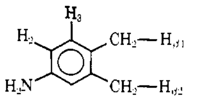
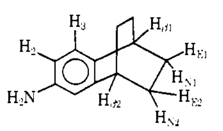
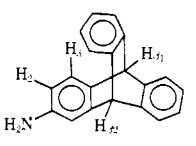
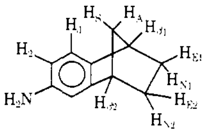








1		2				3		4[10]			
Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$	Proton	$\Delta H_i/\Delta H_2$
2	1.00	2	1.00	E1	−0.331	2	1.00	2	1.00	E1	−0.325
3	−0.49	3	−0.46	E2	0.080	3	−0.44	3	−0.40	E2	0.082
β1	−1.155	β1	0.069	N1	0.029	β1	0.055	β1	−0.156	N1	0.015
β2	0.391	β2	−0.048	N2	−0.033	β2	−0.033	β2	0.075	N2	0.0
										S	0.013
										A	−0.096

the nodal plane, the nickel reagent shifts the resonance of $H_{\beta1}$ upfield and that of $H_{\beta2}$ downfield. Thus, $a_{\beta1}$ is negative and $a_{\beta2}$ is positive. The contact shifts for the endo and exo protons of **2** are similar to the results for the heptane derivative, **4**.[10]

Values of B_0/B_2 may be assessed for $H_{\beta1}$ and $H_{\beta2}$ in both **2** and **3** using eq 2 (see Table II)

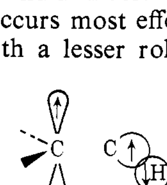
$$\frac{B_0}{B_2} = \frac{1}{2}\left[\frac{\Delta H_{\beta\text{-CH}_3}/\Delta H_2}{\Delta H_{\beta\text{-H}}/\Delta H_2} - 1\right]^{-1} \qquad (2)$$

Table II. Values of B_0/B_2 Calculated from Equation 2

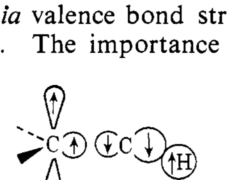
	B_0/B_2	
Amine	$H_{\beta1}$	$H_{\beta2}$
2	−0.028	−0.055
3	−0.023	−0.039

where $\Delta H_{\beta\text{-CH}_3}/\Delta H_2$ and $\Delta H_{\beta\text{-H}}/\Delta H_2$ are the contact shifts for the β protons relative to the shifts for the ortho protons. This analysis assumes that the distribution of spin density in the aromatic nuclei of **1**–**4** is sensibly constant and that $\langle\theta\rangle$ is 90° for $H_{\beta1}$ and $H_{\beta2}$ in the bicyclic molecules **2** and **3** and 45° for the freely rotating methyl groups in the xylene.[13]

The values of B_0/B_2 range from −0.023 to −0.055, with $|B_0/B_2|$ somewhat smaller for the triptycene **3**.[14] With B_2 about 50 G, these observations indicate that B_0 is about −1.5 G for protons constrained to the nodal plane. This finding conflicts with the predictions of the INDO model, but agrees with the analysis presented by Colpa and de Boer.[7] They propose than spin delocalization occurs most effectively *via* valence bond structure IA with a lesser role for IB. The importance of IA may be enhanced by electronegative substituents with a decrease in a_β, for example in a 2-haloethyl radical.[15] In summary, we find B_0 is small, negative, probably only modestly influenced by hybridization changes, and presumably dependent on the dihedral angle.[5a]



$a_{\beta\text{ H}} \sim -1.8$ G
IA



$a_{\beta\text{-H}} \sim +0.50$ G
IB

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(13) Several approaches can be used to estimate B_0/B_2. All analyses, however, yield similar results.

(14) The change may reflect the change in hybridization of the exocyclic carbon bonding orbital from 25% s character in **2** to 28% s character in **3**.

(15) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 2371 (1972).

(16) Fannie and John Hertz Foundation Fellow at the University of Chicago.

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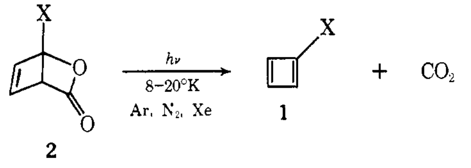
Cyclobutadiene. II. On the Geometry of the Matrix-Isolated Species

Sir:

Lin and Krantz[1] recently provided the first physical evidence for the structure of cyclobutadiene (**1a**) (the object of an intensive search since Kekulé's abortive attempt 100 years ago)[2–11] generated as a primary prod-



a, X = H
b, X = D

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(1) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).

