2904 J. Org. Chem. 1982, 47, 2904–2906

Theoretical Vibrational Spectra of the Dideuteriocyclobutadienes

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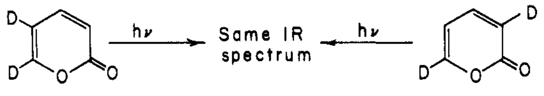
Received February 23, 1982

Vibrational frequencies and infrared intensities of the rectangular ground states of cyclobutadiene-*1,2*-d_2, cyclobutadiene-*1,4*-d_2, and cyclobutadiene-*1,3*-d_2 were calculated by employing a single-configuration SCF wave function and Pople and Hehre's 4-31G basis set. Comparison of these results with the experimental spectrum of Chapman strongly suggests that he has observed a 1:1 mixture of the *1,2*-d_2 and *1,4*-d_2 isomers. The equilibrium constant for the interconversion of cyclobutadiene-*1,2*-d_2 and cyclobutadiene-*1,4*-d_2 was also calculated and agrees with the value assumed by Carpenter.

The experimental infrared spectrum of cyclobutadiene observed by Masamune, Souto-Bachiller, Machiguchi, and Bertie,[1] as well as accurate calculations of its ground-state geometry by Borden, Davidson, and Hart[2] and by Jafri and Newton,[3] and calculated vibrational spectra by Kollmar and Staemmler[4] and Schaad, Hess, and Ewig[5] all indicate a rectangular (D_{2h}) singlet ground state for this molecule.

Earlier work had originally led to the proposal that the ground state is square (D_{4h}).[6,7] This conclusion was based in part on the limited number of lines observed in the IR spectrum of cyclobutadiene. Masamune's finding of additional absorption[1] lines has now ruled out a square geometry. However, experiments by Chapman[8] on dideuteriocyclobutadienes which also appeared to support D_{4h} symmetry have not been resolved in light of the new experimental and theoretical results. Chapman[8] and De La Cruz[9] reported that irradiation of α-pyrone-*5,6*-d_2 (1) and α-pyrone-*3,6*-d_2 (2) in an argon matrix gives rise to product mixtures with identical IR spectra. They concluded that square cyclobutadiene-*1,2*-d_2 (3) had been formed in both cases since if cyclobutadiene had been rectangular, the two α-pyrones would have been expected to yield the isomeric compounds 4 and 5. In addition, they reported the preparation of cyclobutadiene-*1,3*-d_2 (6). In contrast to these results, Whitman and Carpenter[10] have recently obtained evidence by a trapping reaction that indicated cyclobutadiene-*1,2*-d_2 (4) and cyclobutadiene-*1,4*-d_2 (5) to be distinct species.



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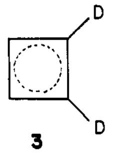

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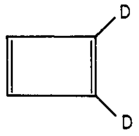

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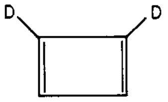

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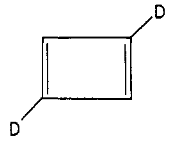

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As an aid to the more exact identification of 4–6, we present here calculated vibrational spectra of these species.

Our previous calculations on the rectangular ground state of cyclobutadiene[5] have been improved by reoptimizing the molecular geometry by using a single-determinant SCF wave function with Pople and Hehre's 4-31G basis set[11] to give an energy of −153.409 299 8 au with C–C bond lengths of 1.5810 and 1.3227 Å, a C–H length of 1.0664 Å, and an exterior angle of 135.32° between the C–H and the shorter C–C bonds.[12] The Cartesian force-constant matrix was approximated by using symmetry-adapted mass-weighted displacements of 0.01 au of each atom. Diagonalization of this matrix led to the computed vibrational frequencies in Table I. The dipole moment changes caused by a variation of 0.1 bohr (atomic mass unit)$^{+1/2}$ in normal coordinates were used to approximate dipole moment derivatives and to give the theoretical relative integrated infrared band intensities (eq 1) in Table I. In

$$I_i \propto |\partial\mu/\partial Q_i|^2 \qquad (1)$$

each case, the intensities in Table I and Figures 1, 2, and 4 were normalized relative to the most intense band in each spectrum. As recommended,[13] the z and y axes were taken through the short and long C–C bonds, respectively.

