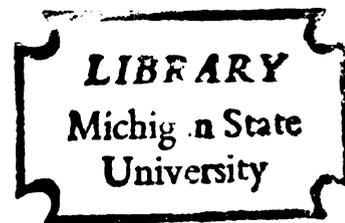


CONFORMATIONAL ANALYSIS OF  
 $\alpha$ -HETEROATOM SUBSTITUTED  
ALDEHYDES BY NUCLEAR MAGNETIC  
RESONANCE SPECTROSCOPY

Thesis for the Degree of Ph. D.  
MICHIGAN STATE UNIVERSITY  
DAVID JOHN FENOGLIO  
1969



This is to certify that the  
thesis entitled  
CONFORMATIONAL ANALYSIS OF  $\alpha$ -HETEROATOM  
SUBSTITUTED ALDEHYDES BY NUCLEAR MAGNETIC  
RESONANCE SPECTROSCOPY  
presented by

David John Fenoglio

has been accepted towards fulfillment  
of the requirements for

Ph.D. degree in Chemistry

G. J. Karabatsos  
Major professor

Date Nov. 10, 1969

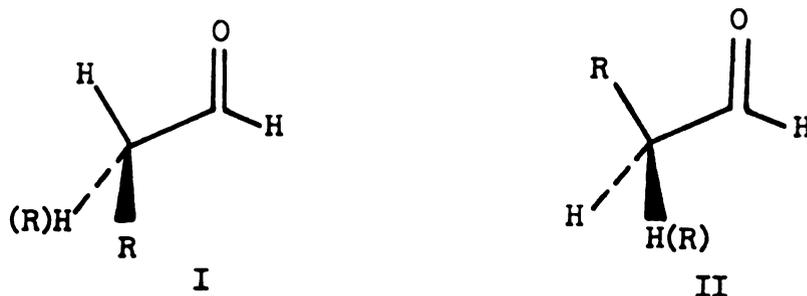


## ABSTRACT

### CONFORMATIONAL ANALYSIS OF $\alpha$ -HETEROATOM SUBSTITUTED ALDEHYDES BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

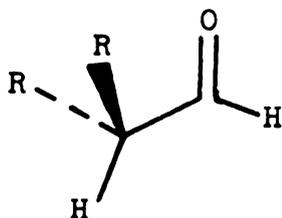
by David John Fenoglio

Nuclear magnetic resonance spectroscopy has been applied to the conformational analysis of  $\alpha$ -heterosubstituted acetaldehydes. The time averaged vicinal spin-spin coupling constants between the aldehydic and  $\alpha$ -proton(s) of chloroacetaldehyde, bromoacetaldehyde, methoxyacetaldehyde, phenoxyacetaldehyde, methylmercaptoacetaldehyde, dichloroacetaldehyde, dibromoacetaldehyde, cyclopropanecarboxaldehyde and glycidaldehyde were studied at 60-Mc as a function of temperature and solvent. The data for the monosubstituted acetaldehydes were interpreted in terms of rotamers I and II, whereby a single bond eclipses the carbonyl group. The data for



the disubstituted acetaldehydes were examined in terms of I and II (threefold barrier to rotation) and I and III (twofold barrier to rotation).

These analyses led to the following conclusions. (A) Chloroacetaldehyde,



III

bromoacetaldehyde, methoxyacetaldehyde and phenoxyacetaldehyde: (1) The data are best interpreted in terms of a threefold barrier to rotation around the  $sp^2$ - $sp^3$  carbon-carbon bond. (2) The most stable rotamer for these compounds is the one with the carbon-heteroatom eclipsing the carbonyl double bond. (3) The free energy and enthalpy differences for  $I \rightleftharpoons II$  are strongly solvent dependent, being much more negative in solvents of high dielectric constant. (B) Methylmercaptoacetaldehyde: (1) A threefold barrier to rotation about the  $sp^2$ - $sp^3$  carbon-carbon bond best fits the data. (2) The most stable rotamer is the one with the carbon-hydrogen bond eclipsing the carbonyl double bond. (3) The free energy and enthalpy differences for  $I \rightleftharpoons II$  are not very sensitive to the dielectric constant of the solvent. (C) Dichloroacetaldehyde and dibromoacetaldehyde: (1) The data are consistent with a threefold barrier to rotation about the  $sp^2$ - $sp^3$  carbon-carbon bond. However, the possibility of a twofold barrier to rotation can not be eliminated. (2) In nonaromatic solvents whose dielectric constant is less than six, the free energy and enthalpy values for  $I \rightleftharpoons II$  are positive, i.e., the rotamer with the carbon-hydrogen bond eclipsing the carbonyl double bond is more stable. (3) In nonaromatic solvents whose dielectric

constant is higher than seven, the free energy and enthalpy values are negative, i.e., the more polar rotamer is more stable. (D) Cyclopropane-carboxaldehyde and glycidaldehyde: (1) No unambiguous decision can be made as to whether there is a dominant twofold or threefold barrier to rotation about the  $sp^2$ - $sp^3$  carbon-carbon bond. (2) The most stable rotamer is the one with the carbon-hydrogen bond eclipsing the carbonyl double bond. (3) The cyclopropyl group acts as an electron donor, whereas the oxirane group acts as an electron withdrawer. Nevertheless, the oxirane ring resembles the cyclopropyl ring more than it does the methoxy group.

Chemical shifts of the aldehydic and methylene (or methine) proton(s) were also measured in conjunction with the coupling constants. It was found that the chemical shift results are in agreement with a new model for the anisotropy of the carbonyl group. This data also reinforce the conclusions derived from the coupling constant data concerning the stability of the rotamers.

CONFORMATIONAL ANALYSIS OF  $\alpha$ -HETEROATOM  
SUBSTITUTED ALDEHYDES BY NUCLEAR MAGNETIC  
RESONANCE SPECTROSCOPY

BY

DAVID JOHN FENOGLIO

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TO MOM AND DAD  
AND MY WIFE,  
JILL

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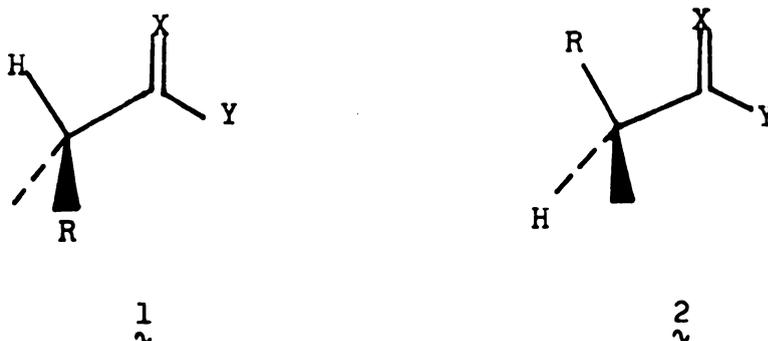
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## INTRODUCTION

Rotational isomerism about a carbon-carbon single bond has been a problem investigated by many techniques. In particular, the relative stabilities of  $\underset{\sim}{1}$  and  $\underset{\sim}{2}$  have been examined with respect to rotation about the carbon-carbon single bond joining the  $sp^2$ - $sp^3$  hybridized carbon atoms as a function of X, Y and R. For example, a few of these



studies include Raman and infrared studies on  $\alpha$ -haloacetones (1, 2, 3), haloacetylhalides (4, 5, 6), N-methylchloroacetamide (7), ethyl haloacetates (8) and 3-halopropenes (9); microwave studies on acetaldehyde (10), acetone (11), propionaldehyde (12) and olefins (13, 14); electron diffraction studies on aliphatic ketones (15) and aldehydes (16, 17); and n.m.r. studies on ketones (18), 3-substituted propenes (19, 20, 21, 22) and aldehydes (23).

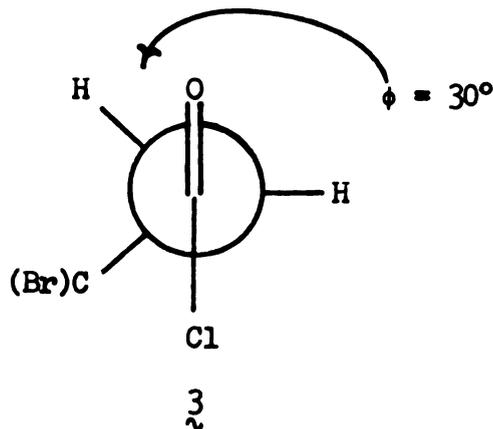
Certain basic factors have been proposed to explain the results from many of these studies. These factors include nonbonded (attractive and repulsive), dipole-dipole and dipole-induced dipole electrostatic interactions. For example, in addition to electrostatic dipole-dipole interactions, nonbonded repulsions between R and Y in rotamer  $\underset{\sim}{1}$  of chloro-

acetone (1), chloroacetyl chloride (4) and N-methylchloroacetamide (7) have been invoked to explain the different  $\frac{1}{2}$  ratios of these compounds. In agreement with these cases is the report (24) that chloroacetaldehyde exists essentially in conformation 1. When this is taken in conjunction with the finding that chloroacetone exists in both 1 and 2, this report is certainly consistent with the concept that nonbonded interactions between R and Y significantly affect the relative stabilities of 1 and 2 of chloroacetone. These same factors have been invoked to correlate and interpret a large number of data (25) on the relative stabilities of the axial and equatorial conformers of 2-halocyclohexanones.

In contrast, nonbonded repulsions in aldehydic systems (X = O and Y = H) (23) have been shown to have only a minor affect on the stability of the rotamers. For example,  $\Delta H^\circ$  for  $\frac{1}{2} \rightleftharpoons \frac{2}{2}$  is -800 and -500 cal/mole when R is methyl or isopropyl, respectively. Out of the 800 cal/mole observed when R is methyl, nonbonded interactions account for less than 200 cal/mole. These interactions become significantly repulsive only when R is *t*-butyl, in which case 1 is favored over 2 by 250 cal/mole.

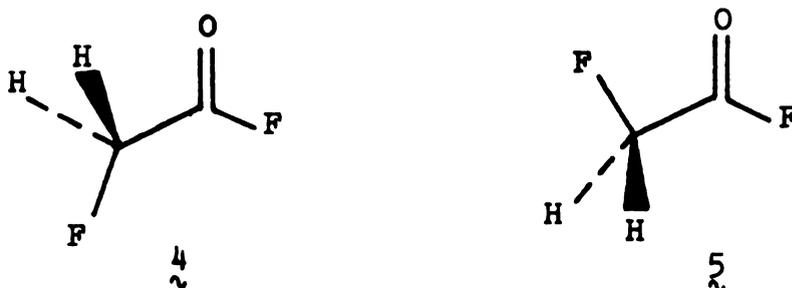
Several compounds containing a single halogen (R = halogen) on the  $\alpha$ -carbon to the double bond have been found to exhibit a threefold barrier to rotation about the  $sp^2$ - $sp^3$  carbon-carbon bond. For example,  $\Delta H^\circ$  for  $\frac{1}{2} \rightleftharpoons \frac{2}{2}$  is -560, -500 and 0 cal/mole for ethyl fluoroacetate, chloroacetate and bromoacetate (8), respectively; it is -1000 and -1900 cal/mole for bromoacetyl chloride and bromoacetyl bromide (1), respectively; and it is -100, +100 and over +100 cal/mole, respectively, for 3-fluoropropene (19, 26), 3-chloropropene (20) and 3-bromopropene (27). In most cases, the data have been interpreted in terms of perfectly eclipsing conformations, i.e., dihedral angles of zero between planes

HCC and CCX in  $\overset{1}{\sim}$  and between planes RCC and CCX in  $\overset{2}{\sim}$ . For chloroacetyl chloride (5) and bromoacetyl chloride (1), a dihedral angle of  $30^\circ$  ( $\overset{3}{\sim}$ ) for  $\overset{1}{\sim}$  was found to best agree with the experimentally determined vibra-



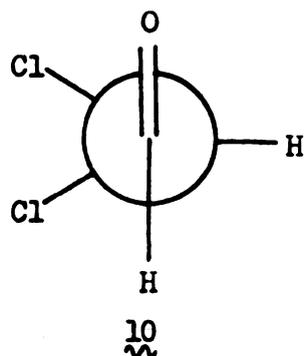
tional frequencies. It was also pointed out (23) that assignments that were made from n.m.r. studies could not make such distinctions in the dihedral angles.

The only monohalosubstituted compound that has been described by a twofold barrier to rotation about the  $sp^2-sp^3$  carbon-carbon bond is fluoroacetyl fluoride (28), whose  $\Delta H^\circ$  for  $\overset{4}{\sim} \rightleftharpoons \overset{5}{\sim}$  is -910 cal/mole.

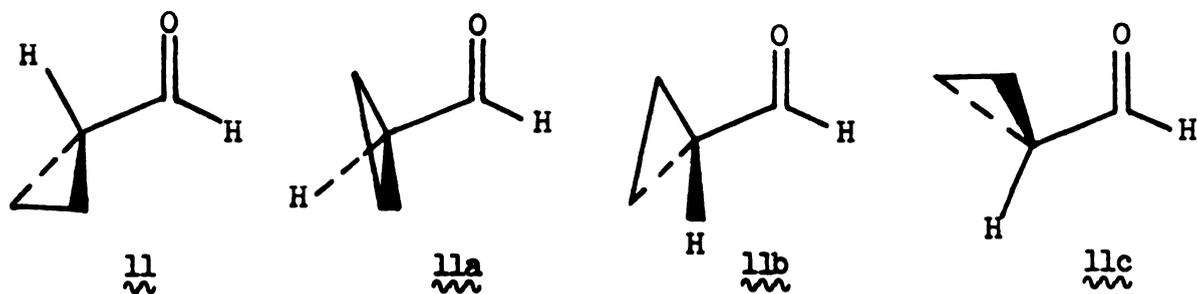


Analogous dihalocompounds differ from the monohalocompounds in two respects: (a) The  $\Delta H^\circ$  values for  $\overset{6}{\sim} \rightleftharpoons \overset{7}{\sim}$  are much more positive than the corresponding ones for  $\overset{1}{\sim} \rightleftharpoons \overset{2}{\sim}$ . In all cases, except for dimethoxypropane (20), the more stable rotamer is the one with the carbon-hydrogen





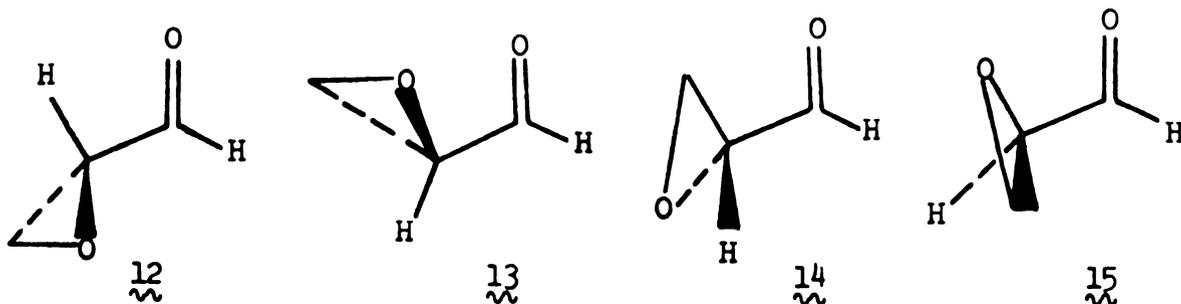
There has also been some question from the n.m.r. results (23) as to whether cyclopropanecarboxaldehyde in the liquid phase is best described in terms of a twofold barrier to rotation (11 and 11c as minimum energy conformations) as found in the gas phase (29), or in terms of a threefold barrier to rotation (11, 11a and 11b as minimum energy conformations).



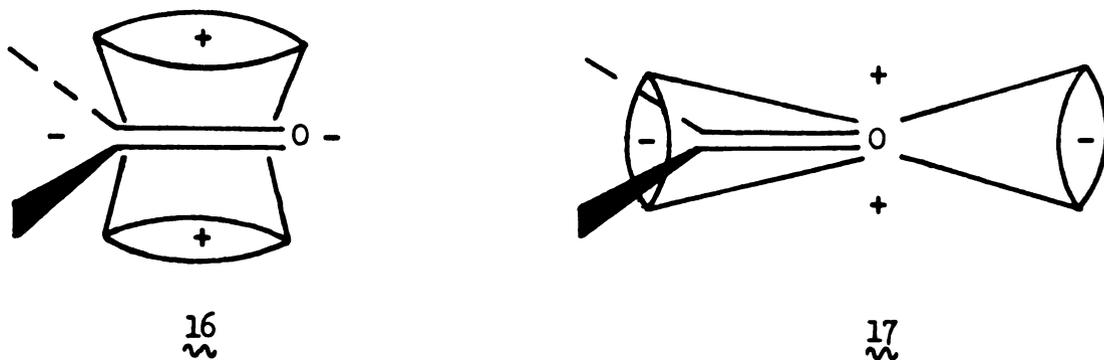
We have investigated chloroacetaldehyde, bromoacetaldehyde, dichloroacetaldehyde, dibromoacetaldehyde, methoxyacetaldehyde, phenoxyacetaldehyde and methylmercaptoacetaldehyde, in order to determine the main factor or factors that control rotamer stabilities.

Cyclopropanecarboxaldehyde was also investigated to see if, in the liquid state, there was a dominant twofold or threefold rotational barrier about the  $sp^2$ - $sp^3$  carbon-carbon bond. The obvious relation of glycidaldehyde to cyclopropanecarboxaldehyde also led to the study of this compound

in order to decide whether a twofold (12 and 13) or threefold (12, 14 and 15) rotational barrier is pertinent.



The effect of the anisotropy of the carbonyl group has been investigated in recent years (30, 31, 32). A model, 16, described by Jackman (33), has been commonly accepted as best describing the anisotropy of the carbonyl group. Recently (34), a more refined model, 17, has been suggested. Studies on rigid cage ketones and ketals (35) seem to agree well with this new model. Along with the measurements of the coupling constants of the



aldehydes mentioned above, the chemical shifts of these aldehydes were measured in order to determine if this new model, 17, was also in agreement with the experimental results.

## RESULTS

### A. Coupling Constants

Summarized in Tables I and II are the vicinal spin-spin coupling constants between the aldehydic and the  $\alpha$ -protons of chloroacetaldehyde, bromoacetaldehyde, dichloroacetaldehyde and dibromoacetaldehyde (Table I); phenoxyacetaldehyde, methoxyacetaldehyde, methylmercaptoacetaldehyde, glycidaldehyde and cyclopropanecarboxaldehyde (Table II). The coupling constants of these aldehydes were observed in 2.5 - 5% solutions in various solvents. All were averages of seven to ten measurements with a precision of  $\pm 0.03$  c.p.s., and were always checked for accuracy and consistency against known values (36, 37) of acetaldehyde; 2.85, 2.88 and 2.90 c.p.s. at 36, 0 and  $-30^\circ$ , respectively.

The coupling constants of chloroacetaldehyde and bromoacetaldehyde are smaller than that of acetaldehyde, as were those of monosubstituted alkylacetaldehydes (23). In contrast, however, to the coupling constants of the monoalkylacetaldehydes that were found to be relatively insensitive to solvent dielectric constant, those of chloroacetaldehyde and bromoacetaldehyde decreased sharply with increase in the dielectric constant of the medium. The coupling constant of bromoacetaldehyde is larger than that of chloroacetaldehyde when compared in the same solvent.

Similar to the monohaloacetaldehydes, the coupling constants of the dihaloacetaldehydes decrease sharply with increasing dielectric constant of the solvent. For example, for dichloroacetaldehyde and dibromoacetaldehyde, the coupling constants are respectively, 4.65 and 5.65 c.p.s. in the low dielectric constant solvent pentane ( $\epsilon \sim 1.8$ ), and 1.10 and 2.17 c.p.s. in the high dielectric constant solvent dimethylsulfoxide

TABLE I. VICINAL SPIN-SPIN COUPLING CONSTANTS<sup>a</sup>, IN C.P.S., OF SOME HALOACETALDEHYDES

Solvent <sup>b</sup>	J <sub>HH</sub> , c.p.s.	
	ClCH <sub>2</sub> CHO	BrCH <sub>2</sub> CHO
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	2.17	
<u>trans</u> -decalin	2.13	2.81
cyclohexane	2.11	2.82
CCl <sub>4</sub>	2.05	2.78
CHCl <sub>3</sub>	1.78	2.62
CH <sub>2</sub> Br <sub>2</sub>	1.59	2.48
CH <sub>2</sub> Cl <sub>2</sub>	1.58	2.47
CH <sub>3</sub> COCH <sub>3</sub>	1.23	2.19
CH <sub>3</sub> CN	1.09	2.06
(CH <sub>3</sub> ) <sub>2</sub> NCHO	0.98	1.97
(CH <sub>3</sub> ) <sub>2</sub> SO	0.83	1.81
H <sub>2</sub> NCHO	0.81	1.80
C <sub>6</sub> H <sub>6</sub>	1.67	2.55
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	1.68	2.54
C <sub>6</sub> H <sub>5</sub> Cl	1.65	2.54
C <sub>6</sub> H <sub>5</sub> CN	1.28	2.25

TABLE I (CONTINUED . . . )

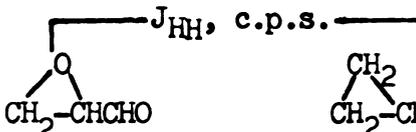
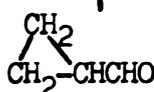
Solvent	$J_{\text{HH}}$ , c.p.s.	
	$\text{Cl}_2\text{CHCHO}$	$\text{Br}_2\text{CHCHO}$
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	4.65	5.65
cyclohexane	4.50	5.56
<u>trans</u> -decalin	4.40	5.47
$\text{CCl}_4$	4.35	5.36
$\text{CHCl}_3$	3.80	4.82
$\text{CH}_2\text{Br}_2$	3.30	4.27
$\text{CH}_2\text{Cl}_2$	3.35	4.25
$\text{CH}_3\text{COCH}_3$	1.90	3.08
$(\text{CH}_3)_2\text{NCHO}$	1.35	3.47
$\text{CH}_3\text{CN}$	1.30	2.89
$(\text{CH}_3)_2\text{SO}$	1.10	2.17
$\text{C}_6\text{H}_6$	3.00	4.16
$\text{C}_6\text{H}_5\text{CH}_3$	3.10	4.24
$\text{C}_6\text{H}_5\text{CN}$	2.10	3.22
$\text{C}_6\text{H}_5\text{NO}_2$	2.30	3.35
Neat	2.90	3.90

<sup>a</sup>Values at  $36 \pm 2^\circ$ .<sup>b</sup>2.5 - 5% solutions.