(2) A. Kekulé, *Justus Liebigs Ann. Chem.*, **162**, 77 (1872).

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(4) Apropros to our studies: E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *ibid.*, **91**, 1875 (1969).

(5) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967); J. Font, S. C. Barton, and O. P. Strausz, *ibid.*, 499 (1970).

(6) G. Maier and M. Schneider, *Angew. Chem., Int. Ed. Engl.*, **10**, 809 (1971); G. Maier, G. Fritschi, and B. Hoppe, *ibid.*, **9**, 529 (1970); G. Maier and U. Mende, *ibid.*, **8**, 537, 539 (1968).

(7) For discussions of cyclobutadiene as an antiaromatic prototype, see R. Breslow, *Sci. Amer.*, **227**, 32 (1972); *Pure Appl. Chem.*, **28**, 111 (1971), and references therein.

(8) For stable cyclobutadienes see R. Gompper and G. Seybold, *Angew. Chem.*, **80**, 804 (1968); H. Kimling and A. Krebs, *Angew. Chem.*, **84**, 952 (1972).

(9) Professor O. L. Chapman has recently obtained similar results from the irradiation of α-pyrone confirming the previously published report of Lin and Krantz.[1]

(10) For reviews of cyclobutadiene, see (a) W. Baker and J. F. W. McOmie in "Non-Benzoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., Chapter II, 1959; (b) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962); (c) G. Subrahonanyam, *J. Sci. Ind. Res.*, **26**, 158 (1967); (d) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

(11) See also, M. Avram, I. G. Dinulescu, E. Marcia, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).

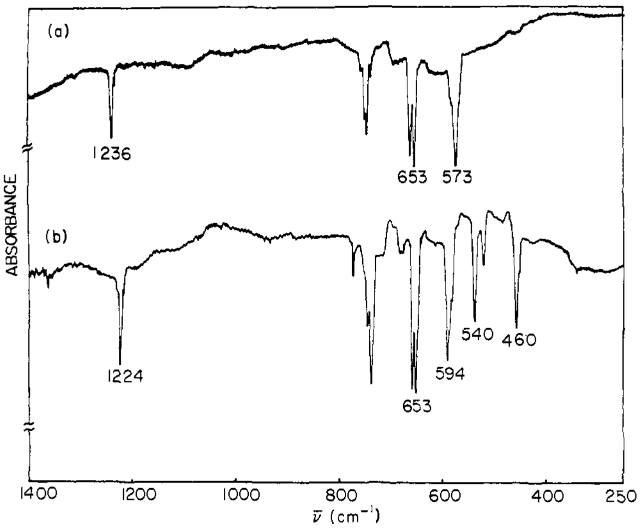

Figure 1. (a) A segment of the ir spectrum of photolyzed **2a** in argon ($M/R \sim 500$) containing bands due to cyclobutadiene. The series of bands centered at 747 cm^{-1} is due to acetylene in different environments. The band at 662 cm^{-1} is due to carbon dioxide. (b) A segment of the ir spectrum of photolyzed **2b** in argon ($M/R \sim 500$) with bands referred to in the text labeled.

uct of the photolysis of bicyclo[2.2.0]pyran-2-one (**2a**).[1, 12] A crucial feature of our initial report was the *complete photoconversion* of starting material **2a** to products. This result allowed inspection of the region in the infrared from 4000 to 250 cm^{-1}, uncontaminated by **2a** or significant side products which might have obscured bands due to **1a**. Cyclobutadiene was in turn photodecomposed to acetylene or converted to the syn dimer (identified by a band for band comparison with the published spectrum;[11] no absorption due to the anti dimer could be detected at 1215 cm^{-1}) upon evaporation of the matrix and redeposition of the photolysate. In this communication we present new experimental and theoretical evidence which supports the assignment of a square (D_{4h}) geometry to **1a**.