Cyclobutadiene results with the 4-31G basis are compared to those of the STO-4G basis[5] and to experiment in Figure 1. Masamune and co-workers[1] did not observe the C–H stretches near 3200 cm^{-1} since other components of their reaction mixture absorb too strongly to separate the cyclobutadiene contribution. Otherwise, the patterns of experimental and observed spectra agree well in symmetry, relative position, and intensity even though calcu-

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(1) Masamune, S.; Souto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 4889–4891.

(2) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388–392.

(3) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012–5017.

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(8) Chapman, O. L.; De La Cruz, D.; Roth, R.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 1337–1338.

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(10) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 4272–4274.

(11) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970**, *54*, 724–728. (b) Hehre, W. J.; Lathan, W. A. *Ibid.* **1972**, *56*, 5255–5257.

(12) We have used the values of the fundamental constants recommended: Cohen, E. R.; Taylor, B. N. *J. Phys. Chem. Ref. Data* **1973**, *2*, 663–734. With these, 1 hartree = 627.5092 kcal/mol, and 1 bohr = 0.529 177 06 Å.

(13) Anonymous *J. Chem. Phys.* **1955**, *23*, 1997–2011. (A reviewer has indicated that the author was R. S. Mulliken.)

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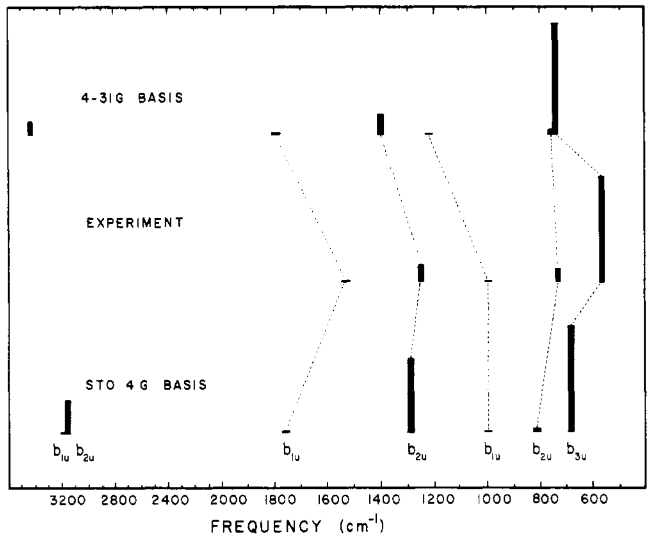

Figure 1. Comparison of theoretical infrared frequencies and intensities of cyclobutadiene in STO-4G and 4-31G basis sets with the experimental results of Masamune.[1]

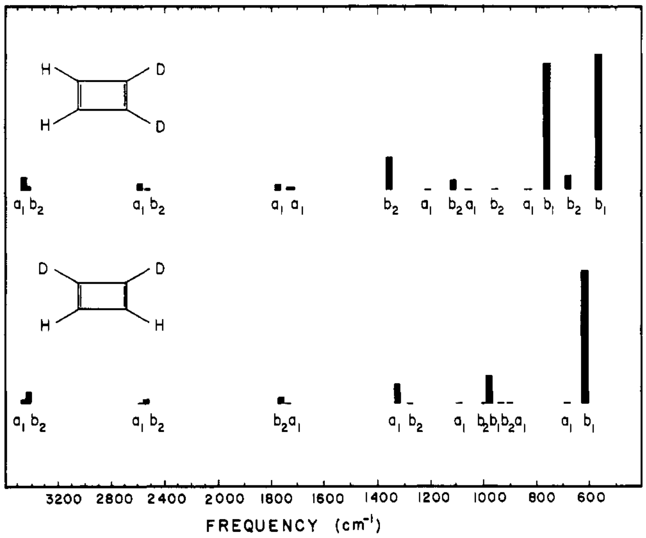

Figure 2. Calculated infrared frequencies and intensities of cyclobutadiene-*1,2*-d_2 and cyclobutadiene-*1,4*-d_2 in the 4-31G basis set.

