(19) Most of the gas solubility measurements were made for H_2 and only representative data were obtained for D_2. The isotope effect on solubility favors D_2 over H_2 by a factor of about 1.05.
(20) R. Stewart and J. R. Jones, *J. Am. Chem. Soc.*, **89**, 5069 (1967).
(21) E. Buncel, E. A. Symons, and A. W. Zabel, *Chem. Commun.*, 173 (1965).
(22) J. F. Bunnett in "Technique of Organic Chemistry", Vol. VII, Part I, 2d ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N.Y., 1961.
(23) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).
(24) E. Buncel and J. P. Millington, *Can. J. Chem.*, **43**, 556 (1965).
(25) O. Exner, *Collect. Czech. Chem. Commun.*, **37**, 1425 (1972).
(26) E. Buncel and E. A. Symons, First IUPAC Conference on Physical Organic Chemistry, Crans, Switzerland, 1972, Abstracts, p 88.
(27) W. A. Jolly, *J. Chem. Educ.*, **44**, 304 (1967).
(28) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972).
(29) R. G. Pearson in "Advances in Linear Free Energy Relationships", Chapman and Shorter, Ed., Plenum Press, London, 1972; T.-L. Ho, *Chem. Rev.*, **75**, 1 (1975).
(30) R. Goitein and T. C. Bruice, *J. Phys. Chem.*, **76**, 432 (1972); E. H. Baughman and M. M. Kreevoy, *ibid.*, **78**, 421 (1974).
(31) J. H. Exner and E. C. Steiner, *J. Am. Chem. Soc.*, **96**, 1782 (1974).
(32) E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2915 (1967).
(33) C. D. Ritchie and H. F. King, *J. Am. Chem. Soc.*, **90**, 833 (1968).
(34) As an alternative to the actual displacement mechanism depicted in eq 6 and in transition state E, an intermediate water molecule may be involved in a general base catalyzed process.[28]
(35) D. D. MacDonald and J. B. Hyne, *Can. J. Chem.*, **49**, 611 (1971).
(36) E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, in press.
(37) L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, **1**, 1 (1963).
(38) A. K. Das and K. K. Kundu, *J. Chem. Soc., Faraday Trans. 1*, 730 (1973).

Normal Coordinates, Structure, and Bonding of Benzyne

Jean Wilcox Laing and R. Stephen Berry*

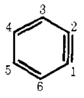
Contribution from the Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637. *Received May 23, 1975*

Abstract: On the basis of the observed matrix-infrared spectrum of benzyne, a structure and set of force constants and bond orders are proposed, other possible structures are ruled out, and predictions are made of yet-unobserved frequencies and of the vibrational spectrum of benzyne-d_4.

Benzyne, or 1,2-dehydrobenzene, has offered a challenge to our capacities to infer structures and bonding, ever since its existence was demonstrated.[1,2] The reactivity of benzyne—the apparently very low or zero activation energy of dimerization, for example—indicates that the species is more like a diradical than a benzene with an extra electron-pair bond.[3,4] Yet there is no indication that the ground state of benzyne is anything but a closed-shell singlet.[1,5] The qualitative picture in vogue supposes that benzyne's "triple" bond is shorter than the 1.39 Å of a normal benzenoid bond because two electrons occupy a *weakly* bonding orbital whose maximum electron density lies in the molecular plane, and whose parentage in benzyne can be traced to the C-atom orbital contributions from the vicinal C–H bonds of benzene that no longer exist in benzyne. If this is so, then presumably there is some strain-induced rehybridization, making the atomic carbon orbitals of the "triple" bond more than one-third p-like, and (see Figure 1) giving the orbitals of the adjacent C–C bonds a hybridization between sp^2 and sp. The bond lengths and bond orders of benzyne were first estimated previously in connection with semiempirical theoretical calculations.[6] Some calculations indicate a shortening of the C_1–C_2 bond and lengthening of the C_4–C_5 bond, and a "triple bond" structure, although one calculation suggests a cumulene-like structure.[7]

The only experimental hints directly cogent to the geometry and bonding of benzyne come from the infrared spectrum of the species frozen in an inert matrix. This spectrum was obtained by Chapman, Mattes, McIntosh, Pacansky, Calder, and Orr.[8] The microwave spectrum has not been reported and the electronic spectrum[9] appears to consist of a featureless continuum whose energy range and intensity are consistent with the interpretation just given for the "triple" bond, that the "in-plane" carbon orbitals form ethylene-like bonding and antibonding orbitals whose bonding and antibonding strength are both significantly weaker than in a normal 2pπ olefinic bond. However, the electronic spectrum contributes no positive information about the structure.