TABLE II. VICINAL SPIN-SPIN COUPLING CONSTANTS<sup>a</sup>, IN C.P.S., OF SOME HETEROACETALDEHYDES AND CYCLOPROPANECARBOXALDEHYDE

Solvent <sup>b</sup>	J <sub>HH</sub> , c.p.s.		
	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CHO	CH <sub>3</sub> OCH <sub>2</sub> CHO	CH <sub>3</sub> SCH <sub>2</sub> CHO
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	1.52	1.37	3.63
cyclohexane	1.49	1.34	3.63
<u>trans</u> -decalin	1.45	1.29	3.63
CCl <sub>4</sub>	1.48	1.27	3.63
CHCl <sub>3</sub>	1.16	0.80	3.54
CH <sub>2</sub> Br <sub>2</sub>	1.05	0.78	3.51
CH <sub>2</sub> Cl <sub>2</sub>	0.94	0.77	3.46
CH <sub>3</sub> COCH <sub>3</sub>	0.73	0.76	3.35
(CH <sub>3</sub> ) <sub>2</sub> NCHO	<u>ca</u> 0.49	<u>ca</u> 0.47	3.25
CH <sub>3</sub> CN	<u>ca</u> 0.44 <sup>c</sup>	<u>ca</u> 0.41	3.25
(CH <sub>3</sub> ) <sub>2</sub> SO			3.18
H <sub>2</sub> NCHO			3.10
C <sub>6</sub> H <sub>6</sub>	1.15	0.99	3.51
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	1.22	0.99	3.51
C <sub>6</sub> H <sub>5</sub> Cl	1.14	0.92	3.48
C <sub>6</sub> H <sub>5</sub> CN	0.71	0.69	3.33
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.71	0.59	3.39
Neat	0.73		3.42

TABLE II (CONTINUED . . . )

Solvent		
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>		4.63
cyclohexane	6.26	4.70
<u>trans</u> -decalin	6.28	4.74
CCl <sub>4</sub>	6.22	4.94
CH <sub>2</sub> Br <sub>2</sub>	6.08	5.75
CH <sub>2</sub> Cl <sub>2</sub>	6.06	5.75
CH <sub>3</sub> COCH <sub>3</sub>	5.90	5.80
(CH <sub>3</sub> ) <sub>2</sub> NCHO	5.85	5.95
CH <sub>3</sub> CN	5.94	6.00
(CH <sub>3</sub> ) <sub>2</sub> SO	5.79	6.15
H <sub>2</sub> NCHO	5.48	6.20
C <sub>6</sub> H <sub>6</sub>	6.41	5.30
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	6.40	5.25
C <sub>6</sub> H <sub>5</sub> Cl	6.23	5.80
C <sub>6</sub> H <sub>5</sub> CN	6.06	5.73
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	6.04	5.60

<sup>a</sup>Values at 36 ± 2°.

<sup>b</sup>2.5 - 5% solutions.

<sup>c</sup>Poor resolution.

( $\epsilon \sim 45$ ). Furthermore, the coupling constants are large in low dielectric constant solvents when compared to the monohaloacetaldehydes or monoalkylacetaldehydes. The only other saturated aldehydes whose coupling constants are large are di-t-butylacetaldehyde ( $J_{\text{HH}} = 6.0$  c.p.s.) and cyclopropanecarboxaldehyde ( $J_{\text{HH}} = 5.75$  c.p.s.). The former exist mainly in conformation  $\zeta$  and the latter exist in over 85% of this same conformation (23). Similarly to the monohaloacetaldehydes, the coupling constant of dibromoacetaldehyde is larger than that of dichloroacetaldehyde when compared in the same solvent.

The coupling constants of phenoxyacetaldehyde and methoxyacetaldehyde are the smallest vicinal coupling constants observed for substituted acetaldehydes. Their dependence on solvent polarity closely parallels that of the vicinal coupling constants of the haloacetaldehydes. The vicinal coupling constant of methylmercaptoacetaldehyde is considerably larger than either phenoxyacetaldehyde or methoxyacetaldehyde. It is even larger than that of acetaldehyde (2.85 c.p.s.). It decreased only slightly with increasing dielectric constant of the medium. This would indicate that the polarities of the rotamers of methylmercaptoacetaldehyde might be quite similar. Since the differences between the electronegativities of hydrogen and sulfur are small, this conclusion is reasonable and consistent with  $\zeta_1$  and  $\zeta_2$  being the minimum energy conformations of this aldehyde. In contrast to the small values of the vicinal coupling constants of phenoxyacetaldehyde, methoxyacetaldehyde, chloroacetaldehyde, bromoacetaldehyde and methylmercaptoacetaldehyde, the corresponding coupling constants of glycidaldehyde and cyclopropanecarboxaldehyde are quite large. The vicinal coupling constant of glycidaldehyde is the largest observed of any aldehyde, other than those of  $\alpha,\beta$ -unsaturated aldehydes, whose values

are about 7.7 c.p.s. (38, 39).

In Table III is shown the effect of temperature on the vicinal spin-spin coupling constants of chloroacetaldehyde and bromoacetaldehyde. The coupling constant of chloroacetaldehyde increases with increasing temperature in all solvents, with the rate of increase being greater in the more polar solvents. From a plot of these trends shown in Fig. 1, the coupling constant seems to become temperature independent at about 2.5 c.p.s. The coupling constant of bromoacetaldehyde increases in N,N-dimethylformamide (high dielectric constant), but is constant, or temperature independent, at 2.75 c.p.s. in trans-decalin (low dielectric constant). This is shown in Fig. 2.

The effect of temperature on the vicinal spin-spin coupling constants of dichloroacetaldehyde and dibromoacetaldehyde are shown in Tables IV and V, respectively. For both aldehydes, increase in temperature causes a decrease in the coupling constant in low dielectric constant solvents and an increase in the coupling constant in high dielectric constant solvents. In Figs. 3 and 4 are plots of temperature vs. coupling constant for dichloroacetaldehyde and dibromoacetaldehyde, respectively. The lines converge toward a temperature independent region of about 3.4 c.p.s. for dichloroacetaldehyde and 4.5 c.p.s. for dibromoacetaldehyde.

The temperature dependence of the vicinal coupling constants of methoxyacetaldehyde, phenoxyacetaldehyde, methylmercaptoacetaldehyde, cyclopropanecarboxaldehyde and glycidaldehyde are shown in Table VI. The coupling constants of the former two aldehydes are observed to increase in all solvents with increasing temperature. From plots of temperature vs vicinal coupling constant in Figs. 5 and 6, respectively, temperature independent regions can be extrapolated to be about 1.5 c.p.s. for methoxyacetaldehyde and 1.6 c.p.s. for phenoxyacetaldehyde. In contrast to the

TABLE III. TEMPERATURE DEPENDENCE OF THE VICINAL SPIN-SPIN COUPLING CONSTANTS OF CHLOROACETALDEHYDE AND BROMOACETALDEHYDE

Solvent <sup>a</sup>	$J_{HH}$ , c.p.s., of Chloroacetaldehyde											
	-30°	-15°	0°	15°	36°	50°	60°	70°	80°	90°	100°	110°
<u>trans</u> -decalin	2.01		2.09		2.13		2.19		2.20		2.23 <sup>b</sup>	
cyclohexane			2.06		2.10		2.17		2.18			
C <sub>6</sub> H <sub>5</sub> Cl	1.34		1.61		1.74		1.88		1.95		1.98 <sup>c</sup>	
(CH <sub>3</sub> ) <sub>2</sub> NCHO			0.71		1.02		1.18		1.30			
CH <sub>3</sub> CN	0.60		0.84		1.16		1.26		1.39			
		$J_{HH}$ , c.p.s., of Bromoacetaldehyde										
<u>trans</u> -decalin	2.83	2.78	2.75	2.76	2.77	2.76	2.77	2.76	2.76	2.75	2.75	2.75
(CH <sub>3</sub> ) <sub>2</sub> NCHO	1.48	1.65	1.75	1.81	1.93	2.06	2.08	2.08	2.09	2.09	2.09	2.09

<sup>a</sup>2.5 - 5% solutions. <sup>b</sup>Value at 130°. <sup>c</sup>Value at 120°.

FIG 1. TEMPERATURE DEPENDENCE OF THE COUPLING CONSTANT FOR CHLOROACETALDEHYDE

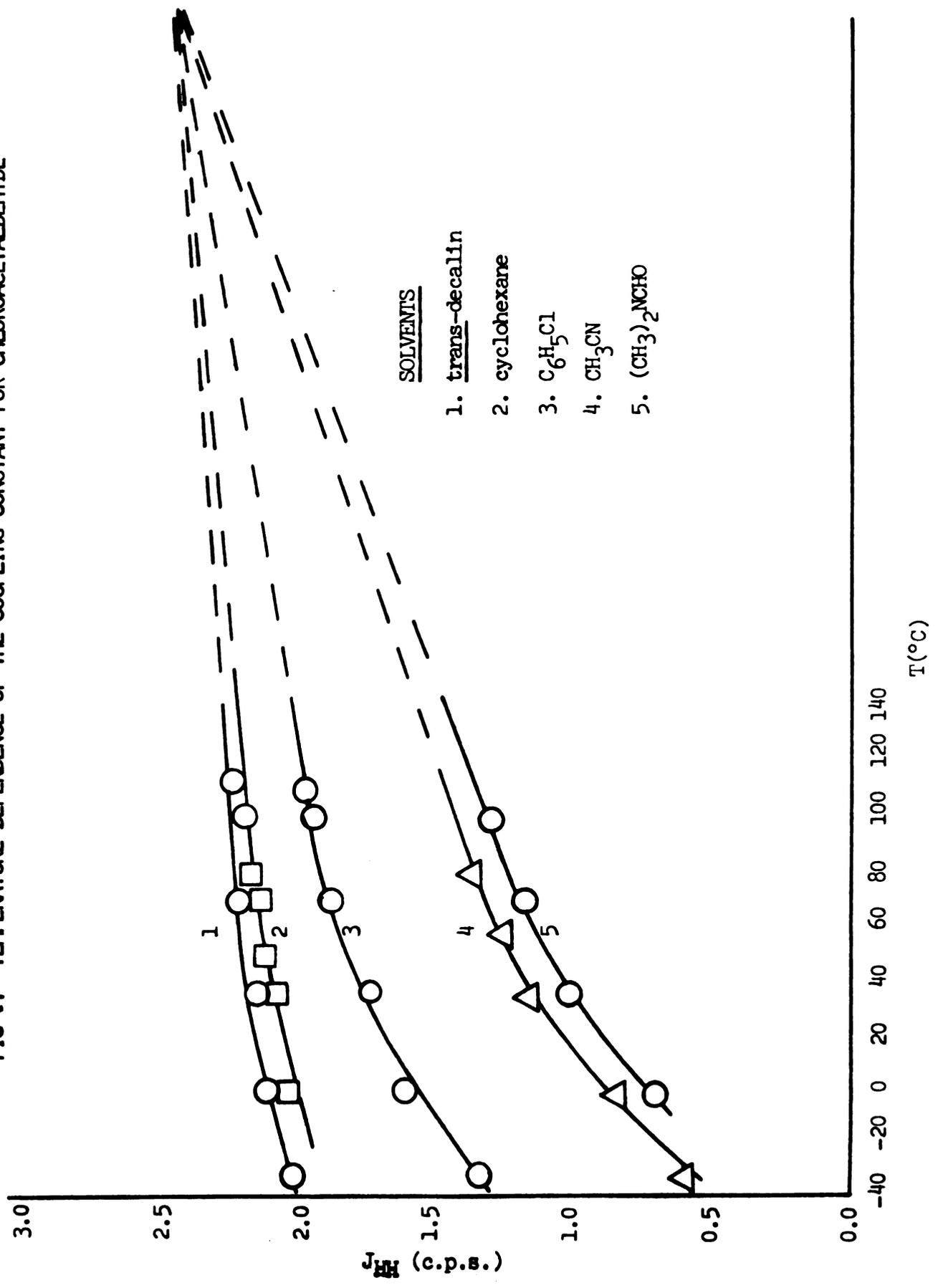


FIG 2. TEMPERATURE DEPENDENCE OF THE COUPLING CONSTANT FOR BROMOACETALDEHYDE

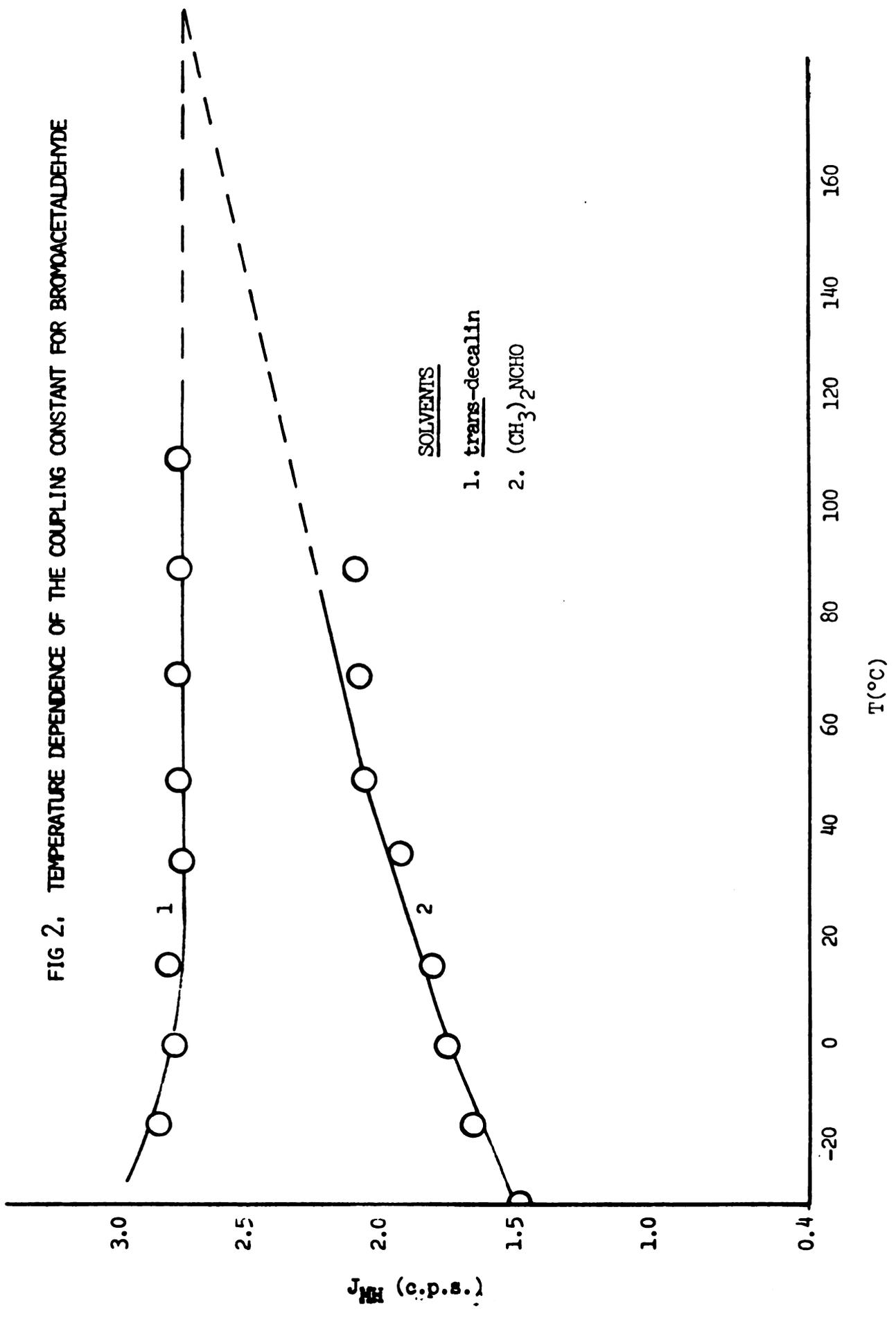


TABLE IV. TEMPERATURE DEPENDENCE OF THE VICINAL SPIN-SPIN COUPLING CONSTANT OF DICHLOROACETALDEHYDE

Solvent <sup>a</sup>	$J_{\text{HHi}}$ , c.p.s.								
	-30°	-15°	0°	15°	36°	50°	70°	90°	110°
cyclohexane			4.52	4.46	4.34	4.33	4.28		
<u>trans</u> -decalin	4.41	4.38	4.37	4.34	4.25	4.18	4.06	4.03	3.99
$\text{C}_6\text{H}_5\text{Cl}$	3.16	3.25	3.29	3.32	3.28	3.37	3.38	3.39	3.38
$\text{C}_6\text{H}_5\text{CH}_3$	2.74	2.90	2.98	3.08	3.09	3.25	3.26	3.28	3.29
$\text{C}_6\text{H}_6$			2.89	2.93	3.04	3.19	3.21		
$\text{C}_6\text{H}_5\text{CN}$		1.69	1.81	1.98	2.04	2.19	2.29	2.35	2.38
$(\text{CH}_3)_2\text{NCHO}$	0.90	1.04	1.13	1.19	1.28	1.41	1.50	1.60	1.70

<sup>a</sup>2.5 - 5% solutions.

TABLE V. TEMPERATURE DEPENDENCE OF THE VICINAL SPIN-SPIN COUPLING CONSTANT OF DIBROMOACETALDEHYDE

Solvent <sup>a</sup>	$J_{HI}$ , c.p.s.						
	-30°	0°	15°	36°	60°	70°	100°
<u>trans</u> -decalin	5.94	5.73		5.43		5.32	5.15
CHCl <sub>3</sub>	5.26	4.98	4.95	4.77			
C <sub>6</sub> H <sub>5</sub> Cl	4.78	4.55		4.46		4.77	4.49 (4.48) <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	4.26	4.38		4.41	4.48	4.48	
CH <sub>2</sub> Br <sub>2</sub>	4.02			4.11		4.14	
(CH <sub>3</sub> ) <sub>2</sub> NCHO	3.15	3.35		3.51		3.59	
CH <sub>3</sub> CN	2.56	2.69		2.94		3.09	

<sup>a</sup>2.5 - 5% solutions.

<sup>b</sup>Value at 130°.

