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VIBRATIONAL ANALYSIS OF O-BENZYNE

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By

Hak-Hyun Nam

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A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

ABSTRACT

VIBRATIONAL ANALYSIS OF O-BENZYNE

By

Hak-Hyun Nam

The infrared spectrum of o-benzyne was obtained via uv matrix isolated phthalic anhydride. Two photolysis of additional frequencies, 1355 and 1395 cm⁻¹, which matches coordinate calculation well were found the normal in addition to all of the frequencies previously reported by Dunkin and MacDonald. Attempts to obtain Raman spectra of this transient species were not successful. The normal coordinate calculation was performed for $o-C_6H_4$ and $o-C_6D_4$ with the experimental data , and with the G-matrix based on a theoretically-calculated molecular geometry. The proposed vibrational force field reproduces experimental infrared frequencies within 2% for in-plane motions and 0.4% for outof-plane fundamentals. In general the stretches of the strained ring system are stiffer and the bends are more pliant than those of benzene. Bond length/bond strength correlations are not strictly followed; this is explicable in terms of pi-electron overlap populations.

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1. Introduction

Benzyne, or bisdehydrobenzene $(C_{4}H_{4})$, is of great chemical interest because of its likely participation as a transient intermediate in organic reactions.¹ Only the ortho isomer (1,2-dehydrobenzene) has been isolated for spectroscopic study, 2^{-4} although theoretical calculations of all three isomers at several levels of sophistication have been reported.⁵⁻⁹ There is now general agreement that the ortho isomer is the most stable, and that it has a singlet ground electronic state. A normal coordinate analysis of obenzyne has been reported ' which is in moderately good agreement with the observed vibrational data.

The first infrared spectrum of o-benzyne (hereafter simply termed benzyne) was reported by Chapman and coworkers 1973.2 photolyzed in They the precursor benzocyclobutenedione, isolated in an Ar matrix at 8 K, with UV light to obtain eight bands in the 400 - 1700 cm⁻¹ range which were attributable to benzyne. One additional band (2085 cm^{-1}) was found two years later by the same group,³ following short wavelength photolysis of 3diazobenzofuranone under similiar matrix conditions. On the basis of those results, Laing and Berry proposed a structure and a set of force constants for benzyne.10 Badger's rule

was used to deduce the $C_{2\sim}$ symmetry geometry, and the complete vibrational spectra of the normal and perdeuterated molecules were calculated. Among the significant predictions was the expectation of two C-C ring stretching modes of A₁ symmetry in the 2000 - 2500 cm⁻¹ region for each isotopomer.

Subsequently, Dunkin and McDonald obtained improved IR spectra of benzyne and tetradeuteriobenzyne by UV photolysis of phthalic anhydride and its perdeuterated analog, isolated in N₂ matrices at 12 K.⁴ The C₆H₄ spectrum reported by the Chapman grouf was generally confirmed, with the addition of a C-H stretch at 3088 cm⁻¹ and the exception of a band previously observed at 1627 cm⁻¹ . Eleven bands were reported for C₆D₄; agreement between observed⁴ and predicted¹⁰ frequencies was reasonably good below 2000 cm⁻¹, but rather poor in the critical higher wavenumber region. Reevaluation of the benzyne force field was suggested, and the normal coordinate analysis of reference 10 was criticized in an independent MNDO study by Dewar, et al. published in the same year.¹¹

Indeed, fatal mistakes were found in ref. 10 by Nam and Leroi¹²: (1)an incorrect proposed geometry for o-benzyne - the $C_{2\nu}$ hexagon was not properly closed; (2) illogical methodology in the calculation (e.g. arbitrary change in force constants from known models, inconsistent calculations

of the G matrix); (3) inconsitencies in the isotopic product rule between calculated $C_{\Delta}H_{4}$ and $C_{\Delta}D_{4}$ vibrations.

The physical data pertaining to benzyne are rather sparese in view of its importance and also the vibrational spectra are not yet complete. This thesis describes further experimental and theoretical work on o-benzyne; two additional bands of benzyne in mid-infrared region obtained by the photolysis of phthalic anhydride (reproduction of Dunkin and MacDonald's work) and a complete reanalysis of the normal coordinate calculation for this important molecule has been made. Measurement of Raman fundamentals was attempted unsuccessfuly.

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2. Experimental

Phthalic anhydride was isolated in N_{2} matrices by simple sublimation into a Displex cryogenic refrigerator as shown in Figure 1. The ratio of phthalic anhydride to nitrogen gas could not be measured exactly, but it is believed to be higher than about 1:300. To determine this ratio pure phthalic anhydride was sublimed for 90 minute and deposited onto the cold CsI window. The weight of the substrate was measured before and after deposition. The weight increase gives the quantity of phthalic anhydride deposited in the inert gas matrix for a compared deposition time. The flow of nitrogen gas was regulated at 2 mM per minute. In this manner matrix-to-solute ratio could be measured approximately.

After recording the infrared spectrum of pure phthalic isolated in N₂ matrix with a Bomem model DA3 anhydride FT-IR, subsequently it was photolyzed with a 200 W mercury-Xenon arc lamp through a water filter . The spectrum of the photolyzed sample was then recorded under the same its precusor. After about 30 conditions minute of as photolysis the matrix began to develop a pale yellowish color matrix and the IR showed a remarkable increase in

intensity at 2348 cm⁻¹,the stretching frequency of carbondioxide, yet no other bands were appreciably enhanced. Frequency at 2140 cm^{-1} , corresponding to the carbonmonoxide - the product of photolysis, was appeared visibly after an hour later. At this time the band at 2082 cm⁻¹. corresponding to carbon-carbon triple bond stretch of obenzyne, began to show up. Figure 2 shows the spectra of phthalicanhydride/N₂ matrix and its photolyzed products after 2 hours of irradiation. The bands due to benzyne are marked by a triangle at the top of the spectra. Identification of those bands made from comparison with the spectrum of the annealed sample (Figure 3), and with the values given by normal coordinate analysis (Tables 4, 6).

In general all the bands reported by Dunkin and MacDonald were confirmed, with the addition of bands at 1355 and 1395 cm⁻¹ which agree very well with the normal coordinate calculation. Among five bands over 2000 cm⁻¹, only two bands, at 2082 and 2090 cm⁻¹ were reproducible for all experiments. Small peaks at 2060, 2067 and 2110 cm⁻¹ may be attributable to site splitting of the two strong bands at 2082 and 2090 cm⁻¹. The band at 2090 cm⁻¹ may be due to a ketene species, which is one of the possible products of the photolysis.²

To find the A_2 frequencies of benzyne, a very crucial source of information to understand the character of C-C



triple bond, Raman experiments were performed with two different type of sample cell as shown in Figure 4. Unfortunately, no attemps were successful due to the extremely weak signals for matrix isolated species.