Cyclobutadiene possesses three bands[13] in the region below 2000 cm^{-1} (Figure 1a), whose positions are identical in xenon (8 to 60°K), argon, and nitrogen matrices. Group theoretical analysis[14,15] predicts four infrared active modes for the square (D_{4h}) [a C-H stretch (E_u), a framework deformation (E_u), an in-plane C-H bend (E_u), and an out-of-plane C-H bending deformation (A_{2u})]. These modes are pictured in Figure 2 for the parent **1a** and the monodeuterated derivative of C_{2v} symmetry. The corresponding analysis for the rectangle[16] (D_{2h}) gives seven infrared allowed fundamentals, as a consequence of breaking the degeneracy of the $3E_u$ modes of the square ($E_u \rightarrow B_{2u} + B_{3u}$, $A_{2u} \rightarrow B_{1u}$), five of which should be observable in the non-C-H stretch region of the ir spectrum. Merely on the basis of the number[13] of bands above 250 cm^{-1} attributable to **1a**, the spectrum is most compatible with a square geometry, provided all of the allowed lines are being observed.

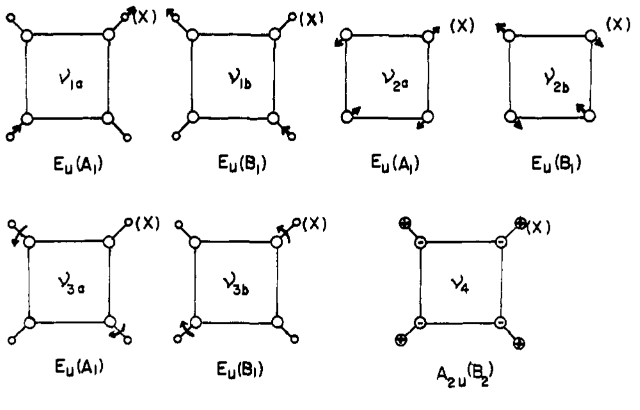

Figure 2. Approximate form of normal modes of infrared active vibrations of square-planar cyclobutadiene (**1a**). The compensating motions of the carbon framework in ν_1 and ν_3 have been neglected for purposes of clarity. Similarly, ν_2 has been represented as principally a framework distortion. Symbols in parentheses correspond to nondegenerate modes which result from descent into C_{2v} symmetry (X = D). The modes are in order of decreasing frequency.

The *location* of the bands is also compatible with a square structure. The band at 1236 cm^{-1} (ν_2), which we attribute to predominantly an in-plane ring deformation, lies between the limits of a C=C double bond (1650 cm^{-1}) and a C—C single bond (1000 cm^{-1}).[17] Furthermore, this frequency, which is somewhat lower than typical values for corresponding vibrations in C_nH_n aromatic rings[18a] of higher bond order, falls closer to the value of 1360 cm^{-1} observed by Hedaya[21] in the cyclopentadienyl radical.

On the basis of analogous ordering of C-H bending modes[15,18] of C_nH_n rings of D_{nh} symmetry, the 653- and 573-cm^{-1} bands are assigned to the in-plane (ν_3) and out-of-plane (ν_4) bending deformations, respectively. The observed bending modes are lower in frequency than those assigned to the related modes in the aromatic series (D_{nh}), but are larger in magnitude than those of the cycloheptatrienyl species studied by Hedaya.[21]

Support for our spectral assignments is also provided by theoretical calculations[22-26] employing C-C stretch-

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[12] (a) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964); (b) W. H. Pirkle and M. Dines, *ibid.*, **90**, 2318 (1968); (c) W. H. Pirkle and L. H. McKendry, *ibid.*, **91**, 1179 (1969).

[13] We wish to defer comment on the weak absorption in the C-H stretching region (which is not crucial to the present argument and is a less sensitive indicator of structure) until the full paper.

[14] G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 92.

[15] H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

[16] All other minor distortions lead to more than four infrared allowed fundamentals: *e.g.*, puckered cyclobutadiene (D_{2d}, 7, five mode, other than C-H stretches); rhomboidal (D_{2h}, 9); trapezoidal (C_{2v}s 15).

[17] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 205.

[18] (a) The infrared active fundamental modes for C_nH_n species of D_{nh} symmetry are tabulated in ref 15, p 305. (b) Note that the reported values for the C=C stretch in the strained species cyclobutene[19] and cyclopropene[20] are 1566 and 1653 cm^{-1}, respectively.