FIG 3. TEMPERATURE DEPENDENCE OF THE COUPLING CONSTANT FOR DICHLOROACETALDEHYDE

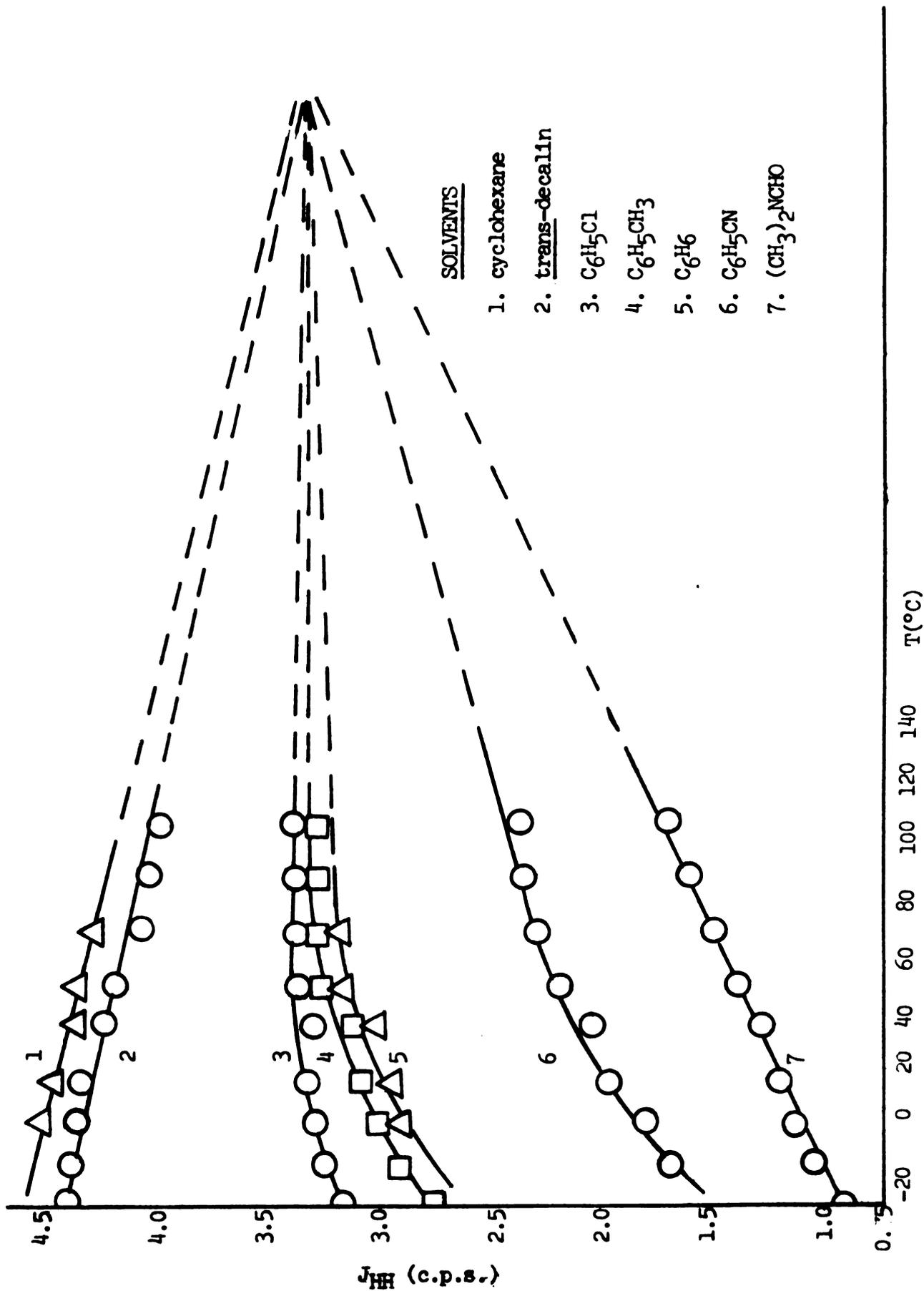


FIG 4. TEMPERATURE DEPENDENCE OF THE COUPLING CONSTANT FOR DIBROMOACETALDEHYDE

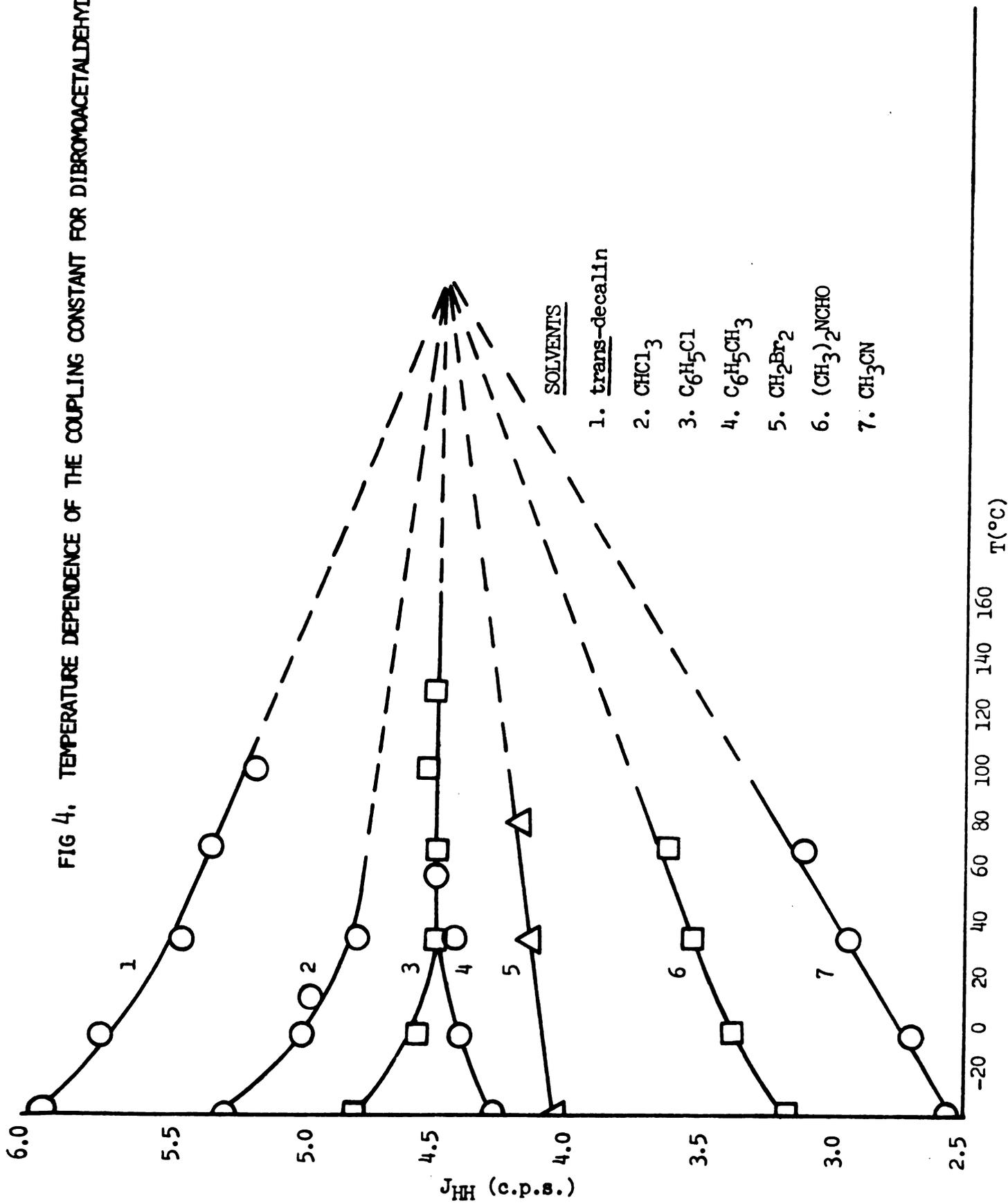


TABLE VI. TEMPERATURE DEPENDENCE OF THE VICINAL SPIN-SPIN COUPLING CONSTANTS OF PHENOXYACETALDEHYDE, METHOXYACETALDEHYDE, METHYLMERCAPTOACETALDEHYDE, GLYCIDALDEHYDE AND CYCLOPROPANE-CARBOXYALDEHYDE

Solvent <sup>a</sup>	$J_{\text{HI}}$ , c.p.s., of Phenoxyacetaldehyde						
	-30°	0°	36°	50°	70°	90°	100° 110° 130°
cyclohexane		1.44	1.46	1.53	1.52	1.52 <sup>b</sup>	
<u>trans</u> -decalin	1.30 <sup>c</sup>	1.38	1.45		1.51	1.53	1.54 (1.53) <sup>d</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	0.79	1.08	1.21		1.32		1.40
C <sub>6</sub> H <sub>5</sub> Cl	0.78	1.07	1.16		1.31		1.36
Neat			0.73	0.80	0.88	0.97	1.05
(CH <sub>3</sub> ) <sub>2</sub> NCHO			0.48	0.54	0.61	0.70	0.78
			$J_{\text{HI}}$ , c.p.s., of Methoxyacetaldehyde				
cyclohexane	1.19	1.29	1.32	1.39	1.39 <sup>b</sup>		
<u>trans</u> -decalin	1.20	1.31		1.34	1.38		1.39
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	0.83	0.99		1.18	1.23		
(CH <sub>3</sub> ) <sub>2</sub> NCHO		0.57		0.75	0.80		

TABLE VI (CONTINUED . . . )

Solvent	$J_{HH}$ , c.p.s., of Methylmercaptoacetaldehyde										
	-30°	-15°	0°	15°	36°	50°	70°	90°	100°	110°	
<u>trans</u> -decalin	3.82		3.77		3.63		3.60			3.47	
$C_6H_5CH_3$	3.74		3.68		3.52		3.50			3.43	
$C_6H_5Cl$	3.69		3.61		3.49		3.43			3.34	
$(CH_3)_2NCHO$	3.46		3.38		3.25		3.25			3.20	
$H_2NCHO$			3.32	3.20	3.16		3.02 <sup>e</sup>	3.05 <sup>b</sup>	3.03		
			$J_{HH}$ , c.p.s., of Glycidaldehyde								
<u>trans</u> -decalin		6.51	6.44	6.40	6.28	6.27	6.18	6.20		6.12	
$(CH_3)_2NCHO$	6.20	6.15	6.12	6.09	5.88	5.86	5.83	5.78		5.64	
			$J_{HH}$ , c.p.s., of Cyclopropanecarboxaldehyde								
<u>trans</u> -decalin	5.39	5.14	5.11	4.95	4.74	4.70	4.60	4.56		4.53	

<sup>a</sup>2.5 - 5% solutions. <sup>b</sup>Value at 80°. <sup>c</sup>Value at -20°. <sup>d</sup>Value at 160°. <sup>e</sup>Value at 60°.

FIG 5. TEMPERATURE DEPENDENCE OF THE COUPLING CONSTANT FOR METHOXYACETALDEHYDE

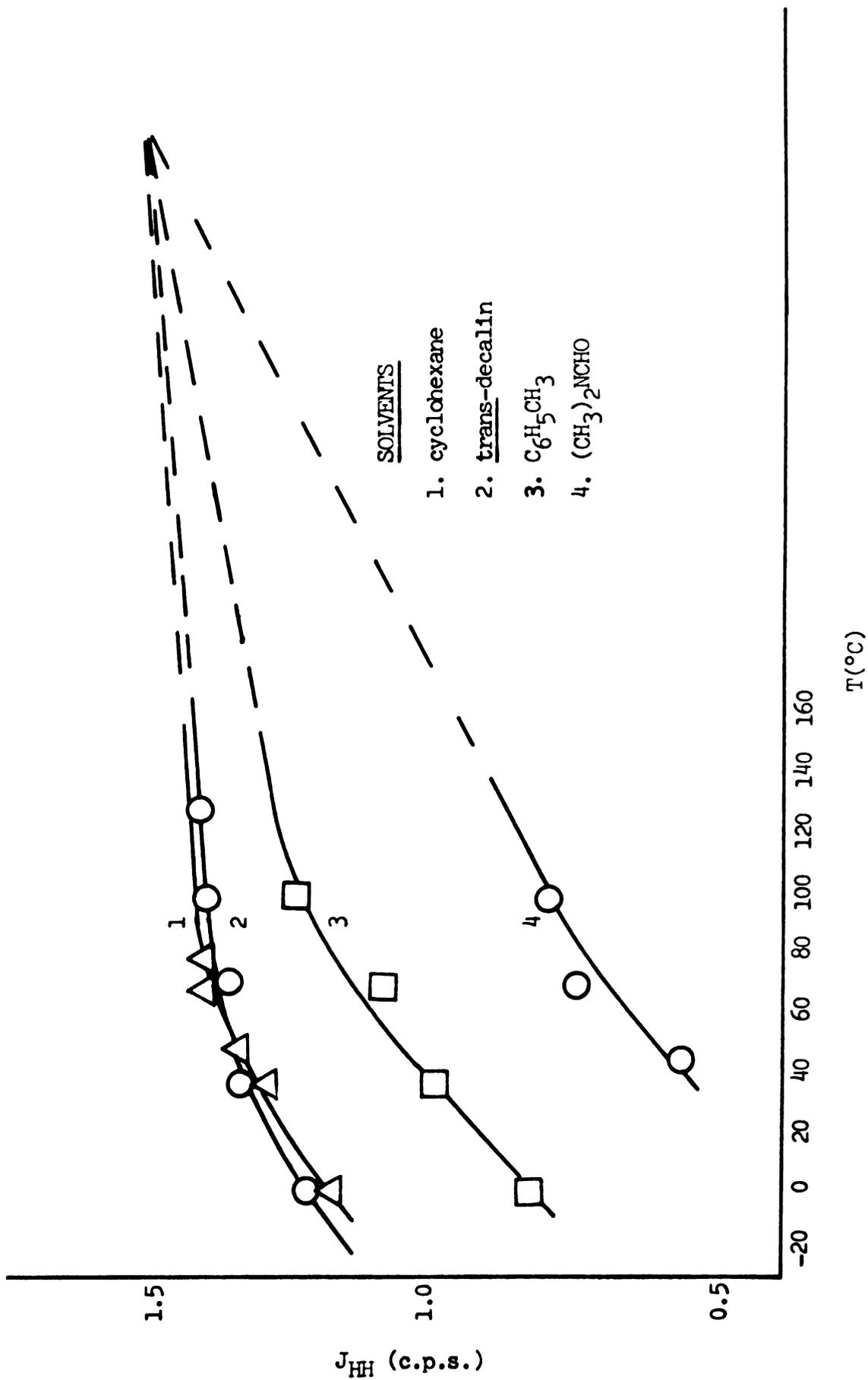
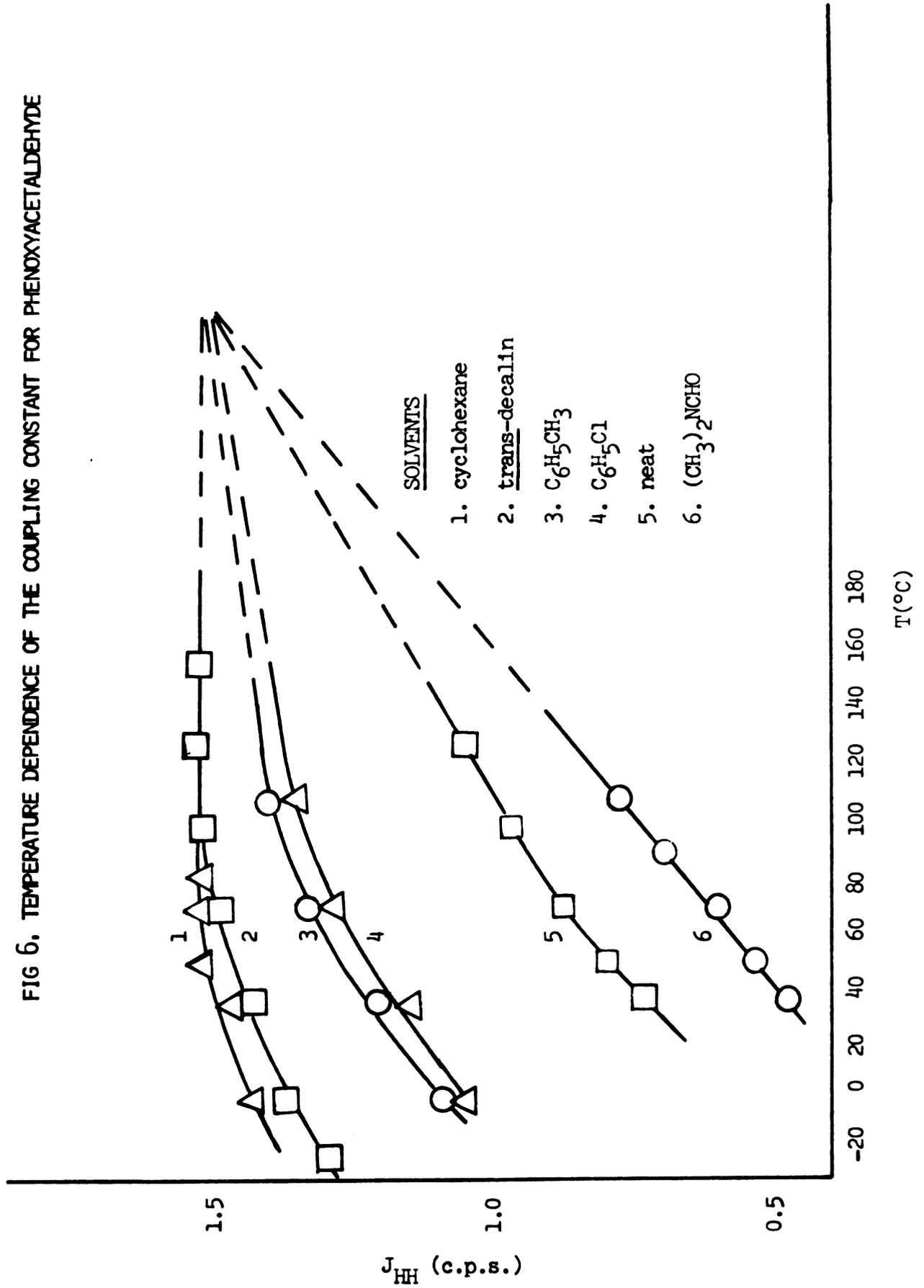
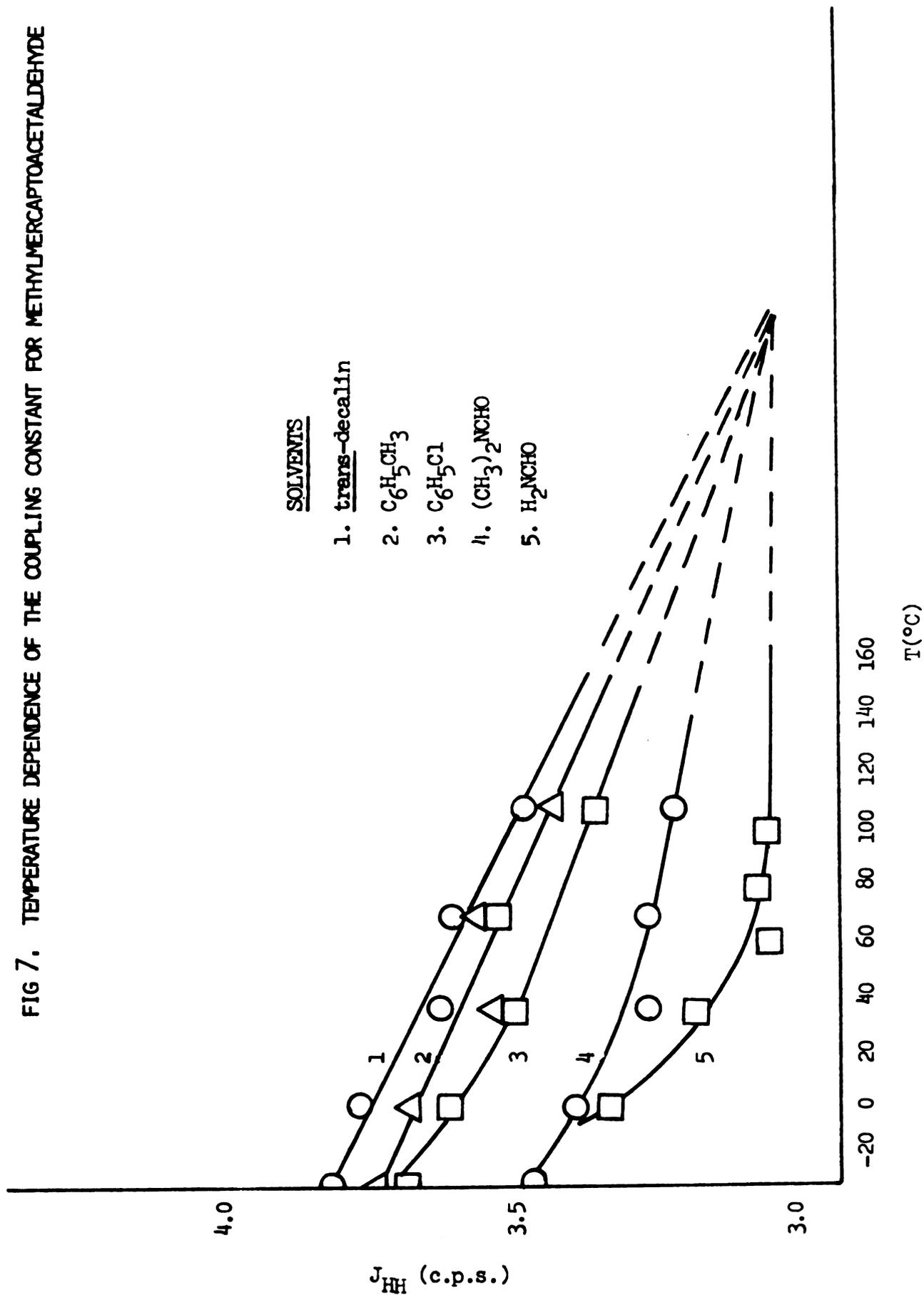


FIG 6. TEMPERATURE DEPENDENCE OF THE COUPLING CONSTANT FOR PHENOXYACETALDEHYDE



two compounds just discussed, the vicinal coupling constants of methylmercaptoacetaldehyde, glycidaldehyde and cyclopropanecarboxaldehyde decrease with increasing temperature in all solvents. When the vicinal coupling constants of methylmercaptoacetaldehyde are plotted against temperature as in Fig. 7, the temperature independent region appears to be at 3.0 c.p.s.