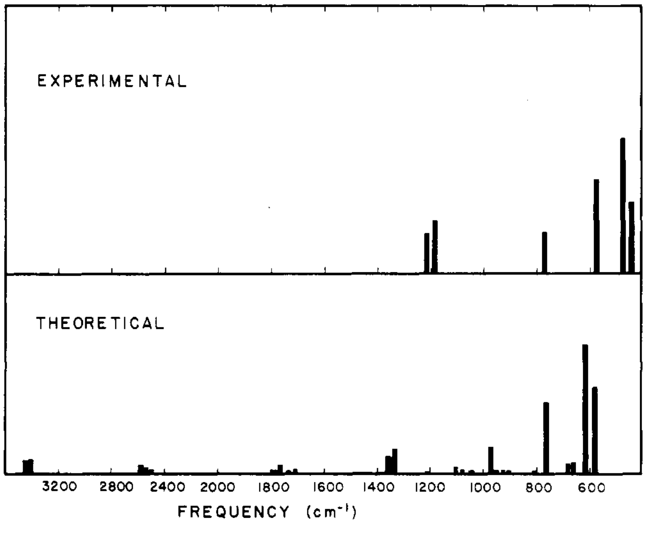

Figure 3. Comparison of the calculated IR spectrum of a 1:1 mixture of cyclobutadiene-*1,2*-d_2 and cyclobutadiene-*1,4*-d_2 in the 4-31G basis set with the observed spectrum of Chapman and De La Cruz.

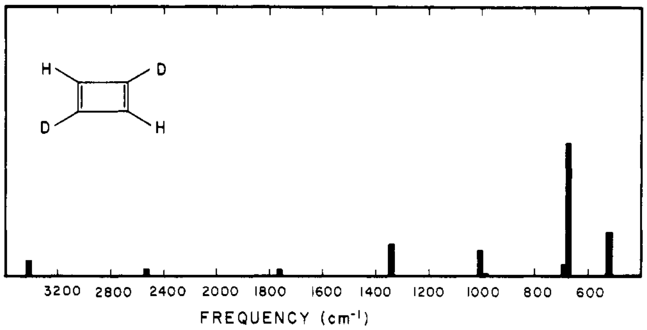

Figure 4. Calculated IR frequencies and intensities of cyclobutadiene-*1,3*-d_2 in the 4-31G basis set.

lated frequencies tend to be too high by as much as 300 cm^{-1}. Vibrational results with the two bases are about the same. Although the intensity of the C–C stretch at 1400 cm^{-1} is improved in the larger basis, the relative position of the two lowest frequency bands is not as good as with the smaller basis.

In the Born–Oppenheimer approximation, cyclobutadiene-*1,2,3,4*-d_4 and **4**–**6** all have the same potential surfaces as cyclobutadiene itself. Different mass weighting and different symmetries give different force-constant matrices. However, these are easily obtained from that of cyclobutadiene; no further energy calculations are required. Diagonalizing these and computing dipole moment derivatives along the new normal modes gives the results in Table I and Figures 2 and 4. The calculated IR spectra of **4** and **5** shown in Figure 2 are sufficiently distinct at lower frequencies to distinguish the two species experimentally. Perhaps this would be most easily done by noting that of the three most intense bands, two are strong and one is medium in **4**, while two are medium and one is strong in **5**. The agreement between theoretical and experimental results in Figure 1 (see also ref 14) suggests that the calculated spectra should be reliable on this major point.