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				-
wavenumber	DM*	<u>Ch**</u>	calc***	L
470	472	469	482	-
739	743	735	743	
848	847	849	845	
1038	1039	1038	1039	
1055	1056	1053	1052	
1355			1360	
1395			1391	
1448	1448	1451	1450	
1596	1598	1607	1599	
2082	2084	2085	2092	

Table 1. The observed wavenumbers of orbenzyne in this work

Reference 4 ×

** Reference 2 *** Section 3

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FIG. 1 SAMPLE CELL FOR MATRIX ISOLATION IR EXPERIMENT



FIG. 2 SPECTRA OF PHTHALICANHYDRIDE AND ITS PHOTOLYZED PRODUCTS

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The bands due to o-benzyne are marked by triangle while cross indicates the bands due to other products.



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FIG. 4 SAMPLE CELLS FOR MATRIX ISOLATION RAMAN EXPERIMENT



3. Normal Coordinate Analysis of o-Benzyne

3.1 Coordinates and Structural Parameters.

The problem was set up in internal valence coordinates. Figure 5 shows the internal coordinates for in-plane and out-of-plane vibrations of the planar cyclic molecule. Coordinates labeled t. are C-C stretches, the α_1 are inplane C-C-C angle bends, the s. are C-H (or C-D) stretches, and the β_1 are the corresponding in-plane C-H (or C-D) rocks. [normalized The a coordinates are linear combinations of the extra ring, adjacent valence angle bends of a given C-H (or C-D) bond.] The 🛃 are C-H (or C-D) outof-plane wags, and the torsional coordinates, $\boldsymbol{\delta}_1$, - numbered consistent with the t₁ stretches - include to be contributions from any C-H (or C-D) bonds attached to the i^{tn} C-C-C frame. Within the C_{2V} point group, the twentyfour fundamental vibrations of benzyne transform as follows: $9A_1 + 4A_2 + 3B_1 + 8B_2$. A₁ and B₂ species represent in-plane normal modes, whereas A_{2} and B_{1} belong to out of plane vibrations; all of the normal modes are Raman-active, but only A_1 , B_1 and B_2 can be observed in the infrared. The symmetry coordinates of benzyne in terms of these four symmetry species are given in Table 2.13

Table 2 Symmetry coordinates for o-benzyne

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<u>^1</u>	A ₂ .	B ₁	^B 2
$T_{15}^{+} = \frac{1}{\sqrt{2}}(t_1 + t_5)$	$\Gamma_{14}^{-} = \frac{1}{\sqrt{2}}(\gamma_1 - \gamma_4)$	$\Gamma_{14}^{+} = \frac{1}{\sqrt{2}}(\gamma_{1}^{+}\gamma_{4}^{-})$	$T_{15}^{-} = \frac{1}{\sqrt{2}}(t_1 - t_5)$
$T_{24}^{+} = \frac{1}{\sqrt{2}}(t_2 + t_4)$	$\Gamma_{23}^{-} = \frac{1}{\sqrt{2}}(\gamma_2 - \gamma_3)$	$\Gamma_{23}^{*} = \frac{1}{\sqrt{2}}(\gamma_{2}^{*}\gamma_{3})$	$T_{24}^{-} = \frac{1}{\sqrt{2}}(t_2 - t_4)$
$T_3 = t_3$	$\Delta_{15}^{+} = \frac{1}{\sqrt{2}} (\delta_1 + \delta_5)$	$\Delta_{15}^{-} = \frac{1}{\sqrt{2}} (\delta_1 - \delta_5)$	$S_{14}^- = \frac{1}{\sqrt{2}}(s_1 - s_4)$
$T_6 = t_6$	$\Delta_{24}^{*} = \frac{1}{\sqrt{2}} (\delta_{2}^{*} \delta_{4}^{*})$	$\Delta_{24}^{-} = \frac{1}{\sqrt{2}} (\delta_2^{-} \delta_4^{-})$	$S_{23}^{-} = \frac{1}{\sqrt{2}}(s_2 - s_3)$
$s_{14}^{+} = \frac{1}{\sqrt{2}}(s_1 + s_4)$	$\Delta_3 = \delta_3$		$A_{16}^{-} = \frac{1}{\sqrt{2}}(\alpha_1 - \alpha_6)$
$s_{23}^{+} = \frac{1}{\sqrt{2}}(s_2 + s_3)$	Δ ₆ = δ ₆		$A_{25}^{-} = \frac{1}{\sqrt{2}}(\alpha_2 - \alpha_5)$
$A_{16}^{+} = \frac{1}{\sqrt{2}}(\alpha_1 + \alpha_6)$			$A_{34}^{-} = \frac{1}{\sqrt{2}}(\alpha_3 - \alpha_4)$
$A_{25}^{+} = \frac{1}{\sqrt{2}}(\alpha_2 + \alpha_5)$			$B_{14}^{+} = \frac{1}{\sqrt{2}}(B_1 + B_4)$
$A_{34}^{+} = \frac{1}{\sqrt{2}}(\alpha_3 + \alpha_4)$			$B_{23}^{+} = \frac{1}{\sqrt{2}}(B_2 + B_3)$
$B_{14}^{-} = \frac{1}{\sqrt{2}}(\beta_1 - \beta_4)$			
$B_{23}^{-} = \frac{1}{\sqrt{2}}(\beta_2 - \beta_3)$			







FIG. 5 INTERNAL VALENCE COORDINATES FOR O-BENZYNE

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FIG. 6 STRUCTURAL PARAMETERS FOR 0-BENZYNE (FROM REFERENCE 6).

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The structural parameters utilized for the benzyne G matrix were taken from the careful review of the calculated geometries of all three isomers published by Noell and Newton; the adopted values are shown in Figure 6. Although there have been numerous theoretical studies of benzyne before and since, the single-determinant 4-31G extended basis geometry given in reference 6 was chosen as most reliable. Other reported structures provided improper ring closure, were predicated on the benzene hexagonal carbon skeleton, or did not specify the bond angles.