FIG 7. TEMPERATURE DEPENDENCE OF THE COUPLING CONSTANT FOR METHYL MERCAPTOACETALDEHYDE



## B. Chemical Shifts

Summarized in Table VII are the chemical shifts of the aldehydic and methylene (or methine) proton(s) of chloroacetaldehyde, bromoacetaldehyde, dichloroacetaldehyde, dibromoacetaldehyde, methoxyacetaldehyde, phenoxyacetaldehyde and methylmercaptoacetaldehyde. They were measured in 2.5 - 5% (vol/vol) solutions with tetramethylsilane as an internal standard. The values were calibrated against a known sample of tetramethylsilane (0.0 c.p.s.), cyclohexane (86.0 c.p.s.), acetone (126.7 c.p.s.), 1,1,1-trichloroethane (164.0 c.p.s.), dioxane (217.0 c.p.s.), methylene chloride (318.0 c.p.s.), and chloroform (439.8 c.p.s.) at a sweep width of 1000 c.p.s.

In nonaromatic solvents, the chemical shifts of the methylene (or methine) proton(s) are shifted down field as the electronegativity of the substituent on the  $\alpha$ -carbon increases. The chemical shifts of the aldehydic protons seem to be fairly insensitive in nonaromatic solvents. Also, as the polarity of the solvent increases, the chemical shifts of the methylene (or methine) proton(s) shift to lower field.

TABLE VII. THE CHEMICAL SHIFTS<sup>a</sup> OF THE HETEROACETALDEHYDES

Solvent <sup>e</sup>	ClCH <sub>2</sub> CHO		BrCH <sub>2</sub> CHO		Cl <sub>2</sub> CHCHO		Br <sub>2</sub> CHCHO	
	H <sub>1</sub> <sup>b</sup>	H <sub>2</sub> <sup>c</sup>	H <sub>1</sub> <sup>b</sup>	H <sub>2</sub> <sup>c</sup>	H <sub>1</sub> <sup>b</sup>	H <sub>2</sub> <sup>d</sup>	H <sub>1</sub> <sup>b</sup>	H <sub>2</sub> <sup>d</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	569	224	572	216	550	335	542	332
cyclohexane	570	224					542	332
<u>trans</u> -decalin	568	224			550	337	541	332
CCl <sub>4</sub>	578	235			558	348	545	339
CHCl <sub>3</sub>	578	241			563	352	541	343
CH <sub>2</sub> Br <sub>2</sub>	580	248					541	
CH <sub>2</sub> Cl <sub>2</sub>	577	244	576	231	563	356	541	
CH <sub>3</sub> COCH <sub>3</sub>	576	248	578	249	572	395	551	383
(CH <sub>3</sub> ) <sub>2</sub> NCHO	580				576	413		348
CH <sub>3</sub> CN	574	253					541	369
(CH <sub>3</sub> ) <sub>2</sub> SO	574	268	573		571	414	551	403
H <sub>2</sub> NCHO			576	255				
C <sub>6</sub> H <sub>6</sub>	531	186					505	292
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	530	184	535	175	502	289	501	287
C <sub>6</sub> H <sub>5</sub> Cl	542	211					516	307
C <sub>6</sub> H <sub>5</sub> CN	576	250					<b>532</b>	365
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	581	253	578	238	569	376	544	362
Neat			576	239	566	366	539	359

TABLE VII (CONTINUED . . . )

Solvent	CH <sub>3</sub> OCH <sub>2</sub> CHO		C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CHO		CH <sub>3</sub> SCH <sub>2</sub> CHO	
	H <sub>1</sub> <sup>b</sup>	H <sub>2</sub> <sup>c</sup>	H <sub>1</sub> <sup>b</sup>	H <sub>2</sub> <sup>c</sup>	H <sub>1</sub> <sup>b</sup>	H <sub>2</sub> <sup>c</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	577		586	257	559	177
cyclohexane	577	223	585	257	557	176
<u>trans</u> -decalin	577	223			558	176
CCl <sub>4</sub>	579	230	588	264		
CHCl <sub>3</sub>	582	241	592	273	566	188
CH <sub>2</sub> Br <sub>2</sub>	582	242	594	280	567	191
CH <sub>2</sub> Cl <sub>2</sub>	580	241			565	190
CH <sub>3</sub> COCH <sub>3</sub>	578	241	590	287	566	190
(CH <sub>3</sub> ) <sub>2</sub> NCHO	579	245	590	293	567	
CH <sub>3</sub> CN	575	242	585	285	565	192
(CH <sub>3</sub> ) <sub>2</sub> SO	574	245	583	292	563	197
C <sub>6</sub> H <sub>6</sub>	558	199	559	226	540	147
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	557	199	559	224	537	
C <sub>6</sub> H <sub>5</sub> Cl	567	215	572	245	551	164
C <sub>6</sub> H <sub>5</sub> CN	581	241	592	278	568	189
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	584	243	596	282	569	191
Neat					563	191

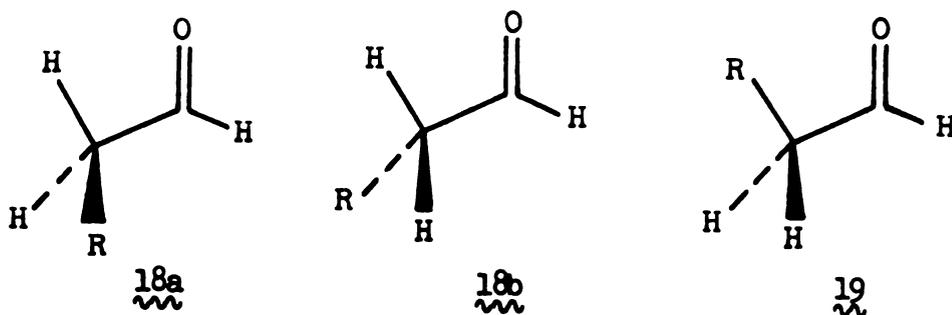
<sup>a</sup>Internal reference is TMS. <sup>b</sup>Chemical shift of aldehydic proton.  
<sup>c</sup>Chemical shift of methylene proton. <sup>d</sup>Chemical shift of methine proton.  
<sup>e</sup>2.5 - 5% solutions.

## DISCUSSION

### A. Coupling Constants

#### I. Monosubstituted Acetaldehydes

The data for the monosubstituted acetaldehydes in Tables I, II, III and VI may be interpreted in terms of  $\overset{18}{\sim}$  and  $\overset{19}{\sim}$  as the equilibrium conformations. By assuming  $J_t > J_g$ , where  $J_t$  is the trans coupling constant and  $J_g$  is the gauche, the observed average vicinal coupling constant would be temperature independent if  $\overset{18a}{\sim}$ ,  $\overset{18b}{\sim}$  and  $\overset{19}{\sim}$  were isoenergetic. Accordingly, the vicinal coupling constant would decrease



with increasing temperature if  $\overset{18a}{\sim}$  (or  $\overset{18b}{\sim}$ ) was more stable than  $\overset{19}{\sim}$ , and would increase with increasing temperature if  $\overset{18a}{\sim}$  was less stable than  $\overset{19}{\sim}$ . From the temperature dependence of the spin-spin coupling constants, the following can be deduced. (a) Chloroacetaldehyde: in both low and high dielectric constant solvents, the most stable rotamer is  $\overset{19}{\sim}$ , i.e., the one with chlorine cis to the carbonyl. (b) Bromoacetaldehyde: in high dielectric constant solvents, the most stable rotamer is  $\overset{19}{\sim}$  and in low dielectric constant solvents, such as trans-decalin, all three rotamers are isoenergetic. (c) Methoxyacetaldehyde and phenoxyacetalde-

hyde: in both high and low dielectric constant solvents,  $\underline{19}$  is the more stable rotamer. (d) Methylmercaptoacetaldehyde: in both high and low dielectric constant solvents,  $\underline{18}$  rather than  $\underline{19}$  is the more stable rotamer.

Rotamer populations and free energy differences,  $\Delta G^\circ$ , between individual rotamers were calculated from equations 1 and 2, respectively, where  $p$  is the fractional population of  $\underline{18}$  ( $\underline{18a} + \underline{18b}$ ) and  $(1 - p)$  that of  $\underline{19}$ . The enthalpy differences,  $\Delta H^\circ$ , between  $\underline{18}$  and  $\underline{19}$  were

$$J_{\text{obsd}} = p(J_t + J_g)/2 + (1 - p)J_g \quad (1)$$

$$\Delta G^\circ = -RT \ln(J_t + J_g - 2J_{\text{obsd}})/(J_{\text{obsd}} - J_g) \quad (2)$$

obtained from plots of  $\log K_{\text{eq}}$  vs  $1/T$ , where  $K_{\text{eq}}$  is given by equation 3.

$$K_{\text{eq}} = 2(1 - p)/p \quad (3)$$

For the above calculations, the  $J_t$  and  $J_g$  coupling constants for each aldehyde must be known. Limits and estimates for these parameters have been made from the experimental data and equation 4, which relates the experimental coupling constant to  $J_t$  and  $J_g$ , either when the three rotamers  $\underline{18a}$ ,  $\underline{18b}$  and  $\underline{19}$  are equally populated, or at free rotation about the carbon-carbon bond (usually at very high temperatures). For

$$J_{\text{obsd}} = 1/3(J_t + 2J_g) \quad (4)$$

bromoacetaldehyde, the temperature independent value ( $J_{\text{obsd}}$  in equation 4) is 2.75 c.p.s. in trans-decalin (Fig. 2). The analogous value for chloroacetaldehyde is greater than 2.23 c.p.s. (highest value within increasing trend in Fig. 1) and is estimated by extrapolation to be

about 2.5 c.p.s. These values are certainly reasonable when compared to the corresponding coupling constant of acetaldehyde (2.85 c.p.s.).

Having established the  $J_{\text{obsd}}$  values for these two aldehydes relating  $J_t$  and  $J_g$  according to equation 4, we can set limits for  $J_t$  and  $J_g$ . For example, the lowest coupling constant of chloroacetaldehyde is 0.6 c.p.s. (in acetonitrile at  $-30^\circ$ ). In absolute magnitude, therefore,  $J_g$  must be equal to or smaller than 0.6 c.p.s. for chloroacetaldehyde. If  $J_t$  and  $J_g$  have the same sign, then, from equation 4,  $J_g \leq 0.6$  c.p.s. and  $J_t \geq 6.3$  c.p.s.; if  $J_t$  and  $J_g$  have opposite signs,  $J_g \leq 0.6$  c.p.s. and  $J_t \geq 8.7$  c.p.s. From the analogous coupling constants of acetaldehyde (23),  $J_g = 0.5$  c.p.s. and  $J_t = 7.6$  c.p.s., a reasonable estimate of the coupling constants of chloroacetaldehyde would be:  $J_g = 0.3$  c.p.s. and  $J_t = 6.9$  c.p.s., both having the same sign.

For bromoacetaldehyde, the smallest coupling constant observed is 1.48 c.p.s. (in N,N-dimethylformamide at  $-30^\circ$ ). Thus,  $J_g \leq 1.48$  c.p.s. and  $J_t \geq 5.28$  c.p.s., if the signs are the same; and  $J_g \leq 1.48$  c.p.s. and  $J_t \geq 11.2$  c.p.s., if the signs are opposite. Since the coupling constants of acetaldehyde and bromoacetaldehyde satisfying equation 4 are 2.85 and 2.75 c.p.s., respectively, reasonable estimates for  $J_g$  and  $J_t$  of bromoacetaldehyde are 0.4 c.p.s. and 7.5 c.p.s., respectively.

The values ( $J_{\text{obsd}}$ ) which satisfy equation 4 for phenoxyacetaldehyde, methoxyacetaldehyde and methylmercaptoacetaldehyde are about 1.6, 1.5 and 3.0 c.p.s., respectively. These values were obtained from extrapolations in Figs. 5, 6 and 7. With these  $J_{\text{obsd}}$  values and equation 4, limits and or estimates can be set for  $J_t$  and  $J_g$  as follows: Since the lowest experimentally measured vicinal coupling constant of phenoxy-

acetaldehyde is about 0.5 c.p.s.,  $J_g$  must be equal to or smaller than 0.5 c.p.s. By using equation 4 as before: if  $J_t$  and  $J_g$  have the same sign, then  $J_g \leq 0.5$  c.p.s. and  $J_t \geq 3.8$  c.p.s. and if they have the opposite sign,  $J_g \leq 0.5$  c.p.s. and  $J_t \geq 5.8$  c.p.s. For methoxyacetaldehyde, the smallest observed coupling constant is about 0.4 c.p.s.

Again,  $J_g$  must be equal to or smaller than 0.4 c.p.s. Thus, if  $J_t$  and  $J_g$  have the same sign,  $J_g \leq 0.4$  c.p.s. and  $J_t \geq 3.7$  c.p.s.; if  $J_g$  and  $J_t$  have the opposite sign,  $J_g \leq 0.4$  c.p.s. and  $J_t \geq 5.3$  c.p.s.

The coupling constant of methylmercaptoacetaldehyde did not vary extensively with solvent polarity and therefore, it is difficult to set reasonable limits for  $J_t$  and  $J_g$ . However, due to the similarity of the  $J_{\text{obsd}}$  values of acetaldehyde (2.85 c.p.s.), bromoacetaldehyde (2.75 c.p.s.) and methylmercaptoacetaldehyde (3.0 c.p.s.), reasonable values for methylmercaptoacetaldehyde of 0.6 and 7.8 c.p.s. can be estimated for  $J_g$  and  $J_t$ , respectively.

By using the previous values for  $J_t$  and  $J_g$ , the effects of solvent polarity on the relative population of the rotamers for chloroacetaldehyde and bromoacetaldehyde were calculated and are given in Table VIII. The values in columns B and E were calculated using the best estimates, those in A and D were calculated from coupling constants with the same sign, and those in C and F were calculated from coupling constants of opposite signs. As had been noted previously from the coupling constants, the population of the more polar rotamer increases as the dielectric constant of the solvent increases. This same effect is seen for chloroacetaldehyde and bromoacetaldehyde in Table IX in terms of the free energy differences,  $\Delta G^\circ$ , that were calculated from equation 2. However, this same trend exists to a smaller extent for bromoacetaldehyde. For example,

TABLE VIII. SOLVENT DEPENDENCE OF THE RELATIVE ROTAMER POPULATIONS<sup>a</sup> OF CHLOROACETALDEHYDE AND BROMOACETALDEHYDE

Solvent	ClCH <sub>2</sub> CHO			BrCH <sub>2</sub> CHO		
	A <sup>b</sup>	B <sup>c</sup>	C <sup>d</sup>	D <sup>e</sup>	E <sup>f</sup>	F <sup>g</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	45	40	40			
<u>trans</u> -decalin	46	44	41	30	32	32
cyclohexane	47	45	42	29	32	32
CCl <sub>4</sub>	49	47	43	32	33	33
CHCl <sub>3</sub>	59	55	49	40	37	35
CH <sub>2</sub> Br <sub>2</sub>	65	61	53	47	41	38
CH <sub>2</sub> Cl <sub>2</sub>	66	61	53	48	42	38
CH <sub>3</sub> COCH <sub>3</sub>	78	72	61	63	50	42
CH <sub>3</sub> CN	83	76	64	69	53	44
(CH <sub>3</sub> ) <sub>2</sub> NCHO	87	79	66	74	56	46
(CH <sub>3</sub> ) <sub>2</sub> SO	92	84	69	83	60	48
H <sub>2</sub> NCHO	93	85	70	83	61	48
C <sub>6</sub> H <sub>6</sub>	63	58	51	44	39	36
C <sub>6</sub> H <sub>5</sub> Cl	63	59	52	44	40	37
C <sub>6</sub> H <sub>5</sub> CN	76	70	60	59	48	41

<sup>a</sup>All values calculated for 36°. <sup>b</sup>Coupling constants used:  $J_t = 6.3$  and  $J_g = 0.6$  (same sign). <sup>c</sup>Coupling constants used:  $J_t = 6.9$  and  $J_g = 0.3$  (same sign). <sup>d</sup>Coupling constants used:  $J_t = 8.7$  and  $J_g = 0.6$  (opposite sign). <sup>e</sup>Coupling constants used:  $J_t = 5.28$  and  $J_g = 1.48$  (same sign). <sup>f</sup>Coupling constants used:  $J_t = 7.5$  and  $J_g = 0.4$  (same sign). <sup>g</sup>Coupling constants used:  $J_t = 11.21$  and  $J_g = 1.48$  (opposite sign).

TABLE IX. SOLVENT DEPENDENCE OF THE FREE ENERGY DIFFERENCE<sup>a</sup>,  $\Delta G^\circ$ , BETWEEN ROTAMERS OF CHLOROACETALDEHYDE AND BROMOACETALDEHYDE

Solvent	ClCH <sub>2</sub> CHO			BrCH <sub>2</sub> CHO		
	$\Delta G^\circ$ , cal/mole, for $\text{18a} \rightleftharpoons \text{19}$			$\Delta G^\circ$ , cal/mole, for $\text{18a} \rightleftharpoons \text{19}$		
	A	B	C	D	E	F
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	-310	-170	-170			
<u>trans</u> -decalin	-325	-300	-200	+100	+40	+40
cyclohexane	-350	-310	-225	+100	+40	+40
CCl <sub>4</sub>	-400	-350	-250	+40	~0	~0
CHCl <sub>3</sub>	-650	-560	-400	-170	-100	-50
CH <sub>2</sub> Br <sub>2</sub>	-800	-700	-500	-360	-200	-100
CH <sub>2</sub> Cl <sub>2</sub>	-835	-710	-500	-375	-230	-100
CH <sub>3</sub> COCH <sub>3</sub>	-1200	-1000	-700	-800	-430	-230
CH <sub>3</sub> CN	-1400	-1100	-780	-950	-500	-275
(CH <sub>3</sub> ) <sub>2</sub> NCHO	-1600	-1250	-830	-1100	-570	-300
(CH <sub>3</sub> ) <sub>2</sub> SO	-1900	-1450	-920	-1400	-680	-400
H <sub>2</sub> NCHO	-2000	-1500	-940	-1400	-700	-400
C <sub>6</sub> H <sub>6</sub>	-750	-640	-450	-300	-150	-80
C <sub>6</sub> H <sub>5</sub> Cl	-750	-650	-475	-300	-180	-100
C <sub>6</sub> H <sub>5</sub> CN	-1130	-950	-675	-650	-380	-200

<sup>a</sup>Calculated for 36° using the corresponding data in Table VIII.

whereas in the least polar solvents  $\overset{\sim}{18a}$  is slightly favored, in the most polar solvent formamide,  $\overset{\sim}{19}$  is favored by about 700 cal/mole.

In Table X are summarized the enthalpy differences,  $\Delta H^\circ$ , between the rotamers of the two haloacetaldehydes. They were calculated from reasonably linear plots of  $\log K_{eq}$  vs  $1/T$ . It can be noticed in Table IX and X that while the  $\Delta G^\circ$  and  $\Delta H^\circ$  values are about equal in solvents of low dielectric constant,  $\Delta H^\circ$  is appreciably more negative than  $\Delta G^\circ$  in solvents of high dielectric constant. For example,  $\Delta G^\circ$  and  $\Delta H^\circ$  for  $\overset{\sim}{18a} \rightleftharpoons \overset{\sim}{19}$  of chloroacetaldehyde are both -300 cal/mole in trans-decalin, whereas in acetonitrile  $\Delta G^\circ$  is -1000 cal/mole and  $\Delta H^\circ$  -2500 cal/mole. This same trend is observed for bromoacetaldehyde.

In Tables XI, XII and XIII, respectively, are summarized the rotamer populations, free energies and enthalpy differences of phenoxyacetaldehyde, methoxyacetaldehyde and methylmercaptoacetaldehyde. These values were determined by using the respective  $J_t$  and  $J_g$  coupling constants from above in conjunction with equations 1, 2 and 3. The values given in columns A, A' and C were calculated by using coupling constants of the same sign. From these results, the most stable rotamer of phenoxyacetaldehyde and methoxyacetaldehyde is  $\overset{\sim}{19}$ . As was the case for chloroacetaldehyde and bromoacetaldehyde, the stability of this rotamer increases with increasing dielectric constant of the solvent. However,  $\overset{\sim}{18}$  is the more stable rotamer of methylmercaptoacetaldehyde, but decreases in stability as the dielectric constant of the solvent increases. The stability of  $\overset{\sim}{19}$  of phenoxyacetaldehyde, methoxyacetaldehyde, chloroacetaldehyde and bromoacetaldehyde is greater in the aromatic solvents benzene and toluene, than would be expected from their dielectric constants ( $\epsilon$  of 2.3 and 2.4 for benzene and toluene, respectively). This

TABLE X. ENTHALPY DIFFERENCES<sup>a</sup>,  $\Delta H^\circ$ , BETWEEN ROTAMERS OF CHLOROACETALDEHYDE AND BROMOACETALDEHYDE

Solvent	ClCH <sub>2</sub> CHO			BrCH <sub>2</sub> CHO		
	$\Delta H^\circ$ , cal/mole, for $\underset{\sim}{18} \rightleftharpoons \underset{\sim}{19}$			$\Delta H^\circ$ , cal/mole, for $\underset{\sim}{18} \rightleftharpoons \underset{\sim}{19}$		
	A	B	C	D	E	F
<u>trans</u> -decalin	-400	-300	-250	0	0	0
cyclohexane	-500	-400	-350			
C <sub>6</sub> H <sub>5</sub> Cl	-1300	-900	-700			
(CH <sub>3</sub> ) <sub>2</sub> NCHO	-2700	-2100	-1000	-3850	-1500	-700
CH <sub>3</sub> CN	-2900	-2500	-1200			

<sup>a</sup>These values were obtained by plotting the equilibrium constants calculated from the rotamer populations in Table VIII vs 1/T.