[19] R. C. Lord and D. G. Rea, *J. Amer. Chem. Soc.*, **79**, 2401 (1957).

[20] D. F. Eggers, J. W. Schultz, K. B. Wiberg, E. L. Wagner, L. M. Jackman, and R. L. Erskine, *J. Chem. Phys.*, **47**, 946 (1967).

[21] We thank Dr. E. Hedaya of Union Carbide Research Institute, Tarrytown, N. Y. 10591, for permission to cite, prior to publication, the following data for the cyclopentadienyl and cycloheptatrienyl radicals: C_5H_5, 3101 (m), 1360 (m), 739 (m), and 657 (vs) cm^{-1}; C_7H_7, 3050 (w), 605 ((s), and 510 cm^{-1}.

[22] Seven force constants were used to predict[23] the observed bands of **1a** and **1b**: four diagonal force constants (C-C stretching, f_{RR}; C-C-C bending, $f_{\alpha\alpha}$; C-H bending, $f_{\beta\beta}$; and ring puckering, $f_{\gamma\gamma}$), and three interaction constants (adjacent C-C stretches, f_{RR}'; adjacent C-C stretching and C-H bending, $f_{R\beta}$; and adjacent out-of-plane C-H bends, $f_{\beta\beta}'$). Values assigned to these constants are: f_{RR} = 6.30 mdyn/Å and f_{RR}' = 0.05 mdyn/Å (taken from extended basis[24] SCF-MO calculations for the B_{1g} and A_{1g} distortions of the $^3A_{2g}$ state of

ing force constants from *ab initio* calculations on **1a** and bending force constants obtained by interpolation of pertinent empirical data. These force constants (seven in all) lead to calculated frequencies[23] for **1a** (ν_2 = 1236 cm^{-1}, ν_3 = 661 cm^{-1}, and ν_4 = 576 cm^{-1}) and the monodeuterio derivative (*vide infra*), in excellent agreement with the observed bands. We also note that the SCF *ab initio* calculations lead to a predicted square equilibrium geometry (R_e = 1.434 Å) for the triplet state ($^3A_{2g}$) of **1a**[26] similar to Dewar's semiempirical result.[27] Furthermore, calculations using the general valence bond method (GVB)[31] indicate that the singlet lies 7.7 kcal/mol above the triplet at the triplet equilibrium geometry (D_{4h}) and is unstable to a rectangular distortion.

The above discussion has focused on the likelihood of a square geometry for **1a**; we emphasize that any appreciable rectangular distortion of the square would be expected to cause significant splitting of the degenerate 1236-cm^{-1} mode (ν_2). A mild rectangular distortion (R_{CC} and R_{CC} = 1.37 and 1.46 Å, respectively) leads to a predicted splitting of 100 cm^{-1}, if the above force constants are employed, with f_{RR} being allowed to vary with bond length according to Badger's rule.[32] Correspondingly larger splitting would be likely for more pronounced distortions (*e.g.*, the equilibrium singlet geometry of **1a** for which we calculate C–C bond distances of 1.34 and 1.56 Å using the GVB[31] method).

The above assignments receive strong confirmation from the spectrum of monodeuteriocyclobutadiene (**1b**) obtained by photolyzing bicyclo[2.2.0]pyran-2-one-*6-d* (**2b**)[12b,c] in the manner described for **2a** previously. Not surprisingly, the allowed modes of the parent **1a** also show up as strong bands, appropriately shifted and split in the spectrum (Figure 1b) of **1b**, as confirmed by inspection of the location of the bands and by the theoretical calculations. The slight shift in the frequency of the band at 1236 cm^{-1} in **1a** to 1224 cm^{-1} upon isotopic substitution confirms that it is predominantly a distortion of the carbon framework (ν_2).