We now turn to a discussion of Chapman and De La Cruz' experimental results[8,9] in light of our calculated spectra. Although IR relative intensities of the dideuteriocyclobutadienes were not given in Chapman's original short communication,[8] they are available in the more recent thesis of De La Cruz.[9] The upper half of Figure 3 shows experimental frequencies and relative intensities of the dideuteriocyclobutadiene obtained by irradiation of α-pyrone-*5,6*-d_2 as given by the final points in Figure 5 of De La Cruz' thesis. The band reported earlier[8] at 576 cm^{-1} is no longer present, but two lower frequency absorptions at 447 and 479 cm^{-1} are now shown.[9] We have not included the 654-cm^{-1} band which Masamune,[15,16] Maier,[17] and Krantz,[18] attribute to a perturbed CO_2 vibration.

It is clear that the experimental spectrum of Figure 3 resembles the theoretical spectrum of neither dideuterio derivative in Figure 2. The spectra in Figure 2 are both shown with the strongest bands of unit intensity, though the strongest band in the upper spectrum is in fact computed to be 0.63 as intense as that in the lower. Taking

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(14) Hess, B. A., Jr.; Schaad, L. J.; Ewig, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 2507–2508.

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(17) Maier, G.; Hartan, H.-G.; Sayrac, T. *Angew. Chem.* **1976**, *88*, 252; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 226–228.

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Table I. Vibrational Frequencies and Relative Integrated Infrared Band Intensities of Cyclobutadiene and Deuteriocyclobutadienes Calculated with a 4-31G Wave Function

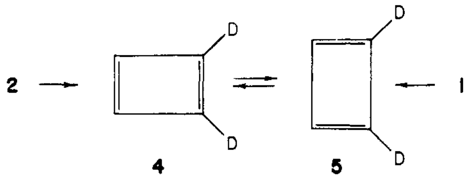
symmetry	frequency,[a,b] cm⁻¹ cyclobutadiene	frequency,[a,b] cm⁻¹ cyclobutadiene-*1,2,3,4*-d_4
b_{3u}	737 (1.00)	541 (1.00)
b_{2u}	739 (0.04)	632 (0.13)
	1400 (0.18)	1154 (0.15)
	3425 (0.03)	2519 (0.05)
b_{1u}	1217 (0.00)	876 (0.00)
	1794 (0.02)	1735 (0.05)
	3425 (0.10)	2554 (0.07)
b_{3g}	978	924
	1322	1067
	3408	2508
b_{2g}	783	617
b_{1g}	1054	843
a_g	1008	778
	1204	1074
	1764	1697
	3461	2614
a_u	616	507
	1071	922

symmetry	frequency,[a,c] cm⁻¹ cyclobutadiene-*1,2*-d_2	frequency,[a,c] cm⁻¹ cyclobutadiene-*1,4*-d_2
a_1	818 (0.00)	663 (0.08)
	1056 (0.00)	906 (0.00)
	1205 (0.00)	1093 (0.01)
	1712 (0.02)	1332 (0.19)
	1783 (0.04)	1729 (0.00)
	2584 (0.04)	2568 (0.02)
	3444 (0.10)	3444 (0.02)
b_1	575 (1.00)	609 (1.00)
	764 (0.92)	979 (0.22)
b_2	681 (0.10)	928 (0.00)
	956 (0.00)	981 (0.00)
	1106 (0.06)	1284 (0.00)
	1366 (0.22)	1764 (0.04)
	2514 (0.01)	2532 (0.03)
	3416 (0.03)	3417 (0.08)
a_2	557	541
	887	708
	1064	1010

symmetry	frequency,[a,d] cm⁻¹, for cyclobutadiene-*1,3*-d_2
a_u	520 (0.33)
	669 (1.00)
	1009 (0.19)
b_u	672 (0.10)
	995 (0.00)
	1342 (0.24)
	1764 (0.05)
	2538 (0.05)
	3425 (0.13)
a_g	857
	954
	1086
	1272
	1730
	2562
	3436
b_g	669
	980

[a] Relative integrated band intensities are given in parentheses for the infrared-active modes. [b] Species of g symmetry are Raman active. The a_u vibrations are neither IR nor Raman active. [c] All modes are Raman active. [d] Species of g symmetry are Raman active.