TABLE XI. SOLVENT DEPENDENCE OF ROTAMER POPULATIONS<sup>a</sup> OF PHENOXYACETALDEHYDE, METHOXYACETALDEHYDE AND METHYLMERCAPTOACETALDEHYDE

Solvent	$C_6H_5OCH_2CHO$ % 19 ~		$CH_3OCH_2CHO$ % 19 ~		$CH_3SCH_2CHO$ % 19 ~
	A <sup>b</sup>	B <sup>c</sup>	A <sup>d</sup>	B <sup>e</sup>	C <sup>f</sup>
$CH_3(CH_2)_3CH_3$	38	36	46	38	16
cyclohexane	40	37	48	39	16
<u>trans</u> -decalin	42	38	51	41	16
$CCl_4$	41	37	52	41	16
$CHCl_3$	60	47	78	58	18
$CH_2Br_2$	67	52	79	59	19
$CH_2Cl_2$	73	54	80	50	21
$CH_3COCH_3$	86	61	80	59	24
$(CH_3)_2NCHO$	>99	69	96	70	26
$CH_3CN$	>99	70	>99	72	26
$H_2NCHO$					31
$C_6H_6$	61	48	67	51	19
$C_6H_5CH_3$	56	45	67	51	19
$C_6H_5Cl$	61	48	71	54	20
$C_6H_5CN$	87	62	84	62	24
$C_6H_5NO_2$	87	62	90	65	23
Neat	89	62			

<sup>a</sup>All values calculated for 36°. <sup>b</sup>Coupling constants used:  $J_t = 3.8$  and  $J_g = 0.5$  (same sign). <sup>c</sup>Coupling constants used:  $J_t = 5.8$  and  $J_g = 0.5$  (opposite sign). <sup>d</sup>Coupling constants used:  $J_t = 3.7$  and  $J_g = 0.4$  (same sign). <sup>e</sup>Coupling constants used  $J_t = 5.3$  and  $J_g = 0.4$  (opposite sign). <sup>f</sup>Coupling constants used:  $J_t = 7.8$  and  $J_g = 0.6$  (same sign).

TABLE XII. SOLVENT DEPENDENCE OF THE FREE ENERGY DIFFERENCE<sup>a</sup>,  $\Delta G^\circ$ , BETWEEN ROTAMERS OF PHENOXYACETALDEHYDE, METHOXYACETALDEHYDE AND METHYLMERCAPTOACETALDEHYDE

Solvent	$C_6H_5OCH_2CHO$		$CH_3OCH_2CHO$		$CH_3SCH_2CHO$
	$\Delta G^\circ$ , cal/mole, for $\underset{\sim}{18a} \rightleftharpoons \underset{\sim}{19}$		$\Delta G^\circ$ , cal/mole, for $\underset{\sim}{18a} \rightleftharpoons \underset{\sim}{19}$		$\Delta G^\circ$ , cal/mole, for $\underset{\sim}{18a} \rightleftharpoons \underset{\sim}{19}$
	A	B	A'	B'	C
$CH_3(CH_2)_3CH_3$	-130	-70	-340	-120	+600
cyclohexane	-180	-90	-380	-150	+600
<u>trans</u> -decalin	-240	-130	-440	-200	+600
$CCl_4$	-200	-100	-470	-200	+600
$CHCl_3$	-700	-360	-1200	-620	+500
$CH_2Br_2$	-860	-470	-1200	-640	+450
$CH_2Cl_2$	-960	-530	-1200	-650	+400
$CH_3COCH_3$	-1500	-700	-1300	-660	+300
$(CH_3)_2NCHO$		-900	-2400	-930	+200
$CH_3CN$		-950	-3600	-1000	+200
$H_2NCHO$					+80
$C_6H_6$	-700	-370	-870	-460	+500
$C_6H_5CH_3$	-600	-300	-870	-460	+500
$C_6H_5Cl$	-700	-380	-1000	-540	+400
$C_6H_5CN$	-1600	-700	-1400	-700	+300
$C_6H_5NO_2$	-1600	-700	-1700	-800	+330
Neat	-1700	-700			

<sup>a</sup>Calculated for 36° from the corresponding data in Table XI.

TABLE XIII. ENTHALPY DIFFERENCES<sup>a</sup>,  $\Delta H^\circ$ , BETWEEN ROTAMERS OF PHENOXY-ACETALDEHYDE, METHOXYACETALDEHYDE AND METHYLMERCAPTO-ACETALDEHYDE

Solvent	$C_6H_5OCH_2CHO$		$CH_3OCH_2CHO$		$CH_3SCH_2CHO$
	$\Delta H^\circ$ , cal/mole, for $\overset{\sim}{18} \rightleftharpoons \overset{\sim}{19}$		$\Delta H^\circ$ , cal/mole, for $\overset{\sim}{18} \rightleftharpoons \overset{\sim}{19}$		$\Delta H^\circ$ , cal/mole, for $\overset{\sim}{18} \rightleftharpoons \overset{\sim}{19}$
	A	B	A'	B'	C
cyclohexane			-1400	-600	
<u>trans</u> -decalin	-1200	-500	-1400	-600	+1000
$C_6H_5CH_3$	-1700	-700	-2200	-800	+900
$C_6H_5Cl$	-1700	-900			+900
$(CH_3)_2NCHO$		-1300	-2600	-1200	+500
$H_2NCHO$					+300
Neat	-3600	-1200			

<sup>a</sup>These values were obtained by plotting the equilibrium constants calculated from the rotamer populations in Table XI vs  $1/T$ .

is attributed to a type of solute-solvent stereospecific association which will be discussed later.

Large discrepancies are particularly obvious between the free energy (Table XII) and enthalpy values (Table XIII) of phenoxyacetaldehyde and methoxyacetaldehyde in the low dielectric constant solvents. Although entropy differences may be partly responsible for these discrepancies, the choice of  $J_t$  and  $J_g$  probably constitutes the major source of error. These parameters were determined on the basis that  $J_{\text{obsd}}$  satisfying equation 4 is 1.6 c.p.s. for phenoxyacetaldehyde and 1.5 c.p.s. for methoxyacetaldehyde. These values are considerably lower than those for acetaldehyde (2.85 c.p.s.), bromoacetaldehyde (2.75 c.p.s.) and chloroacetaldehyde (2.5 c.p.s.). From electronegativity considerations (40, 41), they ought to be between 2.0 and 2.5 c.p.s. Using values of 2.0 and 2.5 c.p.s. for  $J_{\text{obsd}}$  in equation 4, rotamer populations, free energy and enthalpy differences are summarized in Tables XIV and XV. The much better correspondence between free energy and enthalpy differences suggest that these values are more reliable and that the correct choice of  $J_t$  and  $J_g$  may be critical.

a) Consideration of a Twofold Barrier for Chloroacetaldehyde and Bromoacetaldehyde. The results for chloroacetaldehyde and bromoacetaldehyde can be interpreted in terms of a threefold barrier to rotation about the  $sp^2$ - $sp^3$  carbon-carbon bond. However, the question of a twofold barrier to rotation must also be examined. Among all structurally relevant monohalocompounds studied and reported today, only fluoroacetyl fluoride (28) has been found to have a twofold barrier to rotation about the  $sp^2$ - $sp^3$  carbon-carbon bond. However, if it is assumed that  $\underset{\sim}{19}$  and  $\underset{\sim}{20}$  are the equilibrium conformations (twofold

TABLE XIV. ROTAMER POPULATIONS<sup>a</sup> OF PHENOXYACETALDEHYDE AND METHOXYACETALDEHYDE

Solvent	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CHO		CH <sub>3</sub> OCH <sub>2</sub> CHO	
	A <sup>b</sup>	B <sup>c</sup>	A <sup>d</sup>	B <sup>e</sup>
	$J_{\text{obsd}} = 1/3(J_t + 2J_g) = 2.0 \text{ c.p.s.}$			
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	55	46	53	47
cyclohexane	56	47	55	48
<u>trans-decalin</u>	58	48	56	49
	$J_{\text{obsd}} = 1/3(J_t + 2J_g) = 2.5 \text{ c.p.s.}$			
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	66	55	64	56
cyclohexane	67	56	65	57
<u>trans-decalin</u>	68	57	67	57

<sup>a</sup>All values calculated for 36°. <sup>b</sup>Coupling constants used:  $J_t = 5.0$ ,  $J_g = 0.5$  (same sign) and  $J_{\text{obsd}} = 2.0$ ;  $J_t = 6.5$ ,  $J_g = 0.5$  (same sign) and  $J_{\text{obsd}} = 2.5$ . <sup>c</sup>Coupling constants used:  $J_t = 7.0$ ,  $J_g = 0.5$  (opposite sign) and  $J_{\text{obsd}} = 2.0$ ;  $J_t = 8.5$ ,  $J_g = 0.5$  (opposite sign) and  $J_{\text{obsd}} = 2.5$ . <sup>d</sup>Coupling constants used:  $J_t = 5.2$ ,  $J_g = 0.4$  (same sign) and  $J_{\text{obsd}} = 2.0$ ;  $J_t = 6.7$ ,  $J_g = 0.4$  (same sign) and  $J_{\text{obsd}} = 2.5$ . <sup>e</sup>Coupling constants used:  $J_t = 6.8$ ,  $J_g = 0.4$  (opposite sign) and  $J_{\text{obsd}} = 2.0$ ;  $J_t = 8.3$ ,  $J_g = 0.4$  (opposite sign) and  $J_{\text{obsd}} = 2.5$ .

TABLE XV. FREE ENERGY DIFFERENCE<sup>a</sup>,  $\Delta G^\circ$ , BETWEEN ROTAMERS OF PHENOXY-ACETALDEHYDE AND METHOXYACETALDEHYDE

Solvent	$C_6H_5OCH_2CHO$		$CH_3OCH_2CHO$	
	$\Delta G^\circ$ , cal/mole, for $18a \rightleftharpoons 19$		$\Delta G^\circ$ , cal/mole, for $18a \rightleftharpoons 19$	
	A	B	A'	B'
	$J_{\text{obsd}} = 1/3(J_t + 2J_g) = 2.0$ c.p.s.			
$CH_3(CH_2)_3CH_3$	-540	-320	-510	-350
cyclohexane	-570	-350	-540	-370
<u>trans</u> -decalin	-620	-380	-580	-400
	$J_{\text{obsd}} = 1/3(J_t + 2J_g) = 2.5$ c.p.s.			
$CH_3(CH_2)_3CH_3$	-830	-550	-780	-570
cyclohexane	-880	-570	-810	-590
<u>trans</u> -decalin	-900	-580	-850	-610
	$\Delta H^\circ$ , cal/mole, for $18 \rightleftharpoons 19$			
cyclohexane ( $J_{\text{obsd}} = 2.0$ )			-800	-500
cyclohexane ( $J_{\text{obsd}} = 2.5$ )			-800	-500
<u>trans</u> -decalin ( $J_{\text{obsd}} = 2.0$ )	-600	-400	-600	-400
<u>trans</u> -decalin ( $J_{\text{obsd}} = 2.5$ )	-500	-300	-500	-300

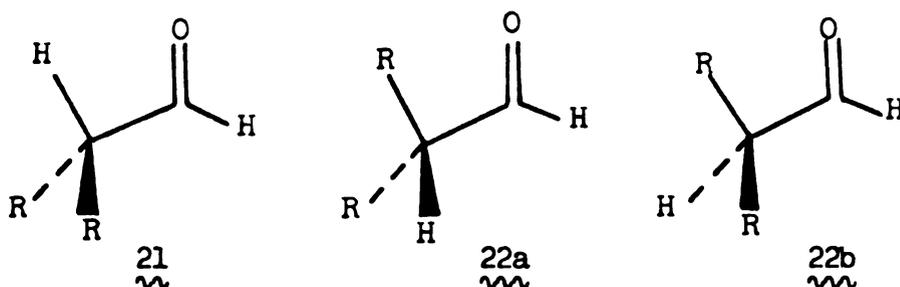
<sup>a</sup>Calculated for 36° from the data in Table XIV.



hydrocarbons. In solvents of high dielectric constant, the methoxy, phenoxy, chloro and bromo groups move ahead of the methyl group in the above given order. For the groups preceeding bromine in the above order,  $\Delta H^\circ$  for  $\overset{\sim}{18a} \rightleftharpoons \overset{\sim}{19}$  is negative and for those groups following bromine, it is positive. The position of the more polarizable methylmercapto group with respect to that of the less polarizable methoxy, as well as that of bromine with respect to chlorine, indicates that dipole-induced dipole interactions play minor roles in determining the relative stabilities of  $\overset{\sim}{18a}$  and  $\overset{\sim}{19}$ . Nonbonded repulsions are partly responsible for the position of the bulky *t*-butyl and methylmercapto groups. However, their relative positions reinforce the conclusion (23) that nonbonded repulsions are not the overriding factor controlling rotamer stabilities. What this factor is, still remains to be determined.

## II. Dihaloacetaldehydes

The data for dichloroacetaldehyde and dibromoacetaldehyde in Tables I, IV and V may be interpreted in terms of a threefold barrier to rotation about the  $sp^2$ - $sp^3$  carbon-carbon single bond with  $\overset{\sim}{21}$  and  $\overset{\sim}{22}$  being the equilibrium conformations of these compounds. As before, by assuming



$J_t > J_g$ , the average vicinal coupling constant would be temperature independent if  $\overset{\sim}{21}$ ,  $\overset{\sim}{22a}$  and  $\overset{\sim}{22b}$  were isoenergetic. If the average vicinal coupling constant increases with increasing temperature, then  $\overset{\sim}{22a}$  (or  $\overset{\sim}{22b}$ ) is more stable than  $\overset{\sim}{21}$ , and if it decreases with increasing temperature,

then  $\overset{\sim}{21}$  is the more stable rotamer. From Tables IV and V, it can be seen that in the non-polar solvents (trans-decalin),  $\overset{\sim}{21}$  is the more stable rotamer, whereas in polar solvents (acetonitrile),  $\overset{\sim}{22}$  is the more stable rotamer for both dichloroacetaldehyde and dibromoacetaldehyde.

Rotamer populations and free energy differences,  $\Delta G^\circ$ , between individual rotamers were calculated, respectively, from equations 5 and 6, where  $p$  is the fractional population of  $\overset{\sim}{21}$  and  $(1 - p)$  that of

$$J_{\text{obsd}} = pJ_t + (1 - p)J_g \quad (5)$$

$$\Delta G^\circ = -RT \ln 1/2(J_t - J_{\text{obsd}})/(J_{\text{obsd}} - J_g) \quad (6)$$

$\overset{\sim}{22a} + \overset{\sim}{22b}$ . As before, the enthalpy differences,  $\Delta H^\circ$ , were calculated from plots of  $\log K_{\text{eq}}$  vs  $1/T$ . The values of  $K_{\text{eq}}$  were determined from equation 7. Determination of these quantities requires knowledge of

$$K_{\text{eq}} = (1 - p)/2p \quad (7)$$

$J_t$  and  $J_g$ , as well as equation 4. Equation 4 relates  $J_t$  and  $J_g$  either when  $\overset{\sim}{21}$ ,  $\overset{\sim}{22a}$  and  $\overset{\sim}{22b}$  are equally populated, or at a state of free rotation about the carbon-carbon single bond (usually at high temperature). The experimental coupling constant ( $J_{\text{obsd}}$ ) satisfying equation 4 is 3.4 c.p.s. for dichloroacetaldehyde and 4.5 c.p.s. for dibromoacetaldehyde as shown in Figs. 3 and 4, respectively. Since the lowest experimentally measured coupling constant of dichloroacetaldehyde is 0.9 c.p.s. (Table IV),  $J_g$  must be equal to or smaller than 0.9 c.p.s. From equation 4, if  $J_t$  and  $J_g$  have the same sign,  $J_g \leq 0.9$  c.p.s. and  $J_t \geq 8.4$  c.p.s.; if they have opposite signs,  $J_g \leq 0.9$  c.p.s. and  $J_t \geq 12.0$  c.p.s. However, a reason-

able estimate would probably be  $J_g = 0.5$  c.p.s.. From this and equation 4,  $J_t = 9.1$  c.p.s. (same sign).

For dibromoacetaldehyde, the smallest observed coupling constant is 2.17 c.p.s. If  $J_t$  and  $J_g$  have the same sign,  $J_g \leq 2.17$  c.p.s. and  $J_t \geq 9.16$  c.p.s.; if the signs are opposite, then  $J_g \leq 2.17$  c.p.s. and  $J_t \geq 17.84$  c.p.s. A reasonable set (estimated  $J_g \sim 1.6$  c.p.s.) of  $J_t$  and  $J_g$  would be 10.3 and 1.6 c.p.s., respectively, (same sign).

The effect of solvent polarity on the relative populations of the rotamers is shown in Table XVI. These were calculated from equation 5. The values in columns B and E were calculated by using the best estimates of the  $J_t$  and  $J_g$  coupling constants. Those in A and D were calculated from the coupling constants with the same sign and those in columns C and F from coupling constants with opposite signs. Inspection of these results are not strongly affected by the choice of the coupling constants,  $J_t$  and  $J_g$ . However, the stability of the rotamers is strongly dependent on solvent polarity. The more polar rotamer 22a (or 22b) is more stable in polar solvents, whereas the nonpolar rotamer, 21, is more stable in the nonpolar solvents.

In Table XVII are summarized the free energy differences,  $\Delta G^\circ$ , between rotamers 21 and 22a (or 22b) calculated from equation 6. In low dielectric constant solvents,  $\epsilon < 5$ , the free energy differences are positive for both aldehydes (21, the less polar rotamer is more stable than 22a, the more polar rotamer). In solvents of dielectric constant greater than 9, the  $\Delta G^\circ$ 's are negative (22a is more stable than 21). The cross-over appears to occur at a dielectric constant of about 6. For example, the  $\Delta G^\circ$  values are positive in chloroform ( $\epsilon$  of 4.8) and negative in methylene bromide ( $\epsilon$  of 7.4). The values in aromatic solvents are anomalous, as they were

TABLE XVI. SOLVENT DEPENDENCE OF THE RELATIVE ROTAMER POPULATIONS<sup>a</sup>  
 OF DICHLOROACETALDEHYDE AND DIBROMOACETALDEHYDE

Solvent	Cl <sub>2</sub> CHCHO			Br <sub>2</sub> CHCHO		
	A <sup>b</sup>	% 21 B <sup>c</sup>	C <sup>d</sup>	D <sup>e</sup>	% 21 E <sup>f</sup>	F <sup>g</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	50	48	43	50	47	39
cyclohexane	48	47	42	49	46	39
<u>trans</u> -decalin	47	45	41	47	45	38
CCl <sub>4</sub>	46	45	41	46	43	38
CHCl <sub>3</sub>	39	38	36	38	37	35
CH <sub>2</sub> Br <sub>2</sub>	32	33	33	30	31	32
CH <sub>2</sub> Cl <sub>2</sub>	33	33	33	30	30	32
CH <sub>3</sub> COCH <sub>3</sub>	13	16	22	13	17	26
(CH <sub>3</sub> ) <sub>2</sub> NCHO	6	10	18	19	21	28
CH <sub>3</sub> CN	5	9	17	10	15	25
(CH <sub>3</sub> ) <sub>2</sub> SO	3	7	16	1	7	22
C <sub>6</sub> H <sub>6</sub>	28	29	30	29	29	32
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	29	30	31	30	30	32
C <sub>6</sub> H <sub>5</sub> CN	16	19	23	15	19	27
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	19	21	25	17	20	28
Neat	27	27	29	25	26	30

<sup>a</sup>All values calculated for 36°. <sup>b</sup>Coupling constants used:  $J_t = 8.4$  and  $J_g = 0.9$  (same sign). <sup>c</sup>Coupling constants used:  $J_t = 9.1$  and  $J_g = 0.5$  (same sign). <sup>d</sup>Coupling constants used:  $J_t = 12.0$  and  $J_g = 0.9$  (opposite sign). <sup>e</sup>Coupling constants used:  $J_t = 9.16$  and  $J_g = 2.17$  (same sign). <sup>f</sup>Coupling constants used:  $J_t = 10.3$  and  $J_g = 1.6$  (same sign). <sup>g</sup>Coupling constants used:  $J_t = 17.85$  and  $J_g = 2.17$  (opposite sign).