We report here an interpretation of the infrared vibrational spectrum of benzyne, as reported by Chapman et al.,[8] from which we infer the normal coordinates, the bond lengths, and bond orders and predict the infrared spectrum of benzyne-d_4. We shall show that its infrared spectrum implies that benzyne has alternating bond lengths consistent with the aryne-like structure I.



I

Analysis of Data

The infrared spectrum of benzyne between 400 and 1700 cm^{-1} was reported by Chapman et al. to exhibit eight bands, at 469, 736, 849, 1038, 1053, 1451, 1607, and 1627 cm^{-1}. No spectrum was reported for higher frequencies. We assume that the benzyne molecule has C_{2v} symmetry. The molecule has normal modes of vibration that transform according to the four symmetry species of this point group, as follows: A_1, nine; A_2, four; B_1, three, and B_2, eight. The A_2 and B_1 species represent out-of-plane motion and the A_1 and B_2 species, in-plane motion. The A_2 modes are infrared-inactive but Raman-active; the other three sets of modes are infrared-active.

We carried out a normal mode analysis with a valence force field model, in which we allowed some variation of the bond lengths and angles, as well as of force constants, to optimize the fit between model and observation. Specifically, we assume that

$$t_1 = R(C_3\text{–}C_4) = R(C_5\text{–}C_6)$$

$$t_4 = R(C_1\text{–}C_6) = R(C_2\text{–}C_3)$$

and define

$$t_2 = R(C_4\text{–}C_5)$$

$$t_5 = R(C_1\text{–}C_2)$$

Table I. Force Constants for *o*-Benzyne in Terms of Internal Coordinates[a]

	s_1	s_2	s_3	s_4	t_1	t_2	t_3	t_4	t_5	t_6
s_1	${}^1F_s$	${}^2F_s$	${}^3F_s$	${}^4F_s$	${}^1F_{st}$	${}^2F_{st}$	${}^3F_{st}$	${}^3F_{st}$	${}^2F_{st}$	${}^1F_{st}$
t_1					${}^1F_t$	${}^2F_t$	${}^3F_t$	${}^4F_t$	${}^3F_t$	${}^2F_t$
	β_1	β_2	β_3	β_4	α_1	α_2	α_3	α_4	α_5	α_6
s_1	0	${}^1F_{s\beta}$	${}^2F_{s\beta}$	0	${}^1F_{s\alpha}$	${}^2F_{s\alpha}$	${}^3F_{s\alpha}$	${}^4F_{s\alpha}$	${}^3F_{s\alpha}$	${}^2F_{s\alpha}$
t_1	${}^1F_{t\beta}$	$-{}^1F_{t\beta}$	${}^2F_{t\beta}$	${}^3F_{t\beta}$	${}^1F_{t\alpha}$	${}^1F_{t\alpha}$	${}^2F_{t\alpha}$	${}^3F_{t\alpha}$	${}^3F_{t\alpha}$	${}^2F_{t\alpha}$
β_1	${}^1F_\beta$	${}^2F_\beta$	${}^3F_\beta$	${}^4F_\beta$	0	${}^1F_{\beta\alpha}$	${}^2F_{\beta\alpha}$	0	$-{}^2F_{\beta\alpha}$	$-{}^1F_{\beta\alpha}$
α_1					${}^1F_\alpha$	${}^2F_\alpha$	${}^3F_\alpha$	${}^4F_\alpha$	${}^3F_\alpha$	${}^2F_\alpha$
	γ_1	γ_2	γ_3	γ_4	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
	${}^1F_\gamma$	${}^2F_\gamma$	${}^3F_\gamma$	${}^4F_\gamma$	${}^1F_{\gamma\delta}$	${}^2F_{\gamma\delta}$	$-{}^3F_{\gamma\delta}$	$-{}^3F_{\gamma\delta}$	$-{}^2F_{\gamma\delta}$	$-{}^1F_{\gamma\delta}$
δ_1					${}^1F_\delta$	${}^2F_\delta$	${}^3F_\delta$	${}^4F_\delta$	${}^3F_\delta$	${}^2F_\delta$

[a] Other rows consist of the same force constants in appropriately permuted orders determined by the symmetry. Since β can be (+) or (–), some $F_{n\beta}$ are negative.