3.2 Method of Calculation

The normal coordinate analysis of benzyne was separated into two parts: the in-plane and out-of-plane vibrations. For the planar oscillations the modified valency force field chosen as a model for the in-plane vibrations of benzene by Duinker and Mills¹⁴ was first adopted. Although the benzene parameters are of course not directly applicable to benzyne, the rough calculation of the benzyne in-plane fundamentals from the force constants of C_6H_6 and the geometry of C_6H_4 enables one to identify which experimental frequencies reported by Dunkin and MacDonald⁴ are most likely attributable to in-plane vibrations. There are 17 in-plane modes ($9A_1$, $8B_2$); however of 34 vibrations thus predicted for the two isotopomers studied in reference 4 only 14
observed bands could be readily assigned to in-plane motions.

We therefore tried to minimize the number of force constants utilized in succeeding steps. Again the model force field suggested in reference 14 was chosen, but different force constants were admitted for each bond stretch and angle bend of the ring, consistent with the constraints of C_{2} , symmetry. Interaction force constants were separated into two groups with respect to whether or not they involved the strained bond to and/or $lpha_1$ or $lpha_6$ (see Figure 1); further distinctions would be required in a detailed analysis. Even with these simplifications, 26 different internal coordinate force constants remain to be specified. First the 13-parameter force field of benzenewas assumed, although some of the force constants reported by Duinker and Mills¹⁴ (D_6 , F_{1-3} , G) were altered to better fit the benzyne observed frequencies. From this initial force field (Table 3, last column) band assignments could be made after diagonalization of the Wilson GF matrix. The force constants were then refined to provide a best least-squares fit of the experimental and calculated frequencies, according to an extensively modified computer program (see Appendices) originally written by the Shimanouchi group.15 The definitions of the in-plane force constants in terms of the internal coordinates and their final values are given in Table 3.

Force Constant	Definition ^b	Final Value ^C	Initial Value ^d
D ₁	titi	7.798 (0.144)	7.015
D ₂	t ₂ t ₂	8.389 (0.114)	7.015
D ₃	^t 3 ^t 3	6.677 (0.112)	7.015
⁾ 6	t ₆ t ₆	13.950 (0.103)	14.000*
0	t _i t _i ° (i≠6)	0.660 (0.062)	0.531
2	t_it ^m (1≠6)	-0.488 (0.050)	-0,531
P	títi [₽] (1≠6)	0.147 (0.227)	0.531
	^د و ^د نا ^۵	0.255 (0.060)	0.531
<u>.</u>	t ₆ t1	-0.180 (0.271)	-0.531
-	t ₆ t _i ^p	0.123 (0.294)	0.531
5	tia (atal or a?)	0.331 (0.071)	0.226
	tiao (and or a?)	0.026 (0.128)	0.226
	t ₆ a ⁰	0.134 (0.111)	0.226
_	t _i B ^o	0.305 (0.013)	0.310
)	^s i ^s i	5.155 (0.019)	5.125
	^s i ^α i+1	-0.244 (0.137)	-0.009
L	°1°1	0.708 (0.045)	0.800*
2	°2°2	0.290 (0.074)	0.500*
5	azaz	0.595 (0.019)	0.950*
)	a _i a <mark>0</mark> (i≠1 or 6)	-0.032 (0.013)	-0.098
1	a _i a _i ^d (i=1 or 6)	-0.185 (0.018)	-0.098
3	α _i β ^ο	0.025 (0.011)	0.063
	6:6:	0.752 (0.035)	1.000*

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Table 3. Internal coordinate force constants⁴ for the in-plane vibrations of \underline{o} -benzyne

(continued)

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Table 3. (continued)

Force Constant	Definition ^b	Final Value ^C	Initial Value ^d
٤ 0	β _i β _i °	0.021 (0.036)	0.028
٤ _m	β _i β _i ^m	-0.050 (0.036)	-0.022
۶ _p	β _i β _i ^P	-0.025 (0.034)	-0.032

^astretching force constants - mdyne/Å

stretching-bending interactions - mdyne/rad

bending force constants - mdyne. Å/rad²

^bDefinitions $\chi_i \chi_i^{\circ}$; $\chi_i \chi_i^{m}$, $\chi_i \chi_i^{p}$ indicate the interaction force constants between coordinates χ_i and its ortho or meta or para position.

^CThe values given in parentheses are dispersions of the final values, given in the same units.

^dInitial values from reference 13, except the force constants indicated by *.



Six experimental frequencies remained to be assigned, three each for $o-C_6H_4$ and $o-C_6D_4$.⁴ Their values satisfy the isotopic product rule for the infrared- and Raman- active B₁ out-of-plane vibratins within 0.4%. Table 4 summarizes the isotopic product rule expectations for the symmetry representations of benzyne, as well as the values according to the assignments of reference 10 and our assignment of the B₁ vibrations in the experimental spectra.

The constraints method¹⁶ for the F matrix was then utilized to determine a mathematically correct (although not necessarily unique) force field for the B₁ representation. A G matrix can be written in diagonal form by means of a similarity transformation

$$AGA = T$$
 (1)

whereupon the F matrix can be estimated by the following equation

$$F = (AT^{1/2})^{-1} C^{-1} \wedge \widetilde{C}^{-1} (AT^{1/2})^{-1}, \qquad (2)$$

where C is any orthogonal constraint matrix for F and Λ is the eigenvalue matrix of the experimentally observed frequencies. For a group with n degrees of internal freedom the F matrix contains n(n+1)/2 elements, and the C matrix depends on n(n-1)/2 independent parameters. The F matrix constraints are determined by the choice of the C matrix parameters, for which several methods have been proposed.¹⁶ We chose to set C=E, the identity matrix, which corresponds

o-benzyne
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rule
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Isotopic
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Table

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			7	lue
Representation	Expression	Structure ^a	Expt1. ^b	Calc. ^c
A1	$\frac{m_1 \cdots m_g}{m_1 \cdots m_g} = \left(\frac{m_g}{m_H}\right)^2 \left(\frac{M}{M^2}\right)^2$	3.891		4.108
٨	$\frac{\omega_1 \dots \omega_{13}}{\omega^1 \dots \omega_1} = \left(\frac{m}{m}\right) \left(\frac{1}{T_z}\right)^{\frac{1}{2}}$	1.838	8 9 9 9	
B 1	$\frac{w_{14}w_{15}w_{16}}{w_{14}w_{15}w_{16}} = \left(\frac{m_{0}}{m_{14}}\right) \left(\frac{M}{M^{2}}\right)^{\frac{1}{2}} \left(\frac{1}{\gamma}\right)^{\frac{1}{2}}$	1.843	1.836	0.781
82	$\frac{\omega_{17}}{\omega_{17}^{2}} \cdots \frac{\omega_{24}}{\omega_{24}^{2}} = \left(\frac{\pi_D}{m_H}\right)^2 \left(\frac{M}{M^{1}}\right)^{\frac{1}{2}} \left(\frac{\Gamma}{\Gamma_X}\right)^{\frac{1}{2}}$	\$ 3.626		

²Value calculated from the structural parameters given in Figure 2, from the theoretical geometry of reference 6.