TABLE XVII. SOLVENT DEPENDENCE OF THE FREE ENERGY DIFFERENCE<sup>a</sup>,  $\Delta G^\circ$ , BETWEEN ROTAMERS OF DICHLOROACETALDEHYDE AND DIBROMO-ACETALDEHYDE

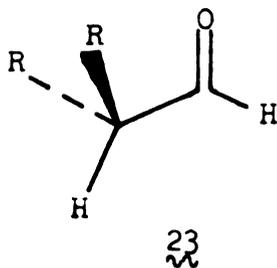
Solvent	Cl <sub>2</sub> CHCHO			Br <sub>2</sub> CHCHO		
	$\Delta G^\circ$ , cal/mole, for $21 \rightleftharpoons 22a$			$\Delta G^\circ$ , cal/mole, for $21 \rightleftharpoons 22a$		
	A	B	C	D	E	F
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	+430	+380	+250	+420	+340	+150
cyclohexane	+380	+350	+220	+390	+320	+140
<u>trans</u> -decalin	+340	+300	+210	+360	+290	+130
CCl <sub>4</sub>	+330	+300	+200	+320	+260	+110
CHCl <sub>3</sub>	+140	+120	+80	+130	+100	+40
CH <sub>2</sub> Br <sub>2</sub>	-40	-15	-20	-90	-75	-30
CH <sub>2</sub> Cl <sub>2</sub>	-17	-14	-11	-100	-80	-40
CH <sub>3</sub> COCH <sub>3</sub>	-730	-590	-360	-740	-550	-210
(CH <sub>3</sub> ) <sub>2</sub> NCHO	-1260	-930	-500	-480	-370	-150
CH <sub>3</sub> CN	-1340	-1000	-540	-900	-650	-240
(CH <sub>3</sub> ) <sub>2</sub> SO	-1800	-1200	-620		-1200	-360
C <sub>6</sub> H <sub>6</sub>	-160	-120	-90	-140	-120	-50
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	-120	-100	-60	-100	-90	-40
C <sub>6</sub> H <sub>5</sub> CN	-600	-340	-300	-640	-480	-190
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	-480	-390	-250	-550	-420	-170
Neat	-200	-190	-110	-260	-210	-90

<sup>a</sup>These values were calculated from the corresponding data in Table XVI.

for the monohaloacetaldehydes, methoxyacetaldehyde and phenoxyacetaldehyde, and will be discussed in a separate section.

In Table XVIII are summarized the enthalpy differences between rotamers  $\underline{21}$  and  $\underline{22}$  calculated from reasonably linear plots of  $\log K_{eq}$  vs  $1/T$ . The enthalpy and free energy differences are about the same in solvents of low dielectric constant, but the enthalpy differences are appreciably more negative than the free energy differences in a medium of high dielectric constant. The effect is greater for dichloroacetaldehyde than for dibromoacetaldehyde. This same effect is also found in the monohaloacetaldehydes.

a) Consideration of a Twofold Barrier. In view of the finding that the rotational isomerism about the  $sp^2-sp^3$  carbon-carbon bond of ethyl dihaloacetates is best described in terms of a twofold barrier to rotation (8), the experimental data for the dihaloacetaldehydes will be examined in terms of minimum energy conformations  $\underline{21}$  and  $\underline{23}$ . The



relevant vicinal spin-spin coupling constants for a twofold barrier to rotation would be  $J_t$  and  $J_c$ , where  $J_t$  is the trans coupling from  $\underline{21}$  and  $J_c$  is the cis coupling from  $\underline{23}$ . Equation 4 now becomes equation 8. As stated earlier, the values of  $J_{obsd}$  for dichloroacetaldehyde and

$$J_{obsd} = 1/2(J_t + J_c) \quad (8)$$

TABLE XVIII. ENTHALPY DIFFERENCES<sup>a</sup>,  $\Delta H^\circ$ , BETWEEN ROTAMERS OF DICHLORO-ACETALDEHYDE AND DIBROMOACETALDEHYDE

Solvent	Cl <sub>2</sub> CHCHO			Br <sub>2</sub> CHCHO		
	$\Delta H^\circ$ , cal/mole, for $\underset{\sim}{21} \rightleftharpoons \underset{\sim}{22}$			$\Delta H^\circ$ , cal/mole, for $\underset{\sim}{21} \rightleftharpoons \underset{\sim}{22}$		
	A	B	C	D	E	F
cyclohexane	+300	+300	+200			
<u>trans</u> -decalin	+300	+300	+200	+600	+500	+230
CHCl <sub>3</sub>				+600	+500	+230
C <sub>6</sub> H <sub>5</sub> Cl	0	0	0	0	0	0
CH <sub>2</sub> Br <sub>2</sub>				-200	-100	-100
C <sub>6</sub> H <sub>6</sub>	-600	-450	-400			
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	-600	-500	-400	-250	-200	-100
C <sub>6</sub> H <sub>5</sub> CN	-1200	-1000	-600			
(CH <sub>3</sub> ) <sub>2</sub> NCHO	-2800	-1400	-600	-700	-500	-200
CH <sub>3</sub> CN				-1500	-800	-300

<sup>a</sup>These values were obtained by plotting the equilibrium constants calculated from the rotamer populations in Table XVI vs  $1/T$ .

dibromoacetaldehyde were found to be 3.4 and 4.5 c.p.s., respectively. When these values are compared to those of acetaldehyde (2.85 c.p.s.), chloroacetaldehyde (2.5 c.p.s.) and bromoacetaldehyde (2.75 c.p.s.), which apply to equation 4, they are found to be larger than substituent electronegativity effects on vicinal proton-proton coupling would have predicted (40, 41). For example, substitution of one hydrogen by chlorine or bromine reduces the average vicinal coupling constant of ethane from 8.0 c.p.s. (43) to 6.5 c.p.s. for chloroethane and 6.6 c.p.s. for bromoethane (40). Substitution of two hydrogens on the same carbon by two chlorines or bromines further reduces the coupling to 6.1 c.p.s. (1,1-dichloroethane) and 6.2 c.p.s. (1,1-dibromoethane) (41). By using this argument of electronegativity, it would be expected that the  $J_{\text{obsd}}$  values of dichloroacetaldehyde and dibromoacetaldehyde would be smaller than 2.5 and 2.75 c.p.s., respectively, for a threefold barrier to rotation. The experimentally observed higher values of 3.4 and 4.5 c.p.s. would seem to contradict a threefold barrier to rotation and would be more aligned with equation 8, i.e., a twofold barrier to rotation about the carbon-carbon bond. However, these predictions based on substituent electronegativity may be quite false. For example, whereas the average vicinal coupling constant of ethanol (hydroxyl substituted for hydrogen) is about 6.6 c.p.s. and of propionic acid (carboxyl substituted for hydrogen) is 7.4 c.p.s., that of lactic acid (hydroxyl and carboxyl substituted on the same carbon) is 7.3 c.p.s., and not about 6.0 c.p.s. as would have been predicted from substituent electronegativity considerations.

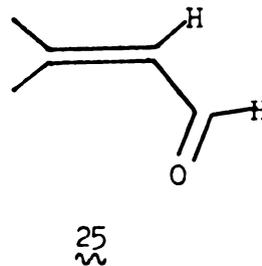
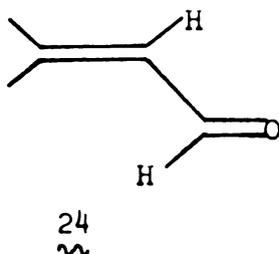
Let the assumption of a twofold barrier still be valid. Since the smallest experimentally observed coupling constant of dichloroacetaldehyde

is 0.9 c.p.s. and  $J_t > J_c$ ,  $J_c$  must be equal to or smaller than this value. From this value for  $J_c$  and equation 8,  $J_t$  must be equal to or greater than 5.9 c.p.s., if  $J_c$  and  $J_t$  have the same sign; and equal to or greater than 7.7 c.p.s., if they have opposite signs. Similar treatment of the data for dibromoacetaldehyde gives:  $J_c \leq 2.17$  c.p.s. and  $J_t \geq 6.83$  c.p.s., if they have the same sign; and  $J_c \leq 2.17$  c.p.s. and  $J_t \geq 11.17$  c.p.s., if they have opposite signs. The question may now be asked whether these values for  $J_t$  and  $J_c$  are reasonable in relation to one another. From valence-bond theory (42), the contact interaction term describing the dihedral angle dependence of vicinal proton-proton coupling is approximated by equation 9. The relative magnitudes

$$J_{HH} = A + B\cos\phi + C\cos 2\phi \quad (9)$$

of  $J_t$  and  $J_c$  depends on the values of A, B and C. For ethane (both carbons  $sp^3$  and a carbon-carbon distance of  $1.54 \text{ \AA}$ ),  $A = 4.22$ ,  $B = -0.5$  and  $C = 4.5$  c.p.s., the treatment predicts  $J_t = 9.22$  c.p.s. and  $J_c = 8.22$  c.p.s. For ethylene (both carbons  $sp^2$  and a carbon-carbon distance of  $1.35 \text{ \AA}$ ), it predicts  $J_t = 11.9$  c.p.s. and  $J_c = 6.1$  c.p.s. Experimentally determined  $J_t$  and  $J_c$  values of ethylenic compounds agree fairly well, if not in absolute value, at least in the relative magnitudes of the two coupling constants with the predicted values. There are no experimental  $J_t$  and  $J_c$  values for systems with one carbon atom  $sp^2$  hybridized and the other  $sp^3$  hybridized to which our calculated values may be compared. Some values are available for systems with both carbon atoms  $sp^2$  hybridized, where the carbon-carbon length is between that of ethane and ethylene. The  $J_t$  of 1,3-butadiene (44) and  $J_c$  (single bond of 1,3-

cyclohexadiene) (45) are 10.41 and 5.14 c.p.s., respectively. For  $\alpha,\beta$ -unsaturated aldehydes (malondialdehyde and acetylacetaldehyde), the analogous coupling constants for  $\overset{24}{\sim}$  and  $\overset{25}{\sim}$  have been estimated by n.m.r. to be about 7.7 and 2.8 c.p.s., respectively (39). If it could be con-



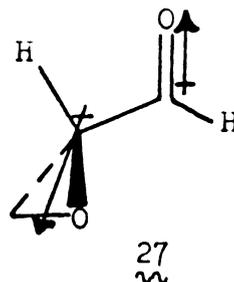
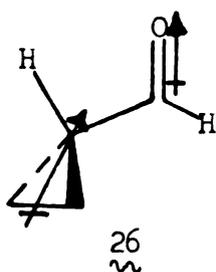
sidered that the 0.9 c.p.s. value for  $J_c$  ( $\overset{23}{\sim}$ ) of dichloroacetaldehyde is an upper limit, then a threefold rather than a twofold barrier to rotation best fits the experimental data. However, the above conclusion may be questioned due to the possibility of the potential well of  $\overset{23}{\sim}$  being quite broad, as in fluoroacetyl fluoride (28), in which case contributions to  $J_c$  from torsional oscillations would make it appear much smaller than it really is.

From the above discussion, the question of a twofold or threefold barrier to rotation is still unanswered, but it does illustrate the major weakness of n.m.r. in rendering an unambiguous conclusion in such cases of rotational isomerism. Irrespective of a twofold or threefold barrier, the conclusion that  $\overset{21}{\sim}$  is the most stable rotamer in the low dielectric constant solvents would remain valid.

### III. Glycidaldehyde and Cyclopropanecarboxaldehyde

The large vicinal coupling constants of glycidaldehyde and cyclopropanecarboxaldehyde and their decrease with increasing temperature (Table VII) indicate that  $\overset{12}{\sim}$  and  $\overset{11}{\sim}$ , respectively, are the most stable rotamers of these compounds in solution. From the dependence of their

coupling constants on solvent dielectric constant (Table II), it can be concluded that the cyclopropane ring donates electronic charge (26) and the oxirane ring withdraws charge (27). From the per cent change of



of the two coupling constants with solvent polarity, it appears that the two effects (donation and withdrawal of charge) are of the same magnitude. If the per cent decrease (ca 10%) of the coupling constant of glycidaldehyde in going from the least polar solvents to the most polar solvents is compared to those of dichloroacetaldehyde (ca 75%), dibromoacetaldehyde (ca 60%), methoxyacetaldehyde (ca 70%), phenoxyacetaldehyde (ca 70%), chloroacetaldehyde (ca 60%) and bromoacetaldehyde (ca 35%), it may be concluded that the oxirane ring acts as a much weaker electron withdrawing group than expected from an alkoxy group.

a) Twofold or Threefold Barrier to Rotation. Knowing that the most stable rotamers of glycidaldehyde and cyclopropanecarboxaldehyde in solution are  $\overset{\sim}{12}$  and  $\overset{\sim}{11}$ , respectively, it is of interest to determine what the nature of the less stable rotamer is. If the less stable rotamer for cyclopropanecarboxaldehyde is  $\overset{\sim}{11c}$ , then there would be a twofold barrier to rotation and equation 8 would apply. From the available experimental data,  $J_{\text{obsd}}$ ,  $J_t$  and  $J_c$  can be estimated. The smallest experimentally measured vicinal coupling constant for cyclopropanecarboxaldehyde is 4.53 c.p.s. (Table VI) in trans-decalin at 110°. If it is assumed that rotamers  $\overset{\sim}{11}$  and  $\overset{\sim}{11c}$  are equally populated at this temperature, which is a false

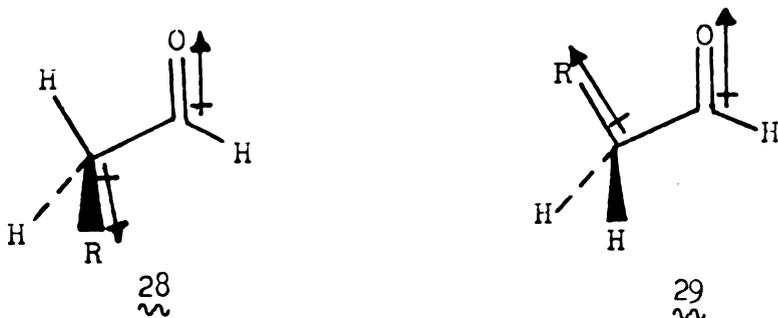
assumption since the coupling constant is still decreasing with increasing temperature, then  $J_{\text{obsd}}$  becomes 4.53 c.p.s. in equation 8. This value of 4.53 c.p.s. would represent an upper limit. The largest experimentally measured coupling constant of this aldehyde is 6.2 c.p.s. (Table II), in formamide at 36°. If this is assumed to be the coupling constant observed for 100% of  $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ , then this value would represent  $J_t$ . Again, this assumption is incorrect and 6.2 c.p.s. represents a lower limit of  $J_t$ . From these two quantities ( $J_t \geq 6.2$  c.p.s. and  $J_{\text{obsd}} \leq 4.53$  c.p.s.) and equation 8,  $J_c$  is calculated to be equal to or smaller than 2.84 c.p.s. From the  $J_t$  values of aliphatic aldehydes (23) and  $\alpha, \beta$ -unsaturated aldehydes (38, 39), the  $J_t$  of cyclopropanecarboxaldehyde may be estimated to be between 7.0 - 7.7 c.p.s. If this is true, then  $J_c$  would be between 1 - 2 c.p.s. As discussed in the section on consideration of a twofold barrier for the dihaloacetaldehydes, the decision of whether such relative values of  $J_t$  and  $J_c$  are reasonable or not is a difficult one to make. Since the more accurate and reliable microwave and electron diffraction techniques have shown that cyclopropanecarboxaldehyde (16), cyclopropyl methyl ketone (46), cyclopropanecarboxylic acid chloride (46) and cyclopropanecarboxylic acid fluoride (17) exhibit twofold barriers to rotation in the gas phase, it is reasonable to assume that the same will be true for cyclopropanecarboxaldehyde in solution. The weakness of the n.m.r. technique to be used as a tool from which to decide such a question is further illustrated by the opposite conclusions drawn regarding the nature of the barrier to rotation, twofold (47) vs. threefold (48, 49), about the analogous  $\text{sp}^2\text{-sp}^3$  carbon-carbon bond of vinyl cyclopropane.

From the similarity between the vicinal coupling constants of cyclo-

propanecarboxaldehyde and glycidaldehyde and on the basis of the microwave and electron diffraction results just mentioned, it may be also assumed that glycidaldehyde exhibits a twofold barrier to rotation.

#### IV. Effect of Solvent Polarity on Rotamer Stabilities

a) Monosubstituted Acetaldehydes. The increase in the rotamer ratio  $\frac{29}{28}$  reflected in the data of Tables VIII, IX, XI and XII as the dielectric constant of the medium increases, is reasonable in view of the higher dipole moment of  $\frac{29}{\sim}$  over that of  $\frac{28}{\sim}$ . It is also



understandable that this increase would be more pronounced for the rotamers of chloroacetaldehyde than for those of bromoacetaldehyde due to the carbon-chlorine bond being more polar than the carbon-bromine bond. This large difference in the dipole moments of the two rotamers is also responsible for  $\Delta H^\circ$  values being much more negative than the corresponding  $\Delta G^\circ$  values in solvents of high dielectric constant. Increase in temperature decreases the dielectric constant of the solvent. This decrease causes a decrease in the ratio  $\frac{29}{28}$  far more rapid than would be expected and causes the coupling constants to increase rapidly with increasing temperature. The result is the calculation of more negative and hence, inaccurate  $\Delta H^\circ$  values. For this reason, in solvents of high dielectric constant,

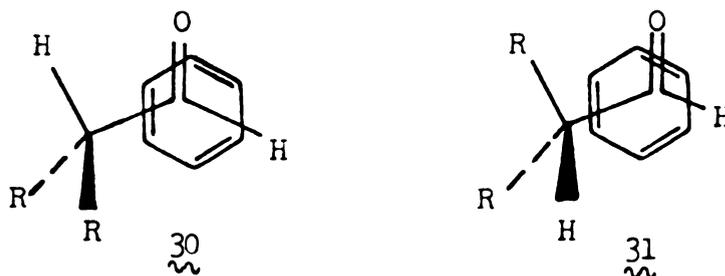
the  $\Delta G^\circ$  values reflect the enthalpy differences to a better degree between rotamers whose dipole moments differ greatly, than do the calculated  $\Delta H^\circ$  values. The only meaningful  $\Delta H^\circ$  values calculated for such rotamers by the temperature dependence of the spin-spin coupling constants are those in solvents of low dielectric constant. Since in trans-decalin,  $\Delta H^\circ \approx \Delta G^\circ$  for monohaloacetaldehydes, the argument that  $\Delta S^\circ$  between rotamers  $\underset{\sim}{18}$  and  $\underset{\sim}{19}$  is zero is indeed valid.

As expected, whereas methoxyacetaldehyde and phenoxyacetaldehyde behave similarly to the haloacetaldehydes, methylmercaptoacetaldehyde does not. The effect of solvent on the enthalpy and free energy differences (Tables XIII and XII, respectively) between the rotamers of methylmercaptoacetaldehyde is not very pronounced and is probably due to the similar polarities of rotamers  $\underset{\sim}{18}$  and  $\underset{\sim}{19}$ .

b) Dihaloacetaldehydes. The increase of the relative stability of rotamer  $\underset{\sim}{22}$  over that of  $\underset{\sim}{21}$  with increasing dielectric constant of the solvent is shown in Tables XVI, XVII and XVIII. In view of the higher dipole moment of  $\underset{\sim}{22}$ , this trend is predictably reasonable, and parallels that observed for methoxyacetaldehyde, phenoxyacetaldehyde and the monohaloacetaldehydes. This large difference in the dipole moments of the rotamers is also responsible for  $\Delta H^\circ$  values being more negative than the corresponding  $\Delta G^\circ$  values in solvents of high dielectric constant.

The inadequacy of the solvent dielectric constant effect to explain all the changes observed in the  $\Delta G^\circ$  values has already been mentioned while discussing the aromatic solvents benzene and toluene. On the basis of the low dielectric constant of these solvents, it would have been expected that  $\underset{\sim}{21}$  would be more stable than  $\underset{\sim}{22}$  rather

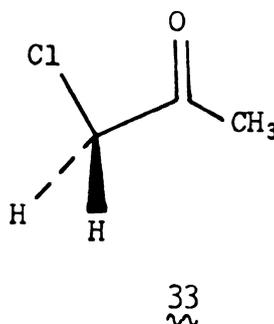
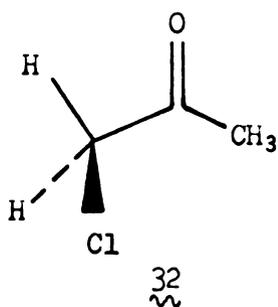
than the reverse which was found experimentally. This reverse effect observed in the aromatic solvent is best interpreted in terms of solute-solvent interactions that destabilize  $\underline{21}$  with respect to  $\underline{22}$ . Some sort of stereospecific association (50), such as pictured in  $\underline{30}$  and  $\underline{31}$ , could rationalize the results in terms of stronger non-bonded repulsions between benzene and halogen in  $\underline{30}$  than in  $\underline{31}$ .



## V. Comparison of Results with Other Systems

a) Monosubstituted Case. The conclusion from the infrared studies (24) that chloroacetaldehyde exists essentially in conformation  $\underline{18}$  is certainly in disagreement with the n.m.r. results here. In fact,  $\underline{18}$  is the major rotamer, about 55%, only in the low dielectric constant hydrocarbon solvents and in carbon tetrachloride. If the degeneracy factor of two that favors  $\underline{18}$  over  $\underline{19}$  is removed, than  $\underline{18}$  would be less stable than  $\underline{19}$  by about 300 cal/mole even in these low dielectric constant solvents.