Table II. Symmetry Coordinates for *o*-Benzyne[a]

A_1 representation	B_2 representation	A_2 representation	B_1 representation
$s_{14+} = (1/\sqrt{2})(s_1 + s_4)$	$s_{14-} = (1/\sqrt{2})(s_1 - s_4)$	$\gamma_{14+} = (1/\sqrt{2})(\gamma_1 + \gamma_4)$	$\gamma_{14-} = (1/\sqrt{2})(\gamma_1 - \gamma_4)$
$s_{23+} = (1/\sqrt{2})(s_2 + s_3)$	$s_{23-} = (1/\sqrt{2})(s_2 - s_3)$	$\gamma_{23+} = (1/\sqrt{2})(\gamma_2 + \gamma_3)$	$\gamma_{23-} = (1/\sqrt{2})(\gamma_2 - \gamma_3)$
$t_{13+} = (1/\sqrt{2})(t_1 + t_3)$	$t_{13-} = (1/\sqrt{2})(t_1 - t_3)$	$\delta_{13+} = (1/\sqrt{2})(\delta_1 + \delta_3)$	$\delta_{13-} = (1/\sqrt{2})(\delta_1 - \delta_3)$
$t_{46+} = (1/\sqrt{2})(t_4 + t_6)$	$t_{46-} = (1/\sqrt{2})(t_4 - t_6)$	$\delta_{46+} = (1/\sqrt{2})(\delta_4 + \delta_6)$	$\delta_{46-} = (1/\sqrt{2})(\delta_4 - \delta_6)$
$t_2 = t_2$	$\alpha_{14-} = (1/\sqrt{2})(\alpha_1 - \alpha_4)$	$\delta_2 = \delta_2$	
$t_5 = t_5$	$\alpha_{23-} = (1/\sqrt{2})(\alpha_2 - \alpha_3)$	$\delta_5 = \delta_6$	
$\alpha_{14+} = (1/\sqrt{2})(\alpha_1 + \alpha_4)$	$\alpha_{56-} = (1/\sqrt{2})(\alpha_5 - \alpha_6)$		
$\alpha_{23+} = (1/\sqrt{2})(\alpha_2 + \alpha_3)$	$\beta_{14-} = (1/\sqrt{2})(\beta_1 - \beta_4)$		
$\alpha_{56+} = (1/\sqrt{2})(\alpha_5 + \alpha_6)$	$\beta_{23-} = (1/\sqrt{2})(\beta_2 - \beta_3)$		
$\beta_{14+} = (1/\sqrt{2})(\beta_1 + \beta_4)$			
$\beta_{23+} = (1/\sqrt{2})(\beta_2 + \beta_3)$			

[a] $\alpha_1 = -(\phi_1 + \phi_2)$, etc.; $\beta_1 = (1/2)(\phi_1 - \phi_2)$, etc.; γ_i = out-of-plane C–H bend; δ_i = torsion angle of C–C–C–C.

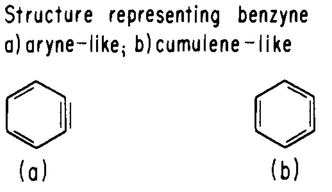


Figure 1. Structures representing benzyne: (a) aryne-like; (b) cumulene-like.

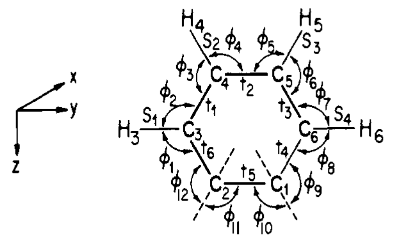


Figure 2. Nomenclature for benzyne.