^bfrum reference 4.

^CFrom frequencies generated by the nurmal coordinate analysis of reference 10.

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to the assumption that the normal coordinates are defined in purely kinematic terms.¹⁶

There are four symmetry coordinates in the B_1 group, while only three vibrational frequencies are allowed. In order to use equation (2) the redundancy was eliminated by use of the transformation U matrix, which has the following properties: ¹⁷

 $U\widetilde{U} = 1$ (3); UR = S (4); $UG_{r}\widetilde{U} = G_{\bullet}$ (5); $UF_{r}\widetilde{U} = F_{\bullet}$ (6).

Here R and subscript r represent the coordinate system which has redundancy and matrices which are defined in R coordinates, respectively; S and subscript s represent the coordinate system without redundancy and matrices which are defined in the S coordinate, respectively. From permutations of the three experimental B_1 frequencies for C_6H_4 six possible trial force fields were obtained. These force fields were substituted in turn into the equation for C_6D_4 :

 $GFL = L \mathbf{\lambda}$

(7)

 $[L = (AT^{1/2})C$ (8)]

and their eigenvalues were compared to the B₁ experimental frequencies for the perdeuterated species. One of the permutations predicted each $C_{\bullet}D_{\bullet}$ fundamental within 25 cm⁻¹ of the observed value, without any adjustments. That particular force field was chosen as an approximate solution for the B₁ vibrations, and was refined by least-squares



adjustment. The out-of-plane force constants generated by this procedure are listed in Table 5.

3.3 Results and Discussion

A. In-plane vibrations

The in-plane (A₁, B₂) vibrational fundamentals predicted for o-C₆H₄ and o-C₆D₄ by the force field given in the third column of Table 3 are listed in Table 6, where they are compared to the experimental results.²⁻⁴ Agreement between observed and calculated wavenumbers is very good (within 2%), although a definitive test of the force field cannot be made until additional bands are experimentally observed. The refined force constants (Table 3) indicate that in general the ring stretching motions become stiffer, and the ring bending motions more pliant, in comparison with typical aromatic systems.¹⁰ This is in good agreement with theoretical expectation for a strained ring system,¹⁰ here due to the strong, short C₆-C₁ bond (t₆ in Figure 5).

Unlike the previous normal coordinate analysis, ¹⁰ only one benzyne ring stretching vibration above 2000 cm⁻¹ is calculated in this work [Table 6: 2094 cm⁻¹ (C₆H₄), 2084 cm⁻¹ (C₆D₄)]. The MNDO study also predicted only one such mode.¹¹ Inspection of the force constant potential energy



	•	<u>e</u> -C6H	l4	
Calc.	Obs. ^a	۵ŧb	P.E.D.C	Assignment
3081	3083	+0.23	5 ⁺ 2362 5 ⁺ 1436	A ₁ CH stretch
3074			5 ₁₄ 75 5 ₂₃ 24	B ₂ CH stretch
3059			s ⁺ ₁₄ 63 s ⁺ ₂₃ 37	A _l CH stretch
3050			5 ₂₃ 76 5 ₁₄ 24	B ₂ CH stretch
2092	2084 (2085)	-0.38	T ₆ 84 T ⁺ 1517	A ₁ ring stretch
1657	(1627)		T ₂₄ 47 T ₁₅ 43	B ₂ ring stretch
1599	1598(1607)	-0.06	$B_{14}^{-}54 B_{23}^{-}28$	A ₁ CH bending
1549			$B_{23}^{+}76 T_{15}^{-}43$	B_2 CH bend + ring stretc
1510			T ⁺ ₂₄ 66 T ₃ 34	A ₁ ring stretch
1450	1448(1451)	-0.14	$B_{14}^+ 87 T_{24}^- 17$	B ₂ CH bend + ring stretc
1391 .			$B_{23}^{-}76 \ B_{14}^{-}37$	A ₁ CH-bending
1360			T ₂₄ 40 T ₁₅ 39	B ₂ ring stretch
1245			T ⁺ 15 ⁵² T ₃ 19	A ₁ ring stretch
1052	1056(1053)	+0.28	T ₃ 46 T ⁺ ₁₅ 29	A ₁ ring stretch
839			A ₁₆ 53 A ₃₄ 13	B ₂ C-C-C bend
482	472(469)	-2.12	A_3475 A_1621	B ₂ C-C-C bend
395		·	A ⁺ ₂₅ 38 A ⁺ ₃₄ 18	A ₁ C-C-C bend

Table 3 Calculated and observed wavenumbers (cm⁻¹) of in-plane vibrations of <u>o</u>-benzyne

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(continued)

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<u>o</u> -C ₆ D ₄				
Calc.	Obs. ^a	۵ ۴ ⁶	P.E.D. ^C	Assignment
2296	2293	-0.13	S ⁺ 23 ⁴⁸ S ⁺ 14 ⁴⁵	A ₁ CD stretch
2288			S ₁₄ 71 S ₂₃ 23	B ₂ CD stretch
2257			S ⁺ ₁₄ 48 S ⁺ ₂₃ 48	A ₁ CD stretch
2237			\$2375 \$1425	B ₂ CD stretch
2084	2093	+0.43	T ₆ 83 T ⁺ 1514	A ₁ ring stretch
1640			$T_{15}^{-}54 T_{24}^{-}47$	B ₂ ring stretcl
1483	1483	0.00	T ⁺ 24 ⁷⁸ T ₃ 45	A ₁ ring stretch
1360			T ₂₄ 51 T ₁₅ 37	B ₂ ring stretch
1291	1293	+0.15	T ⁺ ₁₅ 43 T ₃ 16	A _l ring stretch
1107	1108	+0.01	$B_{23}^{+}61 \ B_{14}^{+}35$	B ₂ CD bend
1102			$B_{14}^{-47} B_{23}^{-32}$	A ₁ CD bend
1029	1029	0.00	$B_{14}^+66 B_{23}^+37$	B ₂ CD bend
1011			T ₃ 41 T ⁺ 1521	A _l ring stretch
1002			$B_{23}^{-}69 B_{14}^{-}45$	A ₁ CD bend
822	822	0.00	$A_{16}^{-52} A_{34}^{-13}$	B ₂ C-C-C bend
462	471	+1.91	A_3475 A_1620	B ₂ C-C-C bend
381			$A_{25}^{+}37 A_{34}^{+}18$	A ₁ C-C-C bend

Table 5 (continued)

^aFrom reference 4; values in parentheses are from references 2 and 3.