The suggested nonbonded repulsions (24) between chlorine and carbonyl oxygen cannot be a controlling factor of the relative stabilities of  $\underline{18}$  and  $\underline{19}$ . It was found (1) that for chloroacetone in the liquid state ( $\epsilon \sim 30$ ),  $\underline{32}$  and  $\underline{33}$  are of comparable stability. It was suggested (7) that  $\underline{32}$  might have been more stable had it not been



for the nonbonded repulsions between the gauche chlorine and the methyl. However, if this interpretation were correct, then chloroacetaldehyde would have been expected to exist predominately in  $\overset{18}{\sim}$  rather than  $\overset{19}{\sim}$ , as the gauche chlorine-methyl interactions in chloroacetone are absent in chloroacetaldehyde. If these nonbonded interactions between the gauche chlorine and methyl groups of chloroacetone are affecting the rotamer stabilities, then to account for the results, these interactions would have to be attractive rather than repulsive.

The enthalpy differences (Table X) for  $\overset{18}{\sim} \rightleftharpoons \overset{19}{\sim}$  of bromoacetaldehyde are shown to be less negative by 300 cal/mole than the corresponding  $\Delta H^\circ$  for chloroacetaldehyde (trans-decalin). This observation mitigates against the polarizability of the R group (dipole-induced dipole interactions) being very important in controlling the ratio  $\overset{18}{\sim} / \overset{19}{\sim}$ . Also, if one were to consider that in these low dielectric constant solvents ( $\epsilon \sim 2$ ), the electrostatic dipole-dipole interactions would destabilize  $\overset{19}{\sim}$  of chloroacetaldehyde more than  $\overset{19}{\sim}$  of bromoacetaldehyde with respect to their other rotamers.

Summarized in Table XIX are the energy differences (either in low dielectric constant solvents or in the gaseous state) between the rotamers of  $RCH_2COY$  compounds, where R is halogen. In all cases,

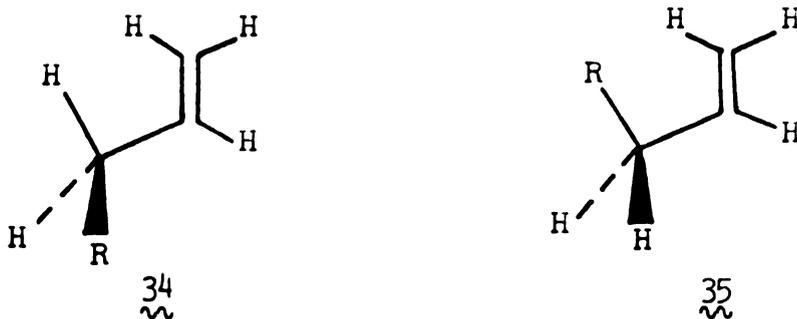
TABLE XIX. ENERGY DIFFERENCES BETWEEN ROTAMERS OF SOME RELATED SYSTEMS<sup>a</sup>

1 ~	System	2 ~	R	$\Delta H^\circ$ , cal/mole	Method	Reference
	$\rightleftharpoons$		Cl	-350	NMR	This work
	$\rightleftharpoons$		Br	0	NMR	This work
	$\rightleftharpoons$		F	-560	IR	8
	$\rightleftharpoons$		Cl	-500	IR	8
	$\rightleftharpoons$		Br	0	IR	8
	$\rightleftharpoons$		Cl (Y = Cl)	ca -1200 <sup>b</sup>	Raman & IR	5
	$\rightleftharpoons$		Br (Y = Cl)	-1000	Raman & IR	1
	$\rightleftharpoons$		Br (Y = Br)	-1900	Raman & IR	1
	$\rightleftharpoons$			-910	Microwave	28

<sup>a</sup>These values are either in low dielectric constant solvents, such as pentane and  $\text{CCl}_4$ , or in the gaseous state. <sup>b</sup>Estimated from ref 5.

except fluoroacetyl fluoride, the results have been interpreted in terms of a threefold rather than twofold barrier about the  $sp^2-sp^3$  carbon-carbon bond. In all cases,  $\Delta H^\circ$  for  $1 \rightleftharpoons 2$  is negative or zero. The only exception appears to be N-methylchloroacetamide (7), where  $\Delta H^\circ$  is quite positive. It is impossible to decide from the published results (1, 2, 3, 4) whether  $\Delta H^\circ$  for  $1 \rightleftharpoons 2$  of the monohaloacetones is positive or negative in the gaseous state, although it appears that it is negative in the liquid state.

Minor differences of the results may be explained in terms of nonbonded and dipole-dipole electrostatic interactions. For example, substitution of bromine for chlorine in the monohaloacetaldehydes and in the ethyl acetates (8) causes  $\Delta H^\circ$  for  $1 \rightleftharpoons 2$  to become more positive. This same trend has been observed in the 3-halopropenes, where  $\Delta H^\circ$  for  $34 \rightleftharpoons 35$  is -100 cal/mole for 3-fluoropropene (19, 26), +100 cal/mole for 3-chloropropene (20) and progressively more positive in 3-bromopropene and 3-iodopropene (9, 27). The best rationalization of these results is increase in the nonbonded repulsions between halogen and

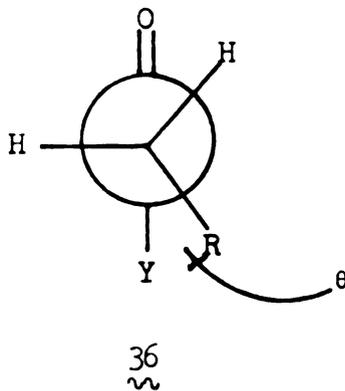


oxygen (or methylene) in rotamer 2 (or 35) as the size of the halogen increases.

The observation that the  $\Delta H^\circ$  values of the haloacetaldehydes are less negative than those of the ethyl acetates (8) and haloacetyl halides

(1, 4, 5, 28) can be explained in terms of dipole-dipole interactions. The difference between the dipole moments of  $\overset{\sim}{1}$  and  $\overset{\sim}{2}$  would be greater for the haloacetaldehydes than the haloesters and haloacetyl halides. The ratio of  $\overset{\sim}{1}/\overset{\sim}{2}$  would then be smaller for the haloacetaldehydes than the haloesters and haloacetyl halides. This same argument (7) has been used to partly explain the differences in the relative stabilities of the rotamers of chloroacetyl chloride, chloroacetone and N-methyl-chloroacetamide.

Nonbonded interactions between the gauche groups R and Y in rotamer  $\overset{\sim}{1}$  have been used (28) to explain why fluoroacetyl fluoride exhibits a twofold barrier to rotation, when all other haloacetyl halide studies exhibit a threefold barrier to rotation. As shown in  $\overset{\sim}{36}$ , when both R and Y groups are the small fluorine atoms, the repulsion between them is very small and, hence,  $\theta = 0^\circ$ . However, when

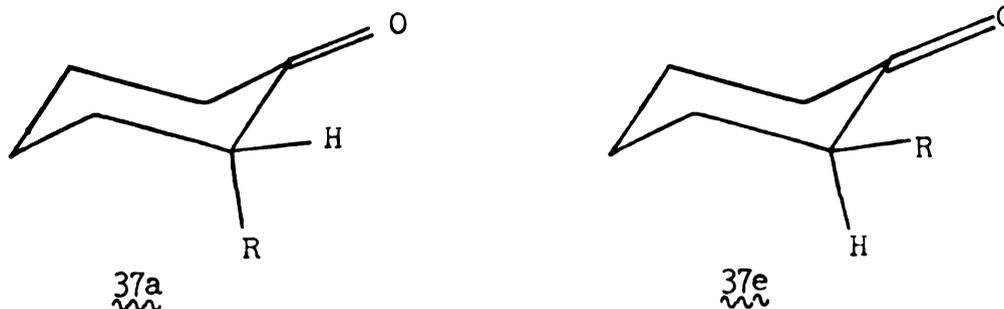


they are the larger atoms chlorine and bromine, the nonbonded repulsions change the equilibrium configuration to  $\theta = 30^\circ$  (1, 4).

Even though these arguments show some success in rationalizing some of the trends observed, they are still inadequate to explain why, in most cases,  $\overset{\sim}{2}$  is so much more stable than  $\overset{\sim}{1}$ .

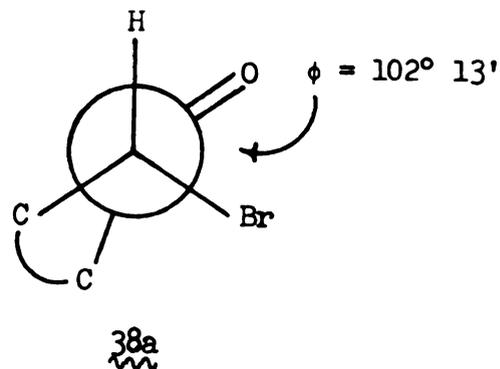
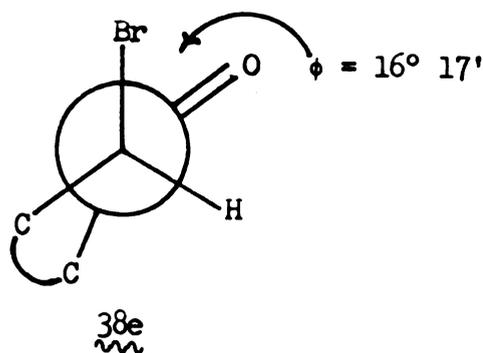
b) Monohaloacetaldehydes vs 2-halocyclohexanones. Several investigations (25) have established that the ratio  $\overset{\sim}{37a}/\overset{\sim}{37e}$  increases when R is

changed from fluorine to chlorine to bromine. In solvents of low

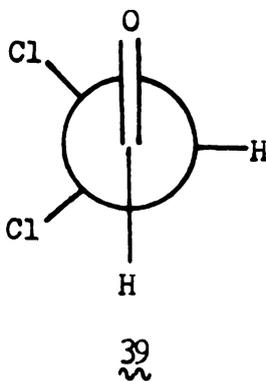


dielectric constant (51), when R is fluorine, the equatorial rotamer is more stable than the axial (25d, f) and when it is chlorine or bromine, the axial rotamer is more stable (24a-c, f). In hydrocarbon solvents, the free energy difference,  $\Delta G^\circ$ , for  $\text{37a} \rightleftharpoons \text{37e}$  was found (25f) to be -170 cal/mole, +740 cal/mole and +1280 cal/mole for 2-fluorocyclohexanone, 2-chlorocyclohexanone and 2-bromocyclohexanone, respectively. The corresponding values calculated (25f) by taking into account nonbonded, dipole-dipole and dipole-induced dipole interactions were +1130, +1130 and +1100 cal/mole. Irrespective of how the results are interpreted, if the same criteria are applied to chloroacetaldehyde and bromoacetaldehyde, the  $\Delta H^\circ$  values for  $\text{18} \rightleftharpoons \text{19}$  would turn out to be similar to those of 2-chlorocyclohexanone and 2-bromocyclohexanone. However, the experimental values are -300 and about +40 cal/mole for chloroacetaldehyde and bromoacetaldehyde, respectively. It seems therefore, that the basic factor, in addition to all those discussed, controlling rotamer stabilities, might be the same one restricting the barrier to rotation about carbon-carbon single bonds and also associated with the nature of the axial bonds (52). The differences between monohaloaldehydes and 2-halocyclohexanones may very well arise from torsional strain. The dihedral angles calculated (25f) for the equatorial (38e)  $\phi = 16^\circ 17'$ ,

and axial (38a), =  $102^{\circ} 13'$ , bromocyclohexanones are different than those of the corresponding acyclic rotamers 19 and 18. From all indications (1, 4, 5, 28) the corresponding dihedral angles ( $\phi$ ) for 19 and 18 are zero and  $150^{\circ}$ , respectively.



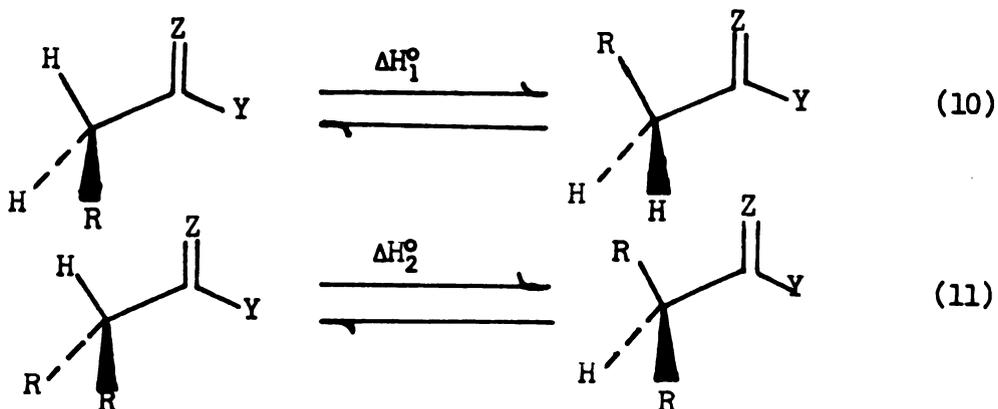
c) Disubstituted Cases. From infrared studies (24), it was suggested that dichloroacetaldehyde exists in essentially one conformation, probably 39. This however, is in disagreement with the n.m.r. results presented here. In low dielectric constant solvents, both 21 and 22 (or 39) are



present in about equal concentrations if the degeneracy of 22 is not taken into account.

Comparison of monochloroacetaldehyde with dichloroacetaldehyde shows that whereas the rotamer with the hydrogen eclipsing the carbonyl group is more stable for dichloroacetaldehyde in saturated hydrocarbon solvents,

it is the less stable one in monochloroacetaldehyde, i.e.,  $\Delta H_1^\circ - \Delta H_2^\circ$  (equations 10 and 11) is negative. Summarized in Table XX are several



$\Delta H_1^\circ - \Delta H_2^\circ$  values for related systems, either in the gas phase or in solvents of low dielectric constant. In all cases, the  $\Delta H_1^\circ - \Delta H_2^\circ$  values are negative and of comparable magnitude.

In the case of the halopropenes, no. 6 and 7, the differences were attributed (19, 20) to less favorable van der Waals attractions between halogen and hydrogen of the methylene group in 7 than in 6 due to the C-R bond being less polar in 7 than in 6. This explanation would lead to the opposite results for no. 1 - 5, unless it was applied only to 1 and 6. A possible explanation for 1 - 5 would be electrostatic dipole-dipole interactions that favor 1 over 2 and 6 over 7. The dipole moment difference for 6 and 7 would be much larger than between 1 and 2 and would lead to a greater energy difference between 6 and 7 than between 1 and 2.

TABLE XX. COMPARISON OF ENTHALPIES<sup>a</sup> BETWEEN MONOHALOSUBSTITUTED AND DIHALOSUBSTITUTED SYSTEMS

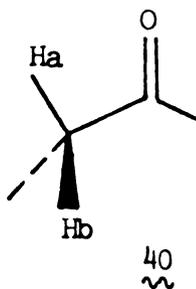
No.	Systems	$\Delta H_1^\circ - \Delta H_2^\circ$ (cal/mole) <sup>b</sup>	Reference
1	CH <sub>2</sub> ClCHO <u>vs</u> CHCl <sub>2</sub> CHO	-600	This work
2	CH <sub>2</sub> BrCHO <u>vs</u> CHBr <sub>2</sub> CHO	-500	This work
3	CH <sub>2</sub> FCO <sub>2</sub> Et <u>vs</u> CHF <sub>2</sub> CO <sub>2</sub> Et	-500	8
4	CH <sub>2</sub> ClCO <sub>2</sub> Et <u>vs</u> CHCl <sub>2</sub> CO <sub>2</sub> Et	-500	8
5	CH <sub>2</sub> ClCOCl <u>vs</u> CHCl <sub>2</sub> COCl	<u>ca</u> -1200 <sup>c</sup>	5,6
6	CH <sub>2</sub> FCH=CH <sub>2</sub> <u>vs</u> CHF <sub>2</sub> CH=CH <sub>2</sub>	-600 to -1500	19,26
7	CH <sub>2</sub> ClCH=CH <sub>2</sub> <u>vs</u> CHCl <sub>2</sub> CH=CH <sub>2</sub>	-700	20

<sup>a</sup>The enthalpies are either in the gas phase or in low dielectric solvents.

<sup>b</sup>For  $\Delta H_1^\circ$  and  $\Delta H_2^\circ$  see text, equations 10 and 11. <sup>c</sup>The enthalpy for the monohalo compound was estimated from the data of reference 5.

## B. Chemical Shifts

The chemical shift data for the monosubstituted and disubstituted acetaldehydes best agree with model 17, rather than 16. The latter model would predict that  $H_a$ , (40) in the plane of the carbonyl group, would be deshielded. The former model would predict the opposite.



From Table VII, it can be seen that in nonaromatic solvents, the chemical shifts of the methylene (or methine) protons move upfield as the polarity of the solvent decreases. From the previous results on the stability of rotamers, it was established that for chloroacetaldehyde, bromoacetaldehyde, dichloroacetaldehyde, dibromoacetaldehyde, methoxyacetaldehyde, phenoxyacetaldehyde and methylmercaptoacetaldehyde the stability of 18 increased with decrease in the dielectric constant. Therefore,  $H_a$  is shielded with respect to  $H_b$ . This shielding effect can be seen graphically in Figs. 8, 9, 10 and 11 for each of the aldehydes. By using the aldehydic and methylene (or methine) chemical shifts in pentane as a reference position, the chemical shifts of these protons in other solvents have been plotted against the per cent population of the rotamer which was obtained from the coupling constant data. The per cent populations plotted for chloroacetaldehyde, bromoacetaldehyde, dichloroacetaldehyde, dibromoacetaldehyde and methylmercaptoacetaldehyde

FIG 8. DEPENDENCE OF THE CHEMICAL SHIFTS OF THE ALDEHYDIC AND METHYLENE PROTONS ON ROTAMER POPULATIONS FOR CHLOROACETALDEHYDE AND BROMOACETALDEHYDE

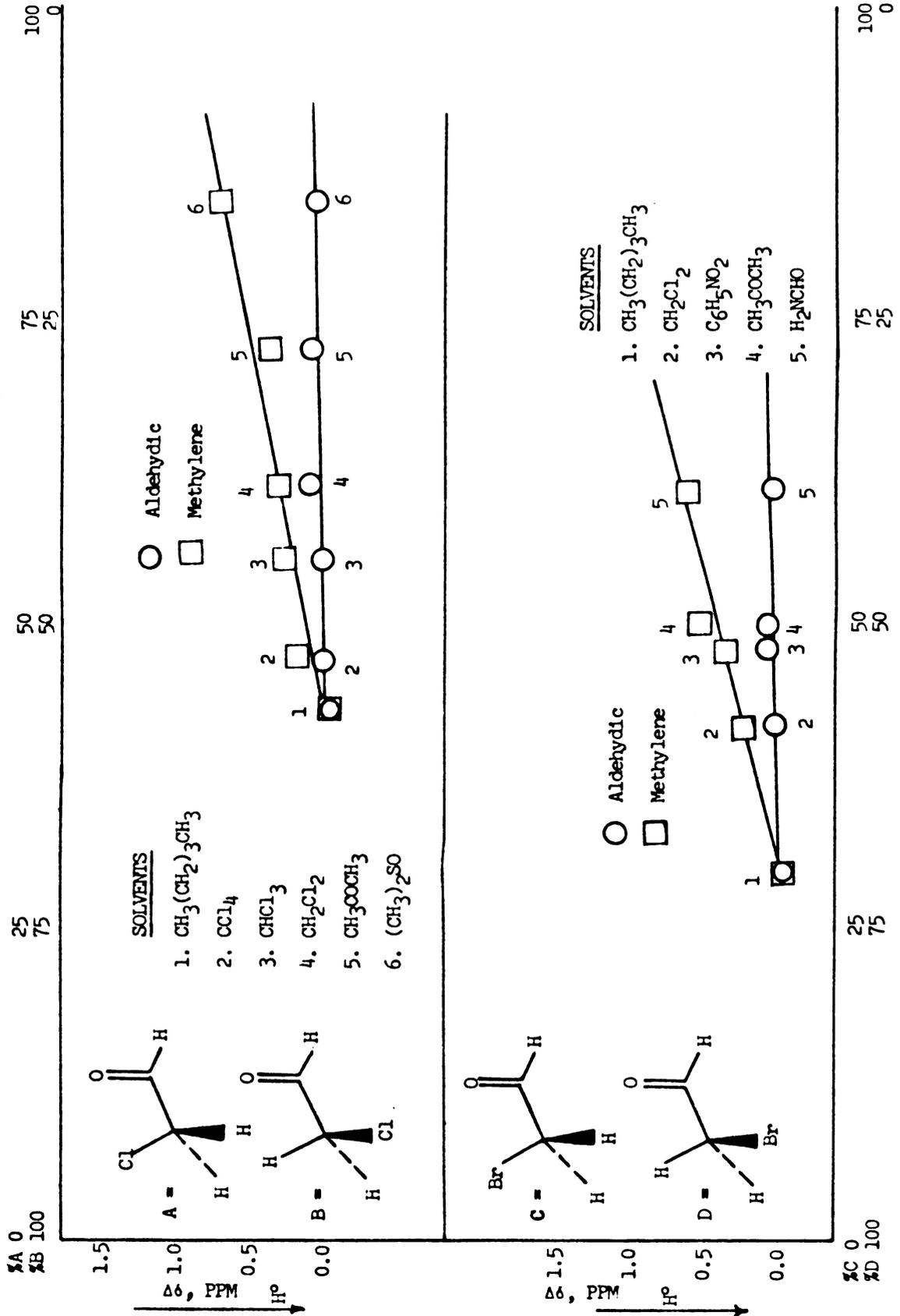


FIG 9. DEPENDENCE OF THE CHEMICAL SHIFTS OF THE ALDEHYDIC AND METHINE PROTONS  
ON ROTAMER POPULATIONS FOR DICHLOROACETALDEHYDE AND DIBROMOACETALDEHYDE