We explored both possibilities, that $t_4 > t_1$, the conventional "triple bond" model, and that $t_1 > t_2$, corresponding to a cumulene-like structure. We also supposed that ∠123 = ∠612 ≥ ∠234 = ∠561 and that ∠345 = ∠456. As it worked out, we could say that ∠234 = ∠345, within our limits of sensitivity.

The computations were carried out by diagonalizing the product of the kinetic energy matrix G and the potential energy matrix F, as described by Wilson, Decius, and Cross.[10]

The valence force coordinate system is defined in Figure 2. The corresponding force constants are defined by their position in the matrix of Table I, and the symmetry coordinates are defined in Table II. The F matrix, G matrix, and scaling are presented elsewhere.[11] Because the molecular point group symmetry is C_{2v}, rather than D_{6h}, the symmetry coordinates and F and G matrices differ from those giving the simplest description of benzene. Our starting trial set of valence force constants was based on that set derived for benzene by Crawford and Miller[12] which they considered most reliable. We did have to estimate some of the constants; the full set is given in Table III. Then the skeletal force constants, bond lengths, and bond angles were varied, and the frequencies of the vibrational spectrum were computed and compared with the experimental set until the fit was satisfactory, as described in the next section. We did not extensively explore variations in the force constants involving the C–H stretching motion, in part for reasons of economy and in part because the high-frequency C–H stretching motions were not observed and are necessarily only weakly coupled to the low-frequency modes. Thus, within the sensitivity of our computations, the C–H stretching force constant of benzyne can be taken to be equal to that of benzene. However, none of the other constants has the same values in both benzene and benzyne.

While it is rarely possible to demonstrate that a set of force constants gives a unique representation of a spectrum, one can get some sense of the reliability of a set by comparing one's "best" fit with the predictions based on physically reasonable but somewhat different values of the parameters. Some such comparisons are made in Table IV, to illustrate the sensitivity of the predicted spectrum to changes in bond lengths, bond angles, and various force constants, all corresponding to about the same basic structure. Frequencies corresponding to other proposed structures fit less well; these are discussed in the following section. We find, without surprise, that the correlation of calculated and observed frequencies is much more sensitive to variations in force constants than to variations of bond lengths and angles. The

Table III. Internal Force Constants of Benzene

${}^1F_s = 5.0645$ dyn/cm × 10^5	${}^1F_\beta = 1.0143$ dyn cm × 10^{-11}
${}^2F_s = 0.0173$	${}^2F_\beta = -0.0193$
${}^3F_s = -0.0310$	${}^3F_\beta = 0.0119$
${}^4F_s = -0.0342$	${}^4F_\beta = -0.0314$
${}^1F_t = 12.720$	${}^1F_\gamma = 0.4409$
${}^2F_t = 0.530$	${}^2F_\gamma = -0.0665$
${}^3F_t = 0.918$	${}^3F_\gamma = 0.0082$
${}^4F_t = 0.473$	${}^4F_\gamma = -0.0303$
${}^1F_{st} = -0.0990$	${}^1F_{t\beta} = -0.0871$ dyne × 10^{-3}
${}^2F_{st} = -0.0990$	${}^2F_{t\beta} = 0.0191$
${}^3F_{st} = -0.0990$	${}^3F_{t\beta} = 0.0871$
${}^1F_\delta - {}^2F_\delta = 0.339$ dyn cm × 10^{-11}	${}^2F_\delta - {}^3F_\delta = -0.023$ dyn cm × 10^{-11}
${}^1F_\delta - {}^3F_\delta = 0.316$	${}^3F_\delta - {}^4F_\delta = 0.033$
${}^1F_\delta - {}^4F_\delta = 0.349$	${}^2F_\delta - {}^4F_\delta = 0.011$
Estimated Values	
${}^1F_\alpha = 1.528$ dyn cm × 10^{-11}	${}^1F_{\gamma\delta} = -0.185$ dyn cm × 10^{11}
${}^2F_\alpha = 0.0076$	${}^2F_{\gamma\delta} = -0.0428$
${}^3F_\alpha = -0.144$	${}^3F_{\gamma a} = -0.0542$
${}^4F_\alpha = -0{,}0895$	${}^nF_{s\beta} = 0$ for all n
${}^1F_{t\alpha} = 0.1532$ dyn × 10^{-3}	${}^nF_{s\alpha} = 0$ for all n
${}^2F_{t\alpha} = -0.0531$	${}^nF_{\alpha\beta} = 0$ for all n
${}^3F_{t\alpha} = 0.0965$	