^bPercent deviation: 100 (obs-calc)/obs.

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^CPotential energy distribution, with major symmetry coordinate contributions, in percent.

distribution shows that this band is dependent primarily on the t_o bond stretching force constant, D_o. The magnitude of this force constant, D_o = 13.95 mdyne/A, indicates that the C_o-C₁ bond is very nearly triple bond in character. It is slightly lower than the theoretically calculated value (16.9 mdyne/A), consistent with the trend exhibited by symmetric C-C stretching force constants for other unsaturated systems.¹⁹ The experimentally observed frequencies can thus be cited as evidence of the strained ring structure of benzyne, as first claimed by Chapman, et al.;³ their inverted positions⁴ [Table 6: 2084 cm⁻¹ (C_oH_o), 2093 cm⁻¹ (C_oD_o)] may reflect interaction between t_o and the C-D displacements (s₁, s₄, g₁, g₂), which were not taken into consideration in these calculations.

In the theoretical structure of benzyne⁴ (Figure 2) the adjacent bond lengths, t_1 and t_2 as well as t_4 and t_5 , are identical and close in value to t_3 ; they differ little from the benzene C-C bond length. Yet the force constants differ markedly from one another, alternating in strength as one goes around the ring. This departure from the bond length/ bond strength (Badger's rule) correlation is explicable in terms of the theoretical electron population analysis, which shows that the *e*-contribution remains fairly constant, but that the *c*-electron overlap alternates strongly^{6,17} in the strained ring system.

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B. Out-of-plane Vibrations

In the absence of data for the A_2 vibrations, which are Raman-active only, the out-of-plane vibrational potential for benzyne is necessarily incomplete. The frequencies predicted for the B_1 out-of-plane modes by the force field given in TAble 4 are compared to the observed frequencies in Table 7. The agreement (within 0.4%) is excellent. As is well known, although the B₁ force field generated by the procedure given in section 3.2 is mathematically correct, it is not unique.²⁰ However, one can apply some general criteria to check its likely applicability. For example, one expects the C-H (or C-D) out-of-plane wagging force constants to be little changed from benzene. If the $d_1 d_4$ interaction force constant is assumed to be negligible (it is actually a very small negative number), then the benzyne C-H wagging force constant is 0.49 mdyne A/rad^2 . This value is close to the reported experimental and theoretical values for benzene,²¹ 0.44-0.45 mdyne A/rad².

Unfortunately, the torsional force constants cannot be similarly compared, since they are not separable in the B_1 symmetry block alone. The individual torsional force constants (\mathfrak{s} 's) can be estimated only after the A_2 , Ramanactive out-of-plane vibrations are available. Moreover, the B_1 block potential constants do not include the torsion about the $t_{\mathfrak{s}}$ bond, which is most critical for the



Force Constant ^a	Value ^b	_
$f_{\gamma_1\gamma_1} + f_{\gamma_1\gamma_4}$	0.493	
$f_{\gamma_1\gamma_2} + f_{\gamma_1\gamma_3}$	-0.018	
$f_{\gamma_1\delta_1} - f_{\gamma_1\delta_5}$	-0.386	
$f_{\gamma_1\delta_{22}} - f_{\gamma_1\delta_4}$	0.335	
$f_{\gamma_2\gamma_2} + f_{\gamma_2\gamma_3}$	0.317	
$f_{\gamma_2 \delta_1} - f_{\gamma_2 \delta_5}$	0.212	
$f_{\gamma_2\delta_2} - f_{\gamma_2\delta_4}$	-0.018	
$f_{\delta_1\delta_1} - f_{\delta_1\delta_5}$	0.841	
$f_{\delta_1\delta_2} - f_{\delta_1\delta_4}$	-0.658	
$f_{\delta_2 \delta_2} - f_{\delta_2 \delta_4}$	0.598	

Table 6. Force field for out-of-plane vibrations of o-benzyne

^aUnits: mdyne Å/rad²

^bDispersions are not included since this force field was transformed directly from the F matrix. r



-					-
Calc.	Obs, ^a	۵sb	P.E.D. ^C	Assignment	-
1039	1039(1038)	0.00	Δ_24,55 Γ+33	CH wag + ring torsio	n
845	847 (849)	+0.24	Γ ⁺ ₂₃ 53 Δ ⁻ ₁₅ 23	CH wag + ring torsion	a <u>o</u> -C ₆ H ₄
743	743 (735)	0.00	Γ ₁₄ 122	CH wag	_
788	792	+0.50	∆ ₁₅ ²⁶ ∆ ₂₄ 12	Ring torsion	_
730	730	0.00	Γ ⁺ ₁₄ 73 Γ ⁺ ₂₃ 51	CD wag	<u>o-</u> C ₆ D ₄
616	616	0.00	$\Gamma_{14}^{+}87 \Gamma_{23}^{+}27$	CD wag	

Table 7 Calculated and observed wavenumbers (cm^{-1}) of infrared-active (B_1) out-of-plane vibrations of <u>o</u>-benzyne

^aFrom reference 4; values in parentheses from reference 2.

^bPercent deviation: 100 (obs-calc)/obs.

^CPotential energy distribution, with major symmetry coordinate contributions, in percent.



calculation of the strained ring structure of benzyne. On the basis of frequency shifts of bands attributed to benzyne out-of-plane deformations from the positions of corresponding bands in benzenoid systems, Chapman, et al.² concluded that benzyne is less rigid with respect to out-ofplane distortion. The bands used in that comparison were not specified, and we feel that it is therefore more prudent to postpone discussion of the flexibility of the benzyne ring until the A_2 vibrations are observed. Then the torsional force constants can be compared to other aromatic systems. In addition, the results can be used to test Anno's criteria,²² developed by Kydd,²³ relating the torsional force constant to the product of the c bond order and the carbon 2pc orbital overlap integral.

APPENDICES

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Appendix 1

Computer program for the calculation of the torsional coordinate s vector according to Hildebrandt's method.