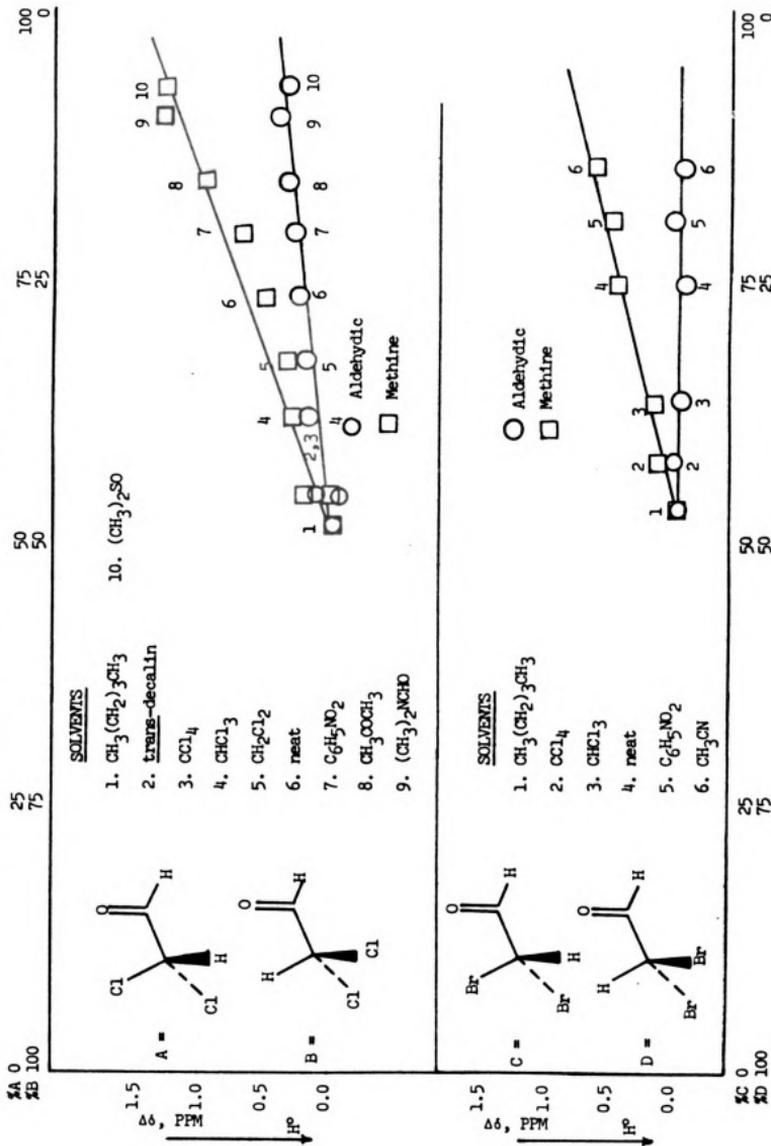


FIG 10. DEPENDENCE OF THE CHEMICAL SHIFTS OF THE ALDEHYDIC AND METHYLENE PROTONS ON ROTAMER POPULATIONS FOR PHENOXYACETALDEHYDE AND METHOXYACETALDEHYDE

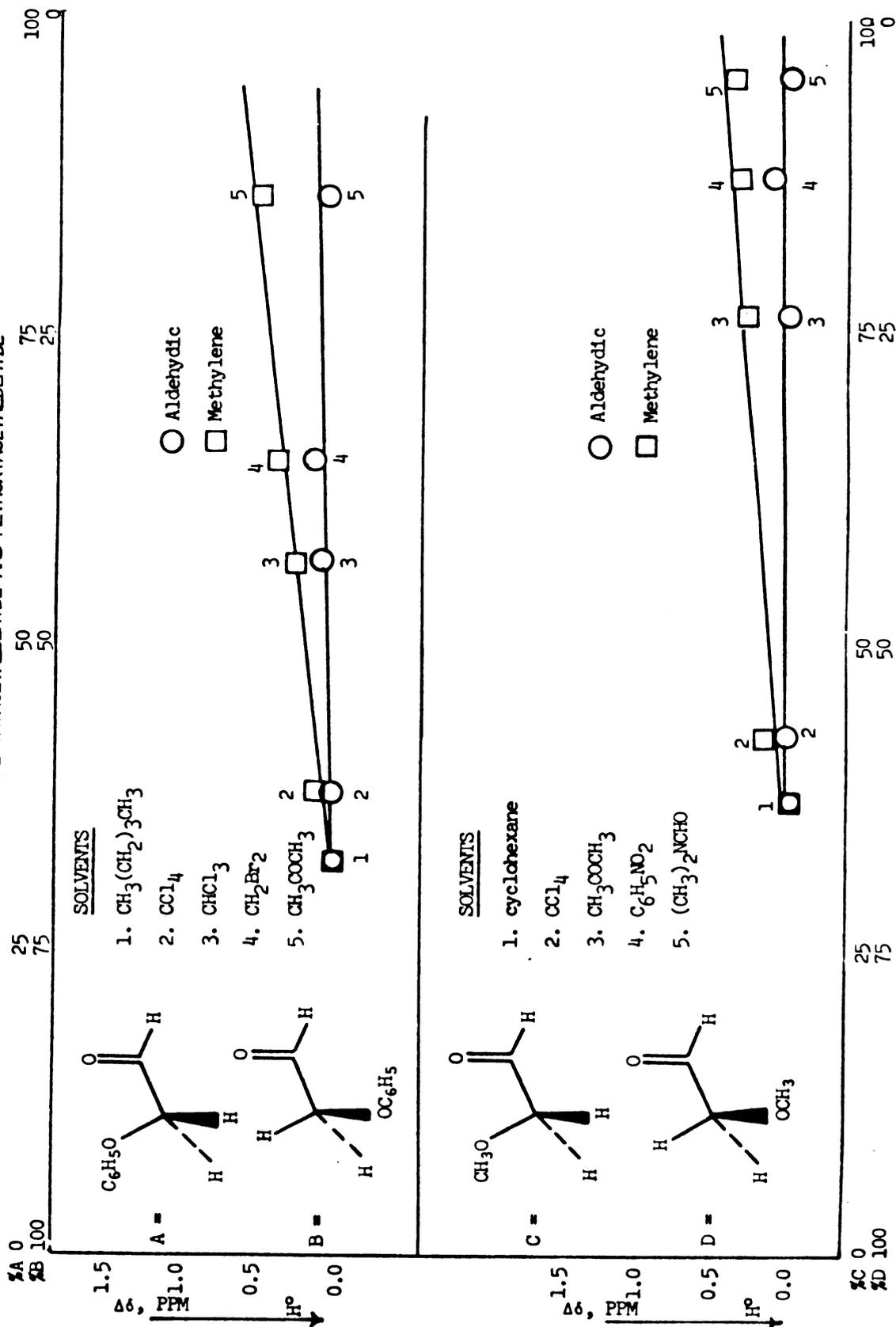
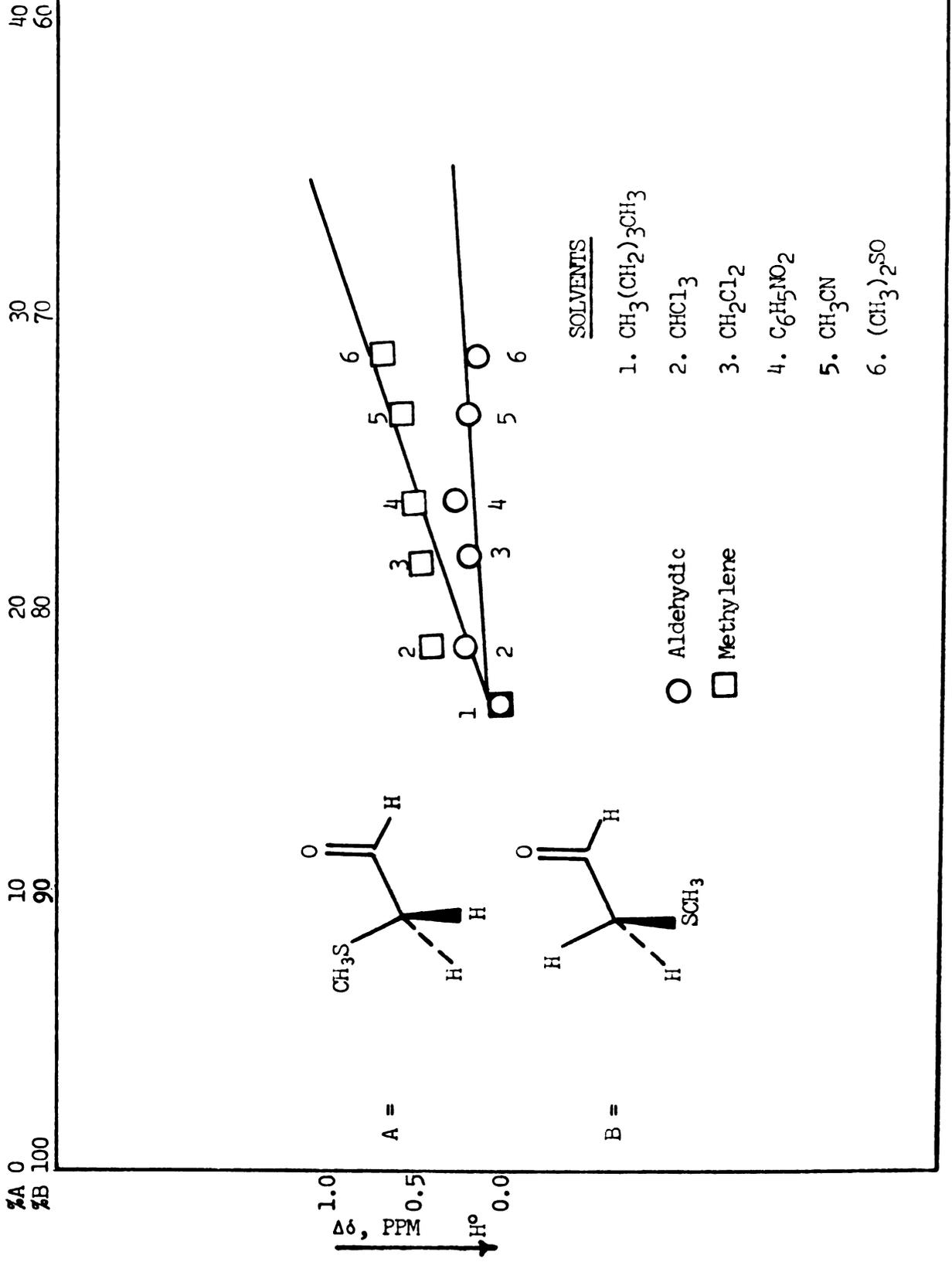


FIG 11. DEPENDENCE OF THE CHEMICAL SHIFTS OF THE ALDEHYDIC AND METHYLENE PROTONS ON ROTAMER POPULATIONS FOR METHYLMERCAPTOACETALDEHYDE



were those calculated from best estimates of  $J_t$  and  $J_g$  (Table VIII, column B and E for chloroacetaldehyde and bromoacetaldehyde, respectively; Table XII, column C for methylmercaptoacetaldehyde; Table XVII, column B and E for dichloroacetaldehyde and dibromoacetaldehyde, respectively). The upper limit per cent populations were used for methoxyacetaldehyde and phenoxyacetaldehyde (Table XII, column A' and A, respectively).

## EXPERIMENTAL

### A. Reagents and Compounds

All aldehydes used in this research were purified by either distillation or preparative gas chromatography immediately prior to use. Dichloroacetaldehyde (Columbia Organic Chemical Co.), methoxyacetaldehyde (Jefferson Chemical Co.), and glycidaldehyde (Aldrich Chemical Co.) were all available commercially. Bromoacetaldehyde diethylacetal and cyclopropyl cyanide were obtained from the Aldrich Chemical Company. Methyl mercaptan was obtained from the City Chemical Corporation.

### B. Solvents

All solvents used in these studies were purified by standard methods (53) and checked for purity by gas chromatography. The purified solvents were stored over molecular sieves in glass stoppered bottles.

### C. Synthesis

#### I. Chloroacetaldehyde

Chloroacetaldehyde was prepared according to a procedure similar to that of Schukina (54). In a flame dried, 50 ml, three-necked, round-bottom flask, equipped with a thermometer, condenser and an adapter allowing the flow of nitrogen and chlorine, was placed 44 g (1.0 mole) of acetaldehyde. The flask was cooled to 15 - 17° and chlorine was passed through the solution at such a rate as to allow the temperature to rise to 39° (refluxing) after about 30 minutes. The addition was maintained for about one extra hour. After the colorless fuming liquid

had been fractionally distilled, the fraction boiling at 80-90° was redistilled under vacuum, b.p. 24-26° (3.0 mm). The fresh distillate was then placed in the freezer section of a refrigerator and was allowed to stand for two to four days, until a white solid had formed. The white solid, presumably the trimer of chloroacetaldehyde, was dried under vacuum at room temperature to yield about 2.0 g (2.5%) of material. Cautious heating of the solid, either at atmospheric pressure or under vacuum, yielded pure chloroacetaldehyde, which was used immediately, as it resolidified on standing.

## II. Bromoacetaldehyde

The procedure of Yanovskaya, Terentiev and Belenskiy (55) was followed. To 200 g (194 ml) of freshly distilled dioxane in a 1-l. flask, maintained at 0° with an ice-bath, was added with stirring 360 g (2.0 mole) of bromine. The resulting hot dark brown solution was poured, with stirring, into 500 ml of ice and water. A crystalline, orange precipitate (dioxane-bromine complex) was collected and dried on a Büchner funnel. After 300 g of the solid was dissolved in ether, two layers formed. Both layers were slowly added through a dropping funnel to a solution of 54 g (1.35 mole) of acetaldehyde in 50 ml of ether maintained at 5-10°. Approximately one hour after addition, the dark red solution turned light yellow. The ether layer was washed first with water, then a 5% sodium carbonate solution and again with water and dried over anhydrous magnesium sulfate. After careful removal of the ether by distillation, the residue was gas chromatographed (preparative chromatography) through a 20% silicon column at 45°. The yield based on preparative chromatography was 31%. The pure bromoacetaldehyde collected was used immediately, as it rapidly decomposed on standing.

### III. Dibromoacetaldehyde

The procedure of Shchukina (54) was followed. To 44 g (1.0 mole) of freshly distilled acetaldehyde maintained at 0° and stirred with a magnetic stirrer was added dropwise 80 g (0.5 mole) of bromine. The reaction mixture was then allowed to come to room temperature. After dropwise addition of another 80 g (0.5 mole) of bromine, the reaction mixture was stirred for 20-25 hours. The resultant two layers were separated and the upper layer was discarded. Prepurified nitrogen was bubbled through the lower layer for about one hour in order to purge it of any hydrogen bromide present. After three to four vacuum distillations, 11.5 g (5.7%) of pure dibromoacetaldehyde was obtained, b.p. 26° (3.0 mm), lit. (54) 137-40°.

### IV. Phenoxyacetaldehyde

The procedure of Dey (56) was followed. Bromoacetaldehyde diethylacetal (65.7 g, 0.33 mole) and an alcoholic solution of sodium phenoxide (31.3 g, 0.33 mole, of phenol, 7.7 g, 0.33 mole, of sodium, 63.3 ml of ethanol) were heated at 150-60° in an autoclave for four hours. The white solid in the pale solution was filtered and the solvent of the filtrate was removed by vacuum distillation. The residue was poured into water and an oily product separated which was extracted with ether. The ether layer was dried with anhydrous magnesium sulfate and the ether was evaporated. Distillation of the residue gave 55 g (78.6%) of phenoxyacetaldehyde diethylacetal, b.p. 117° (3.0 mm), lit. (56) 132-34° (10.0 mm).

Phenoxyacetaldehyde diethylacetal (20.0 g, 0.01 mole) was mixed with 120 ml of 10% sulfuric acid, refluxed at 80° and distillate was collected up to 90°. The residue was cooled, extracted with ether and

the ether layer dried with anhydrous magnesium sulfate. The ether was evaporated and the residue was vacuum distilled to give 5.0 g (38.6%) of phenoxyacetaldehyde, b.p.  $90^{\circ}$ , (7.0 mm), lit. (56)  $105^{\circ}$  (10.0 mm).

#### V. Cyclopropanecarboxaldehyde

Cyclopropanecarboxaldehyde was prepared according to the procedure of Brown (57). In a 1-l., three-necked, round-bottomed flask, equipped with a condenser, dropping funnel and stirrer, was placed 11.4 g (0.3 mole) of lithium aluminum hydride in 300 ml of ether. A nitrogen atmosphere was maintained throughout the reaction. To this stirred solution, 66.6 g (0.9 mole) of 1-butanol was added dropwise over a period of seventy-five minutes at a temperature of  $-10$  to  $-5^{\circ}$ . The reaction was stirred for another fifteen minutes. To this reaction at  $-10^{\circ}$ , 20.1 g (0.3 mole) of cyclopropyl cyanide was added dropwise over a period of fifteen minutes with a temperature rise up to  $8^{\circ}$ . The reaction was stirred for an additional hour at  $0^{\circ}$  and then decomposed by 300 ml of 5N sulfuric acid. The ether layer was separated and the heterogeneous layer was extracted three times with 25 ml portions of ether. The combined ether extracts were washed with sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. The ether was concentrated by distillation and the distillate extracted with 130 ml of sodium bisulfite solution (40%) to remove as adduct any aldehyde which may have passed over with the ether. Finally, this solution was used to make the adduct of the aldehyde. This adduct was extracted four times with 35 ml portions of ether to remove 1-butanol. The solution was decomposed by 42 g of sodium bicarbonate suspended in 50 ml of water at  $0^{\circ}$ . Cyclopropanecarboxaldehyde was steam distilled and the distillate extracted with ether and dried with anhydrous magnesium sulfate. The ether was evaporated and 4.3 g (20.6%) of

cyclopropanecarboxaldehyde was obtained after distillation, b.p. 95-97°, lit. (57) 97-98°.

#### VI. Methylmercaptoacetaldehyde

The procedure of Wick (58) was followed. Bromoacetaldehyde diethylacetal (51.2 g, 0.26 mole) was added dropwise to a solution of sodium mercaptide (11.0 g, 0.48 mole, of sodium, 120 ml of ethanol, 25.2 g, 0.53 mole, of methyl mercaptan) chilled in a dry ice bath. The mixture was allowed to come to room temperature and was heated at 50-60° for one hour. The mixture was then allowed to stand at room temperature overnight. An orange solution was obtained with a white solid which was filtered. The filtrate was diluted with water to twice its volume, extracted with ether and the ether layer dried with anhydrous magnesium sulfate. The ether was evaporated and the residue was vacuum distilled to give 23.1 g (54.2%) of methylmercaptoacetaldehyde diethylacetal, b.p. 53-55° (10.0 mm), lit. (58) 55° (10.0 mm).

Methylmercaptoacetaldehyde diethylacetal (25.0 g, 0.15 mole) and 50 ml of 1% hydrochloric acid were refluxed at 80° and distillate collected up to 86°. The mixture was allowed to cool to room temperature and was extracted with ether and the ether layer was dried with anhydrous magnesium sulfate. The ether was evaporated and the residue was vacuum distilled to give 4.0 g (29.2%) of methylmercaptoacetaldehyde, b.p. 26-27° (8.0 mm), lit. (58) 35° (10.0 mm).

#### D. N.M.R. Spectra

All samples measured were 5% vol/vol using purified solvents. Nuclear magnetic resonance spectra were determined at 60-Mc on a Varian Associates Model A-60 Analytical Spectrometer (Varian Associates, Palo Alto, Calif.). Undegassed samples were run with tetramethylsilane (TMS) as an internal

standard. Coupling constants ( $J$ ) were recorded at a 50 c.p.s. sweep width. The recorded coupling constants were averages of seven to ten measurements and were calibrated against known values of acetaldehyde (36, 37). Chemical shifts were obtained at a sweep width of 1000 c.p.s. and were calibrated against a known sample of tetramethylsilane (0.0 c.p.s.), cyclohexane (86.0 c.p.s.), acetone (126.7 c.p.s.), 1,1,1-trichloroethane (164.0 c.p.s.), dioxane (217.0 c.p.s.), methylene chloride (318.0 c.p.s.), and chloroform (439.8 c.p.s.). Temperature studies were carried out using a Varian Associates V-6040 Variable Temperature Controller with an accuracy of  $\pm 2^\circ$ .

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