bond lengths and angles enter only in the elements of the G matrix (kinetic energy), not in the potential energy or F matrix. For a molecule like benzyne, with a host of molecules to serve as comparisons, it is probably more reliable to ascertain bond lengths through the use of a bond length—bond order—force constant correlation, rather than directly through variation of the bond lengths and angles in a fitting procedure, because the normal mode frequencies are simply too insensitive to changes in distances.

Results and Inferences

The best-fitting set of infrared-active frequencies is shown in Table V, together with the observed frequencies and the percent deviations of calculated from observed frequencies. The eigenvectors are available.[11] The most critical valence coordinate for purposes of interpreting the structure of benzyne, the C-C stretching coordinate called t_5, occurs primarily in the modes with predicted frequencies 2083 and 2450 cm^{-1}, which were outside the region originally observed by Chapman et al. In the 2083 mode, the "C≡C" bond and the "C—C" bond across the ring stretch in phase with each other, and out of phase with the other four C-C bonds. In the 2450-cm^{-1} mode, the "C≡C" bond coordinate t_5 oscillates out of phase with the stretching coordinate t_2 opposite, and out of phase with $(t_4 + t_6)$ but in phase with $(t_1 + t_3)$; this mode is the highest frequency stretching mode of the ring, with alternate bonds moving exactly out of phase.

The best fit of the valence force constants for benzyne is indicated in Figure 3, with the corresponding force constants for benzene. The bond lengths, bond angles, bond orders, and force constants are collected in Table VI. We see that the deviation from a benzenoid structure is not great, far less than models proposed for benzyne on the basis of semiempirical orbital models.

Our selection of the "optimum" geometry, force constants, and bond orders was not totally based on fitting the infrared spectrum. When the magnitudes for satisfactory sets of values were obtained, we applied two additional criteria in an approximate way. One is the empirical connection between bond length and bond order known as Badger's rule: with equilibrium distances R_e in Å and bond-stretching force constants k in mdyn/Å,

Table IV. Predicted Frequencies for A_1 Normal Modes of Benzyne for Various Changes of Parameters[a]

1	2	3	4	5	6
3096	3094	3094	3097	3124	3127
3054	3053	3053	3054	3054	3063
2450	2441	2441	2457	2465	2557
2083	2082	2082	2081	2083	2174
1645	1652	1653	1647	1638	1708
1601	1607	1607	1590	1601	1675
1444	1446	1447	1441	1444	1434
1052	1053	1052	1049	1052	1064
471	476	482	475	471	471

[a] Column 1, best fit; column 2, all angles 120°, t_5 (C≡C) = 1.334 Å; column 3, all angles 120°, t_5 = 1.274 Å; column 4, angles 123 and 612 = 177.5°, angle 165 = 125°, t_5 = 1.334, column 5, best fit structure, force constant for t_4 and t_6, F_{t46+}, taken as 7.47 mdyn/Å instead of 6.56; column 6, force constants for all four A_1, F_{t13+}, F_{t46+}, F_{t2}, and F_{t5}, taken 10% higher than best-fit values.

Table V. Observed Infrared Frequencies of *o*-Benzyne Compared with Calculated Normal Frequencies for the Ir Active Representations of the C_{2v} Point Group

