References and Notes

(1) Originally collected in March 1974 during the Alpha Helix Baja Expedition (AHBE 22-III-74-1-1) and subsequently collected during June 1976 (ITBE 2-VI-76-1-3) and March 1977 (IBE 13-III-77-2-5).
(2) Identified by Dr. G. J. Bakus, Allan Hancock Foundation, University of Southern California, Los Angeles, Calif. 90007, from samples preserved in ethanol.
(3) Assays were carried out by (a) Dr. Robert G. Hughes, Roswell Park Memorial Institute, Buffalo, N.Y., at 100 μg/12.7-mm disk; (b) Dr. P. D. Shaw, Department of Plant Pathology, University of Illinois, under the conditions previously described (P. D. Shaw, W. O. McClure, G. Van Blaricom, J. Sims, W. Fenical, and J. Rude, "Food-Drugs from the Sea Conference Proceedings 1974", Marine Technology Society, Washington, D.C., 1976, p 429); (c) Mr. G. E. Zurenko, The Upjohn Co., at 80 μg/12.7-mm disk.
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On the Structure of Cyclobutadiene. Theoretical Determination of Its Infrared Spectrum

Sir:

The structure of unsubstituted cyclobutadiene is still actively discussed. Originally, a square-planar structure was derived from its IR spectrum.[1-3] On the other hand, x-ray crystallografic investigations found a nonsquare C–C frame for alkylsubstituted cyclobutadienes,[4] and quantum chemical calculations very strongly favored a rectangular singlet ground state for the unsubstituted cyclobutadiene molecule.[5,14] Borden et al.[14] concluded that the interpretation of the experimental IR spectrum might be wrong. A semiempirical calculation of all vibration frequencies both for the rectangular singlet and square triplet was published by Dewar and Komornicki.[6] They

Chart I. Deformations of Cyclobutadiene Which Belong to IR Active Vibrations

No.	Type	Symmetry classification	Representation
1	Asymmetric C=C stretch	B_{3u}	
2	Asymmetric C—C stretch	B_{2u}	
3	CH stretch	B_{3u}	
4	CH stretch	B_{2u}	
5	CCH bending	B_{3u}	
6	CCH bending	B_{2u}	
7	CH out of plane	B_{1u}	

found that the observed spectrum is in fact in good agreement with the spectrum calculated for the square structure.

To resolve the discrepancy we performed ab initio SCF calculations of the vibration frequencies and intensities of the IR active vibrations of the rectangular singlet cyclobutadiene. Our results can be summarized as follows: (1) the observed IR spectrum is compatible with a rectangular structure; (2) the band at 1240 cm^{-1} which so far has been attributed to a C–C stretching deformation of square cyclobutadiene is an in-plane CCH bending deformation of cyclobutadiene.

In a molecule with inversion symmetry only those deformations that produce a dipole moment are IR active. For cyclobutadiene only seven fundamentals are active; they are given in Chart I using the D_{2h} symmetry notation. In the square structure (D_{4h}) the first six deformations are pairwise equivalent and degenerate such that only four fundamental frequencies can be observed. Since the number of observed bands is small (originally[1] just four bands, more recently only three,[3] and even one of them, the C–H stretching vibration, could not be confirmed[7]), it has been assumed that cyclobutadiene must have a square structure.

We have calculated the vibration frequencies in the following way. First, the CEPA method[8] was used to determine the equilibrium C–C bond lengths (C–C, 1.57 Å; C=C, 1.34 Å),[9] whereas the C–H length was fixed at 1.085 Å and the CCH angle at 135°. Starting from this equilibrium geometry we calculated the force constants (and nondiagonal force constants) for the seven IR-active vibrations in harmonic approximation using an ab initio SCF method. The basis used in these two steps had double ζ quality augmented by a set of d functions at the C atoms.[10] With this force constant matrix **F**

Table I. Observed and Calculated IR Bands of Ethylene[a]

Type	Symmetry	No.	Exptl IR spectrum	Calcd frequencies		Relative intensities[b]	
				Harmonic	SCF harmonic	SCF, $(dD/dq_i)^2$	Exptl[12]
CH	B_{2u}	9	3105	3234	3303	0.77	0.61
	B_{3u}	11	3021	3147	3219	0.61	0.34
CCH	B_{2u}	10	826	843	888	0.008	0.012
	B_{3u}	12	1444	1473	1595	0.17	0.24
Out of plane	B_{1u}	7	949	969	1092	2.7	1.93

[a] In cm^{-1}. [b] The dipole moment is in Debye and the normal coordinate in angstrom (atomic mass unit)$^{-1/2}$.