More than one terminal atom, m atoms on j and n atoms on k, constitute m \times n torsional motions around one axis j-k. Contributions from all these motions to axis j-k can be taken into account by taking a normalized linear combinations of the m x n four atom configurations as was used by Snyder and Schachtschneider.²⁴ Hildebrandt, however, proved computationally that this method of normalization does not give a correct reduced moment of inertia from the inverted G matrix and proposed new formulas for the calculation of the torsional coordinate s vector.²⁵ This was confirmed algebraically by Williams.²⁶ Since Shimanouchi's program also uses the same method as Snyder and Schachtschneider, the calculation of the torsional s vector had to be modified according to Hildebrandt's method of normalization.

Modification was made without changing the format of the original program. For one torsional axis this program



distinguishes the type of terminal atoms and calculates them separately by calling subroutines TORS1 and TORS2. Source programs are listed on the following pages. For more complete descriptions of the mathmatical treatment, see reference 25 and 26.

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THIS TORSIONAL B MATRIX ELEMENTS CALCULATION WAS MODIFIED C COMPLETELY ACCORDING TO HILDEBRAND'S NORMALIZATION. С NEW SUBROUTINES TORSI AND TORSE WERE CREATED FOR THIS PART C INSTEAD OF OLD SUBROUTINE TORSM. FOR COMPLETE DISCRIPTION С OF PROGRAM, SEE THE REF. CAN. J. CHEM 56, 1289, 1978 AND NOTE С OF AUTHOR H-H NAM. С 337 IF (NOTOR . EQ. 0) CO TO 363 DO 362 MTOR = 1, NOTOR NI = NITR(MTOR) NL = NLTR(MTOR) TI=1.0/NI TL=1.0/NL JA = JTOR (MTOR) KA = KTOR(MTOR)JJ = MEB(MJ) - 1KK = JJ+3DO 350 MI=1, NI I1 = KK + MI + 3IA=ITOR (MTOR, MI) CALL TORSI IF (JOKER . LE. O) GO TO 340 WRITE(6, 1203) ERROR(5), NOPROB, MTOR, JOKER IERR=1 JOKER=0 GO TO 351 340 DO 350 M =1, 3 N = II + MNCOLB(N) = NCB(1, M)DATB(N)=DATB(N)+BEL(1,M)&TI N=JJ+M NCULB(N) = NCB(2, M)DATB(N)=DATB(N)+BEL(2, M)*TI N=KK+M $NCGI_B(N) = NCB(3, M)$ DATB(N)=DATB(N)+GEL(3, M)*TI 350 CONTINUE 351 CONTINUE DO 351 ML=1, NL LL=KK+(NI+ML)#3 LA=LTOR (MTOR, ML) CALL TORS2 IF (JOKER LE. 0) GO TO 255 WRITE(6, 1203) ERROR(5), NOPROB, MTOR, JOKIN IERR=1 JOKER=0 GO TO 351 355 DO 360 M=1, 3 N=LL+M NCOLB(N) = NCB(4, M)DATB(N)=DATB(N)+BEL(4, M) *TL N= JJ +N NCOLB(N) = NCB(2, M)DATB(N)=DATB(N)+BEL(2, M) +TL N=KK+M NCOLB(N)=NCB(3, M) DATB(N)=DATB(N)+BEL(3, M) *TL 360 CONTINUE 361 CONTINUE MEB(MJ+1) = MEB(MJ) + NI*3 + NL*3 + 6 MJ = MJ + 1362 CONTINUE



#DECK	, TORS
	SUBROUTINE TORS1
С	THIS SUBROUTINE COMPUTES THE & MATTY ELEMENTS FOR THE L-TYPE
С	TORSION ACCORDING TO HILDERPAND & NORMALIZATIO SCHEME
Ċ	THIS WAS CREATED BY HAVE WINN NAM ON A (201 TO UNDERSTAND THE
č	PROCRAM. SEE IN ALL COST ALL COST ALL COST ALL CONDERSIAND (HIS
č	PROCEAM USETTER BY I'M AND HIS AND AND DESCRIPTION OF
č	TE END ATOMS WITCH TO CHART WHICH IS IN DR. LERUI'S GROUP.
•	THE END AN AT A STATE OF THE ATTEND OF THE ATTEND.
	DINERSION RIG(3), RIR(3), EIJ(3), EJR(3), X(3, 30), NCB(6, 3), BEL(6, 3),
•	
	CUTTON NUAT, I, NCB, BEL, IA, JA, KA, LA, JOKER
	IF (IA . GI. NUAT . OR. JA . GT. NOAT . OR. KA . GT. NOAT) GO TO 380
	DJKSG=0.0
	DO 170 M=1, 3
	RIJ(M)=X(M, JA)-X(M, IA)
	RJK(M) = X(M, KA) - X(M, JA)
	DIJSG=DIJSC+RIJ(M)++2
170	DJKSQ=DJKSQ+RJK(M)++2
	DIJ=SGRT(DIJSG)
	DJK=SQRT(DJKSQ)
	CDSJ=0.0
	DO 240 M=1, 3
	EIJ(M)=RIJ(M)/DIJ
	EJK(M)=RJK(M)/DJK
240	COSJ=COSJ-EIJ(M)+EJK(M)
	IF(ABS(COSJ) . GT. 1.0) GO TO 400
	SINJ=SQRT(1.0-COSJ**2)
	C1(1)=EIJ(2)+EJK(3)-EIJ(3)+EJK(2)
	C1(2)=EIJ(3)+EJK(1)-EIJ(1)+EJK(3)
	C1(3)=EIJ(1)+EJX(2)-EIJ(2)+EJK(1)
1	DO 360 M=1, 3
1	NCB(1, M)=(IA-1)*3+M
1	008(2, M)=(JA-1)+3+M
	NCB(3, M)=(KA-1)*3+M
1	BEL(1, M) = -C1(M)/(DIJ + SINJ + 2)
1	BEL(2, M) = C1(M) + (DJK-DIJ+COSJ)/(DIJ+DJK+SINJ++2)
1	BEL(3, M) = C1(H) * COSJ/(DJK * SINJ * * 2)
360 (CONTINUE
G	GD TO 420
380 🗸	JOKER=1
- 6	GO TO 420
400	JOKER=2
420 R	RETURN
E	IND