Obsd freq (cm^{-1}) (ref 8 and 19)	Calcd freq A_1 representation (cm^{-1})	Calcd freq B_2 representation (cm^{-1})	Calcd freq B_1 representation (cm^{-1})
			306
469	471 (0.4%)		
		540	
735			735 (0.0%)
849		854 (0.6%)	
1038		1039 (0.1%)	
1053	1052 (0.1%)		
		1313	
1451	1444 (0.5%)		1449 (0.1%)
1607	1601 (0.4%)		
1627	1645 (1.1%)		
		1856	
		2044	
2085	2083 (0.1%)		
	2450		
		3040	
	3054		
		3087	
	3096		

$$k(R_e - 0.68)^3 = \text{constant (which we fixed from benzene)} \qquad (1)$$

The second is the bond order-bond length relationship of Coulson, coupled to the constraint that the sum of the bond orders p_j for the carbon-carbon bonds must be (roughly) 10. For our system, the relationships have the form

$$p = \frac{1.02 - 0.530R_e}{0.235R_e - 0.160} \qquad (2)$$

$$\sum_{j=1}^{6} p_j \simeq 10 \qquad (3)$$

The best-fitting set of parameters does not conform precisely to eq 3, as Table VI shows. The bond t_5 is significantly shorter than its force constant would imply if Badger's rule held strictly. The other bonds have lengths and orders that are reasonably consistent with eq 1, 2, and 3. Frequencies computed with bond lengths of column 5, Table VI, fit significantly worse than the best-fit set, particularly the calculated 1680 cm^{-1} (obsd 1627) and 1073 cm^{-1} (obsd 1053) modes.

Three previously proposed structures of benzyne are those shown in Figure 4, together with one based on column 5, Table VI. We have calculated hypothetical infrared spec-

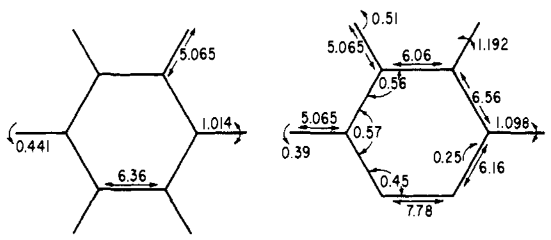


Figure 3. Force constants used to calculate the normal modes of vibration of *o*-benzyne compared to the force constants for benzene. Stretching force constants are in units of dyn/cm × 10^5 and bending force constants are in units of dyn cm × 10^{-11}.

Table VI. Bond Lengths, Bond Angles, Bond Orders, and Carbon–Carbon Bond-Stretching Force Constants for the Best-Fitting Set of Constants, Corresponding to the Frequencies of Table V. Bond Lengths and Bond Orders Derived from the Best-Fitting k's and Eq 1 and 2 Are Given in the Last Two Columns

Bond	R_e(Å)	p	Best-fitting k (mdyn/Å)[a]	Badger's rule bond length (Å)	p
t_1	1.384	1.73	6.56	1.387	1.72
t_2	1.414	1.57	6.06	1.405	1.62
t_4	1.414	1.57	6.16	1.401	1.64
t_5	1.304	2.25	7.78	1.349	1.80
		Σp_i = 10.42			Σp_i = 10.14
∠123 = 123°			∠234 = 118.5°		∠345 = 118.5°

[a] Actual computations and ref 11 were based on a scaling in which stretching force constants have twice this numerical value.

Table VII. Frequencies (cm^{-1}) of the A_1 Modes of Benzyne Based on Structures II, III, and IV and Equations 1 and 2

II	III	IV	V	Best fit	Obsd
3116	3122	3130	3122	3096	
3061	3060	3072	3061	3034	
2356	2981	2814	2429	2450	
1973	2225	2335	2066	2083	2085
1672	1701	1710	1680	1645	1627
1609	1578	1631	1616	1601	1607
1426	1453	1438	1433	1444	1451
1079	1084	1048	1073	1052	1053
456	518	491	474	471	469

tra for the A_1 modes of these structures by using our own best set of force constants for all elements of the F matrix except the C–C stretching constants, for which we used the values based on Badger's rule (above). The spectra so predicted are shown in Table VII. While we did not attempt to optimize the force constants around each of the C–C stretching constants, for structures II, III, and IV, it is clear that none of these structures offers as suitable a model as structure I because the predicted frequencies are so different from the observed spectrum. In the case of III and IV, only very unreasonable force constants for bending and interaction could conceivably bring the calculated values into the range of the observed. Note that the arbitrarily selected symmetric structure used by Hoffmann, Imamura, and Hehre (II) and structure V give quite comparable fits to the data.