this into account, we calculated a 1:1 mixture of these two isomers to have the spectrum shown at the bottom of Figure 3. Although the calculated lines are shifted to higher frequencies as is usual in SCF calculations,[5,14] the pattern of the six most intense lines is very similar to that of the experimental spectrum. This suggests that what Chapman actually obtained was an equilibrium mixture of the two isomeric rectangular cyclobutadienes 4 and 5. While 1 and 2 may initially very well have given rise to 5 and 4, respectively, it appears that each was converted into the other under the experimental conditions to establish an equilibrium mixture. This agreement of the experimental and theoretical spectra in Figure 3 provides further evidence that cyclobutadiene is rectangular rather than square.



4 5

Carpenter[10] assumed 4 and 5 to be in an equilibrium proportion of 1:1 at 10 °C. It is difficult to imagine any isotope effect that could cause a large deviation from this value, but as a check it is simple to compute this equilibrium constant from the theoretical molecular geometries and vibrational frequencies. By use of standard expressions for partition functions

$$K = [4]/[5] = (M_4/M_5)^{3/2}(I_{A4}I_{B4}I_{C4}/I_{A5}I_{B5}I_{C5})^{1/2}\frac{\sigma_5}{\sigma_4} \times \exp\left[\frac{-h}{2kT}\sum_{i=1}^{18}(\nu_{4i}-\nu_{5i})\right]\prod_{i=1}^{18}\frac{1-\exp(h\nu_{5i}/kT)}{1-\exp(h\nu_{4i}/kT)} \quad (2)$$

This assumes classical rigid rotor behavior for 4 and 5 (almost certainly reasonable at 10 °C where Carpenter's experiments[10] were done) and that no excited electronic states lie low enough to make a significant contribution. The molecular weights M and symmetry numbers σ are identical for 4 and 5. There remain the rotational, zero-point vibrational, and excited vibrational factors which we compute to give

$$K = 1.00020 \times 1.02313 \times 1.00291 = 1.026 \quad (3)$$

at 10 °C, in good agreement with the value assumed by Carpenter.[10] Since our force constant matrices were computed by using finite Cartesian displacements, normal modes corresponding to translation and rotation did not have exactly zero frequency. The translation frequencies were quite small, but those for rotation were sometimes as large as 50 cm^{-1}. To get some estimate of the effect of these errors on the computed equilibrium constant, we used the Redlich–Teller product rule to replace the rotational partition function in eq 2 by a product of frequencies as in eq 4. This gave $K = 1.005$, still in good agreement with Carpenter's assumption.

$$(I_{A4}I_{B4}I_{C4}/I_{A5}I_{B5}I_{C5})^{1/2} = \prod_{i=1}^{18}(\nu_{4i}/\nu_{5i}) \quad (4)$$

Equation 2 of course does not apply to an equilibrium mixture in the frozen matrix at 8 K. At that temperature even a small energy difference between the isomers is expected to shift the equilibrium overwhelmingly in favor of the more stable structure. For example, an energy difference of 50 cal/mol (=17.5 cm^{-1}) corresponds to an equilibrium constant of 23 at 8 K. Our vibrational calculations are certainly not accurate to this small of an energy difference. The fact that a 1:1 mixture appears to have been observed at 8 K suggests that equilibrium may have been reached while there was still local heating due to the photolysis and that the high-temperature equilibrium mixture was frozen out on cooling.

The calculated IR spectrum of cyclobutadiene-*1,3*-d_2 is shown in Figure 4. Chapman[8] has also reported the spectrum of this compound, but the intensities are not given, and the spectrum is contaminated with lines of the monodeuterio compound so that it is not possible to make a comparison with our computed result.

Registry No. 4/5, 40522-77-8; 6, 40522-78-9; cyclobutadiene, 1120-53-2; cyclobutadiene-*1,2,3,4*-d_4, 56516-62-2.