	SUBRUUTINE TORS2
С	THIS SUBROUTINE COMPUTES THE B MATRIX ELSISHINTS OF J-TYPE
С	TORSION. L STANDS FOR THE END ATCM ON J.
	DIMENSION $RLK(3)$, $RKJ(3)$, $ELK(3)$, $EKJ(3)$, $NCD(6,3)$, $BEL(6,3)$,
	+X(3,30),C2(3)
	COMMON NOAT, X, NCB, BEL, IA, JA, KA, LA, JOKEK
	IF (JA . GT. NOAT . OR. KA . GT. NOAT . OR. LA . GT. NOAT) GO TO 380
	DLKSG=0. 0
	DKJSG=0. 0
	DO 170 M=1, 3
	RLK(M) = X(M, KA) - X(M, LA)
	RKJ(M) = X(M, JA) - X(M, KA)
	DLKS9=DLKS0+RLK(M)**2
170	DKJSG=DKJSG+RKJ(M) ++2
	DLK=SQRT(DLKSQ)
	DKJ=SQRT (DKJSQ)
	COSK=0. 0
	DD 240 M=1,3
	ELK(M)=RLK(M) ['] /DLK
	EKJ(M)=RKJ(M)/DKJ
240	COSK=COSK-ELK(M)*EKJ(M)
	IF (ABS (COSK) . GT. 1.0) GO TO 400
	C2(1)=ELK(2)+EKJ(3)-ELK(3)*EKJ(2)
	C2(2)=ELK(3)+EKJ(1)-ELK(1)+EKJ(3)
	C2(3)=ELK(1)*EKJ(2)-ELK(2)*EKJ(1)
	SINK=SGRT(1.0-CDSK**2)
	DD 360 M=1,3
	NCB(2, M)=(JA-1)*3+M
	NCB(3, M)=(KA-1)+3+M
	NCB(4, M)=(LA-1)*3+M
	BEL(2,M)=C2(M)+COSK/(DKJ+SINK++2)
	BEL(3,M)=C2(M)+(DKJ-DLK*COSK)/(DLK*DKJ#GIRK+*2)
	BEL(4,M)=-C2(M)/(DLK*SINK**2)
360	CONTINUE
	GD TO 420
380	JOKER=1
	GO TO 420
400	JOKER=2
420	RETURN
	END

.



Appendix 2

The calcualation of the s vector for a rocking coordinate

When three bonds are branched from one common center in the same plane, it is very convenient to define rocking coordinates to reduce the number of redundancies in the internal coordinates. This rocking coordinate is defined by the linear combination of two adjacent external angles.

Since most normal coordinate calculation programs use only five types of vibrational motions, when one has a planar cyclic molecule the number of internal coordinates increase unnecessarily and consumes much longer time for calculation. Thus insertion of a rocking coordinate routine into the program will give more flexibility to handle every type of molecule.

Mathmatical formulas for s-vector calculation for a rocking coordinate are provided in the following pages, along with their derivations.




FIG. A-1 RELATIONS BETWEEN DISPLACED AND EQUILBRIUM VECTORS FOR A ROCKING MODE.



Define the rocking coordinate as

$$\Delta \beta = 1/\sqrt{2} \left(\Delta \phi_1 - \Delta \phi_2 \right) \tag{A-1}$$

The scarlar products of unit vectors directed outwards from the central atom gives twe cosine of the angles m:

$$\cos\phi_1 = e_1 \cdot e_2$$
 (A-2)

$$cos\phi_2 = e_2.e_3$$
 (A-3)

The expression for a small variation in m may be obtained by differentiation of (A-2) and (A-3).

$$\cos\phi_1 = -\sin\phi_1 \Delta\phi_1 = e_1 \Delta e_2 + e_2 \Delta e_1$$
 (A-4)
 $\cos\phi_2 = -\sin\phi_2 \Delta\phi_2 = e_2 \Delta e_3 + e_3 \Delta e_2$ (A-5)

The small variation of the unit vectors appearing on the right side of (A-4) and (A-5) can be replaced in terms of the arbitrary vectors of the atoms: ρ_0, ρ_1, ρ_2 and ρ_3 . It is clear that we must now obtain the expressions for the vectors S_{ϵ} in

 $S_{t} = \Delta \phi_{t} = \sum_{\alpha' \neq i}^{N} S_{t\alpha'} \cdot \rho_{\alpha'}$

by substituting appropriate expressions for e_1 , e_2 and e_3 in equation (A-4) and (A-5). We define r_1 as the vector from atom 0 to atom i. Then the unit vectors

$$\mathbf{e_1} = \mathbf{r_1}/\mathbf{r_1} \tag{A-6}$$

where r_1 is the distance between the atoms i and O. Differentiation of (A-6) yields

 $e_{1} = (r_{1}\Delta r_{1} - r_{1}\Delta r_{1}) / r_{1}^{2}$ (A-7)

A prime can be used to distinguish the vectors r_1 in a displaced configuration (Figure A-1). Thus;

$$r_{1} = r_{1} + (f_{1} - f_{0})$$
(A-8)
$$\Delta r_{1} = (f_{1} - f_{0})$$
(A-9)



To obtain one computes the scalar product of each side of (A-8) by itself, neglecting second order terms in the ho .

 $r_{\star}^{\prime 2} = r_{\star}^{2} + 2r_{\star} \cdot (\rho_{i} - \rho_{o}) \qquad (A-10)$ This equation shows that the small variation in the square of bond length is $2r_{\star} \cdot (\rho_{i} - \rho_{o})$, or

 $r_{1} = (r_{1})^{2}/2r_{1} = e_{1} \cdot (\rho_{1} - \rho_{2})$ (A-11) Substitution of (A-11) and (A-9) into (A-7) gives the small change in e_{1} and of the displacements, ρ_{1} , of the atoms. Then substitution of (A-7). into (A-4) and (A-5) and collection of the vectors which act as scalar product multipliers of the ρ 's gives the desired result for $\Delta \phi_{1}$ and

$$\Delta \phi_{1} = \left\{ \frac{(r_{1} - r_{2}\cos\phi_{1})\mathbf{e}_{1} + (r_{2} - r_{1}\cos\phi_{1})\mathbf{e}_{2}}{r_{1}r_{2}\sin\phi_{1}} \right\} \cdot \rho_{0}$$

$$+ \left(\frac{\cos\phi_{1}\mathbf{e}_{1} - \mathbf{e}_{2}}{r_{1}\sin\phi_{1}} \right) \cdot \rho_{1} + \left(\frac{\cos\phi_{1}\mathbf{e}_{2} - \mathbf{e}_{1}}{r_{2}\sin\phi_{1}} \right) \cdot \rho_{2} \qquad (A-12)$$

$$\Delta \phi_{1} \equiv \left\{ \frac{(r_{2} - r_{3}\cos\phi_{2})\mathbf{e}_{2} + (r_{3} - r_{2}\cos\phi_{2})\mathbf{e}_{3}}{r_{2}r_{3}\sin\phi_{2}} \right\} \cdot \rho_{0}$$