We have explored several structures of the sort like Haselbach's, in which the bond lengths imply that the benzyne molecule is cumulene-like, rather than acetylene-like. These structures are uniformly unsatisfactory. We can say with considerable confidence that the benzyne molecule is properly called a cycloalkyne.

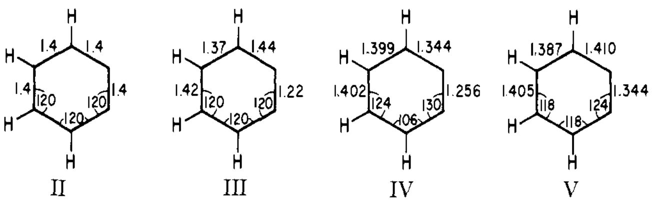


Figure 4. Structures suggested for benzyne. II, Hoffmann, Imamura, and Hehre,[16] also used by Millie, Pradu, and Serre;[17] III, Coulson,[6] also approximately that inferred from computations by Fraenkel and Newton;[18] IV, Haselbach;[7] V, from Table VI, column 5.

Table VIII. Infrared-Active Frequencies Predicted for Perdeuteriobenzyne, Based on the Best Fit to the Observed Spectrum of Normal Benzyne

A_1	B_2	B_1
451		
	546	
		548
		594
714		
	774	
	814	
	1027	
1112		
		1281
1480		
1568		
	1706	
	1978	
2035		
2243		
	2350	
2380		
2452		

The original spectrum[8] was only reported for the region between 450 and about 1700 cm^{-1}. The normal modes that depend most sensitively on the "C≡C" bond t_5 and the bond opposite, t_2, have frequencies in the range of about 2100 and 2600 cm^{-1}, respectively. A truly critical determination of the structure of benzyne from its infrared spectrum requires that the normal frequencies in this higher-frequencies region be measured.

After this work had been submitted for publication, we learned of new work by Chapman and co-workers[19] which extends the range of observation to about 2600 cm^{-1}. The extended spectrum shows a band, with a signal:noise ratio of about 5:1, at 2085 cm^{-1}, which fits very nicely with the predicted value of 2083 cm^{-1}. No other bands at frequencies above 2085 cm^{-1} were attributable to benzyne. However, the nonobservance of the predicted band at 2450 cm^{-1} need not shake our assignment and interpretation. It is entirely plausible from the geometric nature of the 2083 and 2450 modes, that the change in the z-component of the molecule dipole moment during the 2450 cm^{-1} oscillation is considerably smaller than the change associated with the 2085-cm^{-1} band, so that the higher frequency band could easily have less than one-fifth the intensity of the lower-frequency band, and thereby remain unobserved. We conclude from the observation of the band at 2085 cm^{-1} that our general model is probably rather close to the true situation.

As a final check of our proposed structure, we have calculated the infrared-active frequencies for perdeuteriobenzyne. These are given in Table VIII. Hopefully they can be measured in the near future.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

References and Notes

(1) (a) G. Wittig, G. Peiper, and G. Fuhrmann, *Ber. Dtsch. Chem. Ges.*, **73**, 1193 (1940); (b) G. Wittig, *Naturwissenschaften*, **30**, 696 (1942).
(2) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N.Y., 1967.
(3) (a) M. E. Schafer and R. S. Berry, *J. Am. Chem. Soc.*, **87**, 4497 (1965); (b) R. S. Berry, J. Clardy, and M. E. Schafer, *ibid.*, **86**, 2738 (1964).
(4) G. Porter and J. I. Steinfeld, *J. Chem. Soc. A*, 877 (1968).
(5) E. Wasserman (private communication).
(6) C. A. Coulson, *Chem. Soc., Spec. Publ.*, **No. 12**, 85 (1958).
(7) E. Haselbach, *Helv. Chim. Acta*, **54**, 1981 (1971).
(8) O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Am. Chem. Soc.*, **95**, 6134 (1973).
(9) R. S. Berry, G. N. Spokes, and R. M. Stiles, *J. Am. Chem. Soc.*, **84**, 3570 (1962).
(10) E. B. Wilson, Jr., J. Decius, and P. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955, pp. 240–272.
(11) J. W. Laing, Doctoral Dissertation, University of Chicago, 1974.
(12) B. L. Crawford and F. A. Miller, *J. Chem. Phys.*, **14**, 282 (1946); *ibid.*, 17, 249 (1949).
(13) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); *ibid.*, **3**, 710 (1935).
(14) G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, Princeton, N.J., 1950.
(15) C. A. Coulson, R. Daudel, and J. M. Robertson, *Proc. R. Soc. London, Ser. A*, **205**, 306 (1951).
(16) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.*, **90**, 1499 (1968).
(17) P. Millie, L. Praud, and J. Serre, *Int. J. Quantum Chem.*, **4**, 187 (1971).
(18) H. A. Fraenkel and M. D. Newton, *Chem. Phys. Lett.*, **18**, 244 (1973).
(19) O. L. Chapman, C.-C. Chang, J. Kole, N. Rosenquist, and H. Tomioka, *J. Am. Chem. Soc.*, **97**, 6586 (1975).