Table II. Calculated and Observed IR Bands of C_4H_4 and C_4D_4[a]

		C$_4$H$_4$			C$_4$D$_4$	
Type	No. in Chart I	Calcd frequencies, SCF	Calcd rel intensities, $(dD/dq_i)^2$	Obsd bands	Calcd frequencies, SCF	Calcd rel intensities
asym C=C	1	1697	0.08		1612	0.10
asym C—C	2	790	0.21		661	0.24
CH	3	3287	0.37	(3040)	2466	0.14
CH	4	3270	0.06		2407	0.03
CCH	5	1129	0.00		823	0.00
CCH	6	1377	0.86	1240	1161	0.33
Out of plane	7	692	4.20	570	508	2.26

[a] In cm^{-1}.

and the mass matrix M, the harmonic vibration frequencies $\lambda_i = \omega_i/2\pi$ and IR-vibration vectors C_i are calculated from the eigenvalue equation

$$FC_i = \lambda_i^2 MC_i$$

The vectors C_i are then used to estimate the relative intensities of the IR-active fundamentals by calculating the square of the dipole moment change along the corresponding normal vibration.

To test the numerical reliability of our results we performed the same type of calculation for ethylene using the same basis set. The results are collected in Table I, where we have also included both the observed fundamentals and harmonic frequencies[11] which should be compared with our calculated SCF values. Obviously, the SCF approximation leads only to a rather poor agreement with experiment[12] for some ω_i. This is particularly true for the out-of-plane bending vibration ω_7; inclusion of electron correlation by means of the CEPA formalism lowers the force constant by $\sim$15%, reducing the SCF harmonic frequency of 1092 to 998 cm^{-1} which is in reasonable agreement with the experimental value of 969 cm^{-1}. The reason for the rather large deviation of the asymmetric HCH bending vibration ω_{12} is not known so far. Our calculated relative intensities reproduce the experimental results fairly well.

Table II contains the results for cyclobutadiene for the seven IR-active vibrations. Only two of them are expected to give strong bands in the IR spectrum; the CH stretch is already rather weak, much more so the asymmetric C–C stretch. The assignment of the band at 570 cm^{-1} to the out-of-plane deformation and of the band at 3040 cm^{-1} to the CH stretch is evident, particularly since the deviations of observed and SCF frequencies are practically the same as in ethylene. The two IR-active CCH bending vibrations at 1129 and 1377 cm^{-1}, respectively, differ very strongly in their intensities. Only the one in which the two easily polarizable C=C double bonds are deformed along their main axis (B_{2u}, compare Chart I) gives rise to a large dipole moment and to a strong band. Its calculated frequency is almost 140 cm^{-1} higher than that of the observed band at 1240 cm^{-1}. That is about the same deviation from experiment as in the case of ethylene.

Thus, we assign the observed band at 1240 cm^{-1} to an in-plane CCH bending vibration of rectangular cyclobutadiene rather than to the asymmetric C–C stretching vibration of a hypothetical square cyclobutadiene.[1] Though the C–C stretching vibration might appear at that frequency, the strong band of the CCH bending must appear in that region and there is no other band available to account for it (the band at 661 cm^{-1} originally assigned to the CCH bending does not belong to the cyclobutadiene at all[3]). Very recently, Krantz et al.[13] reported the IR spectrum of a ^{13}C substituted cyclobutadiene. The very small shift of 4 cm^{-1} which they found for the band at 1240 cm^{-1} supports also our assignment. Only the spectrum of the so far unknown perdeuteriocyclobutadiene could give

the final answer to the assignment of the CCH bending vibration since in this species the CCH bending vibration should be shifted by $\sim$200 cm^{-1} to longer wavelengths, whereas the C–C stretching vibrations should be much less affected.

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A Novel 5-Fluorouracil–Copper(II)–Peptide Ternary Complex

Sir:

The pyrimidine derivative 5-fluorouracil (5-FU) is presently used as a carcinostat in humans.[1] As a first step in the elucidation of the interactions between a metal ion, a peptide, and a carcinostat related to the natural occurring nucleic acids, we