+
$$\left(\frac{\cos 2\mathbf{e_2} - \mathbf{e_3}}{r_{2}\sin\phi_2}\right) \cdot \left(\mathbf{a} + \left(\frac{\cos 2\mathbf{e_3} - \mathbf{e_2}}{r_{3}\sin\phi_1}\right) \cdot \left(\mathbf{a} - 13\right)\right)$$

From (A-12) and (A-13), and the definition of A_{μ}^{μ} :

42



$$\Delta \beta = 1/\sqrt{2} (\Delta \phi_1 - \Delta \phi_2)$$

= $\frac{1}{\sqrt{2}} \begin{cases} \frac{(r_1 - r_2 \cos \phi_1)e_1 + (r_2 - r_1 \cos \phi_1)e_2}{r_1 r_2 \sin \phi_1} \end{cases}$

$$-\frac{(r_2 - r_3 \cos \phi_2)e_2 + (r_3 - r_2 \cos \phi_2)e_3}{r_2 r_3 \sin \phi_2} \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_3 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_4 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_2 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_2 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_2 \\ e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1 - e_1 \end{array} \right) \cdot \left(\begin{array}{c} \cos 1e_1$$

+

(A-14)

In (A-14), each coefficient corresponds to the s vectors for the particular atom. Thus:

$$S_1 \approx \cos \phi_1 e_1 - e_2$$

 $r_1 \sin \phi_1$

$$S_2 \approx -\sin\phi_1 e_1 + \sin(\phi_1 - \phi_2) e_2 + \sin\phi_1 e_3$$

$$r_2 \sin\phi_1 \sin\phi_2$$

$$S_3 \simeq cos\phi_2e_3 - e_2$$

 $r_3sin\phi_2$

 $S_0 = -(S_1 + S_2 + S_3)$ (A-15)

The Shimanouchi's normal coordinate program was extended to include treatment of the rocking coordinates by this formulas according to subroutine ROCKM, for which the source code follows.



363 IF (NOROC . EQ. 0) CO TU 377 DCI 376 NJ=1, NOROC IA= IROC(NJ) JA= JROC(NJ) KA= KROC(NJ) LA= LROC(NJ) CALL ROCKM IF (JOKER . LE. O) GO TO 366 WRITE(6, 1203) ERROR(6), NOPROB, NJ, JOKER IERR=1 JOKER=0 GO TO 376 356 N= MEB (MJ)-1 DU 370 L=1,4 DO 370 M=1,3 . N=N+1 NCCLB(N) = NCB(L, M) $DATB(N) = BEI_(L, M)$ 370 CONTINUE MEB(MJ+1) = MEB(MJ) + 12MJ=MJ+1 376 CONTINUE 377 IF (IERR. GT. 0) GO TO 10000

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LIST OF REFERENCES

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REFERENCES

- R. W. Hoffmann, Dehydrobenzene and Cycloalkynes (Academic Press, New York, 1967)
- 2. O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G.V. Calder and G. Orr, J. Am. Chem. Soc. <u>95</u>, 6134 (1973)
- 3. O. L. Chapman, C.-C. Chang, J. Kolc, N. Rosenquist and
 H.Tomioka, J. Am. Chem. Soc. <u>97</u>, 6586 (1975)
- I. R. Dunkin and J. G. MacDonald, J. C. S. chem. comm. <u>1979</u>, 772 (1979).
- 5. M. J. S. Dewar and W.-K. Li, J. Am. Chem. Soc. <u>96</u>, 5559 (1974).
- J. O. Noell and M. D. Newton, J. Am. Chem. Soc., <u>101</u>, 51 (1979).
- 7. C. A. Coulson, R. Daudel and J. M. Robertson, Proc. Roy. Soc. (London) <u>A205</u>, 306 (1951); E. Haselbach, Helv. Chim. Acta <u>54</u>, 1981 (1971).
- R. Hoffmann, A. Imamura and W. J. Hehre, J. Am. Chem.
 Soc. <u>90</u>, 1499 (1968).
- 9. W. Thiel, J. Am. Chem. Soc. <u>103</u>, 1420 (1981); M. J. S. Dewar, G. P. Ford and C. H. Reynolds, J. Am. Chem. Soc. <u>105</u>, 3162 (1983).
- 10. J. W. Laing and R. S. Berry, J. Am. Chem. Soc. <u>98.</u> 660

46

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(1976).

- 11. M. J. S. Dewar, G. P. Ford and H. S. Rzepa, J. Mol. Structure <u>51</u>, 275 (1979).
- H.-H. Nam and G. E. Leroi, Spectrochim. Acta, <u>41A</u>,
 67 (1985).
- 13. Slight differences in the definitions of the symmetry coordinates with respect to reference 10 should be noted.
- 14. J. C. Duinker and I. M. Mills, Spectrochim. Acta <u>24A</u>, 417 (1968).
- 15. T. Shimanouchi, Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules, Tokyo University, Tokyo, Japan (1969).
- 16. S. Califano, Vibrational States (John Wiley and Sons, London, 1976), and references cited therein.
- K. Kuczera and R. Czerminsky, J. Mol. Structure <u>105</u>,
 269 (1983).
- G. Varsanyi, Vibrational Spectra of Benzene Derivatives
 (Academic Press, New York, 1969).
- 19. M. D. Newton, in Applications of Electronic Structure Theory, H. F. Schaefer III, ed. (Plenum Press, New York 1977).
- 20. B. Jordanov and Nikolova, J. Mol. Structure <u>13</u>, 21 (1972); <u>15</u>, 165 (1973).
- 21. P. Pulay, G. Fogarasi and J. E. Boggs, J. Chem. Phys. <u>74</u>, 3999 (1981).
- 22. T. Anno, J. Chem. Phys. 28, 944 (1958).

.

- 24. J. H. Schachtschneider. Reports 231/64 and 57/65, Shell Development Co.
- 25. R. L. Hildebrandt, J. Mol. Spectrosc. <u>44</u>, 599 (1972).
- 26. I. H. Williams, J. Mol. Spectrosc. <u>66</u>,288 (1977).

. .