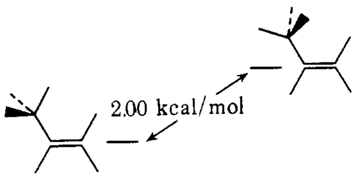
Torsional Potentials of Methyl Rotors Attached to Polar Linkages

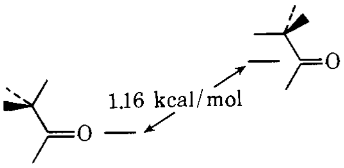
Warren J. Hehre,[*1a] **John A. Pople,**[1b] **and Alain J. P. Devaquet**[1c]

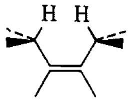
Contribution from the Department of Chemistry, University of California, Irvine, California 92717, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and Laboratoire de Chimie Organique Thêorique, Universitê Pierre et Marie Curie, 75 Paris, France. *Received May 16, 1975*

Abstract: The qualitative orbital arguments presented earlier as one possible rationalization for the observed conformational preference in propene are extended to the case of rotation of a methyl group about a polar double bond. The conclusions of this simple model, regarding variations in the torsional potential of the methyl group, are fully substantiated both by experimental data and by the results of quantitative ab initio molecular orbital calculations. Brief consideration is also given to variation in the barriers of methyl rotors in other molecular environments.

It is generally accepted that a methyl group attached to an unsaturated linkage will adopt a conformation in which one of its CH's eclipses the multiple bond. For example, propene is known to exist in such a methyl-eclipsed equilibrium conformation[2] with a barrier to rotation—through a methyl-staggered form—of some 2.0 kcal/mol.[3] Similarly, one of the C–H bonds in acetaldehyde prefers to eclipse the carbonyl linkage.[4a] In this instance, however, the potential hindering free rotation is considerably smaller than it is in propene.[4] Even the individual methyl rotors in a molecule like *cis*-2-butene prefer to be oriented so as each to eclipse the carbon-carbon double bond, although in doing so one would seem to maximize the steric repulsion between the pair of in-plane methyl hydrogens. Indeed, the barrier to rotation here (0.73 kcal/mol)[3a,5] is far smaller than that found for propene.







We,[6] and others,[7] have already pointed out possible explanations for this preference of *vinylic methyl groups* to eclipse unsaturated linkages. Consider, if you will, the consequences resulting from the interaction of the valence orbitals of a methyl rotor[8] and the π system of a double bond (Figure 1). Restricting ourselves only to the highest occupied and lowest vacant molecular orbitals on each of the two fragments, we see that four interactions result.[9] The first is between filled valence shells. The net repulsion which results—akin to that experienced between approaching rare gas atoms—is greater for the staggered rotamer than it is in the eclipsed. This is because overlap between the two fragments is most effective (and hence destabilization at a maximum) in the arrangement where the out-of-plane methyl hydrogens are positioned directly over the double bond, rather than being trans disposed. It should be emphasized that the diagram below and the ones which follow are constructed to represent individual interactions between specific orbitals on a methyl group and a polar unsaturated linkage. They should not be taken as representations of the total molecular orbitals which result. In this regard it is important to realize that the *energy of interaction* is proportional to the square of the overlap between fragments