Assuming that bands at 653, 594, and 540 cm^{-1} arise from the ν_3 and ν_4 modes of the parent **1a**, their location is only consistent (in the harmonic approximation) with the assignment of the band at 540 cm^{-1} to ν_4, and the bands at 653 and 594 cm^{-1} to the two split components (ν_{3a} and ν_{3b}) of the degenerate parent mode (ν_3).[33] The calculations described above are in good agreement with this analysis, predicting only a small splitting of the 1236-cm^{-1} band. (Similar calculations for the 1,2- and 1,3-dideuterio derivatives give splittings of 17 and 32 cm^{-1}, respectively.) A much larger splitting is predicted for the in-plane bending mode (ν_3), with the unshifted line (in which the C–D bend does not participate) assigned to the A_1 component (calcd value, 661 cm^{-1}), and the 594-cm^{-1} band assigned to the B_1 component (calcd, 616 cm^{-1}). The calculations yield a value of 527 cm^{-1} for the remaining parent mode (ν_4), thus completing the confirmation of the above assignment. In addition to the aforementioned intense bands in Figure 1b, arising from the active parent modes, we also note an intense band at 460 cm^{-1} which, from our calculations (477 cm^{-1}), is indicated to be almost a pure CH bending mode of B_1 symmetry. The appearance of spectra **1a** and **1b**, combined with theoretical predictions of the splittings of E_u modes upon descent into C_{2v} symmetry, solidly support assignment of the 1236- and 653-cm^{-1} bands to degenerate modes of square cyclobutadiene.

Although the present results are consistent with a square equilibrium geometry, there remains the possibility of an *effective* square geometry arising, perhaps, from rapid equilibration between slightly distorted squares separated by small barriers. The present *ab initio* calculations rule out such a possibility for any distortion of the triplet; since the equilibrium singlet corresponds to a *strongly distorted* square (a rectangle with normal single and double bond lengths), the larger barrier separating the two rectangular forms should prohibit rapid equilibration between them.

Acknowledgment. The award of a Frederick Gardner Cottrell Grant from the Research Corporation to A. Krantz is gratefully acknowledged This work was performed in part under the auspices of the U. S. Atomic Energy Commission (M. D. N.).

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1a and scaled by the same factor (0.877) which brings the calculated and experimental benzene force constants into agreement; the remaining interaction constant between the C–C bonds was assumed to be zero);[25] $f_{\beta\beta}$ = 0.30 mdyn Å/rad^2 (estimated from standard values[28] on the basis of calculated[29] s character (sp$^{1.6}$) for the C–H bonds); $f_{\alpha\alpha}$ = 1.30 and $f_{\gamma\gamma}$ = 1.30 mdyn Å/rad^2 (based on available data for cyclobutane[30a] and benzene[30b]); $f_{R\beta}$ = 0.36 mdyn/rad (from benzene,[30b] with signs determined by assuming hybrid orbital following); and $f_{\beta\beta}'$ = −0.05 mdyn Å/rad^2 (based on the out-of-plane benzene modes[30c]). This unbiased selection from *a priori* and standard empirical values adequately reproduces the observed bands.

(23) The computer program was written by J. H. Schactschneider as described in Technical Report No. 231-64 and 57-65, Shell Development Co., Emeryville, Calif., 1964.

(24) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(25) The C–C force constants were based on the square equilibrium triplet calculation,[26] since the calculated equilibrium geometry (D_{2h}) and force constants for the singlet were not consistent with the observed spectrum of **1a**; *vide infra.*

(26) (a) A previous minimal basis *ab initio* calculation (limited CI) suggested a slightly rectangular equilibrium triplet.[26b] However, the more flexible, extended basis[24] used in the present calculations predicts a square geometry. (b) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(27) M. J. S. Dewar, M. C. Kahn, and N. Trinjastic, *J. Amer. Chem. Soc.*, **93**, 3437 (1971).

(28) Reference 14, p 193.

(29) From the localized molecular orbitals; see, *e.g.*, M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 773 (1972).

(30) (a) T. P. Wilson, *J. Chem. Phys.*, **11**, 369 (1943); (b) J. C. Duinker and I. M. Mills, *Spectrochim. Acta, Part A*, **24**, 417 (1968); (c) F. A. Miller and B. L. Crawford, *J. Chem. Phys.*, **14**, 282 (1946).

(31) W. J. Hunt, P. J. Hay, and W. A. Goddard, III, *J. Chem. Phys.*, **57**, 738 (1972). We thank the authors for providing us with a version of their program.

(32) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966.

(33) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 190.

Prostaglandin Synthesis. I. An Improved Synthesis through Bicyclo[3.1.0]hexane Intermediates

Sir:

The potent pharmacological properties of the various members of the prostaglandin family and their limited supply from natural sources have prompted intensive