Table III. Optical States of Bicyclo[1.1.0]butane

State	Vibronic components	Frequency^a range, cm^{-1}	Oscillator strength	Assignment
A	α, β	43 600–48 160	5.3×10^{-4}	A_2
B^b		48 160–57 875	7.4×10^{-2}	B_1
C^c	δ	57 875–61 780	2.2×10^{-2}	A_2 + ?
D		61 780–65 000	2.8×10^{-2}	?
E		6 500–74 000	1.8×10^{-2}	?

[a] Frequency range for integration to give oscillator strength. [b] The γ bands ride on this broad transition. [c] The δ bands appear to ride on a continuum. The oscillator strength for just the δ bands is 6.6×10^{-4}. The δ bands are assigned as A_2, and the underlying continuum presumably corresponds to a different state.

120 lock-in amplifiers which used the 7-Hz signal from the beam modulator driver as the reference.

The sample and reference signals (I and I_0) were digitized and recorded using a PDP-12 computer. In order to improve the signal to noise ratio, the signals were sampled many times (typically 50–1000) and the I/I_0 ratio was derived from the averaged signals. The wavelength marker also was recorded by the computer. After a scan, the sample cell was emptied and the base line was recorded in the same fashion. The final corrected spectrum was obtained as the ratio of the I/I_0 values for the sample run and the base line run.

The spectra shown were plotted using the above data (stored on magnetic tape) as input, along with the sample pressure, cell length, and temperature. The optical cross sections are defined by:

$$\sigma_\nu = \left(\frac{760}{p}\right)\left(\frac{T}{273.15}\right)\left(\frac{1}{9.0L_0}\right)\ln\left(\frac{I_0(\nu)}{I(\nu)}\right)$$

where the pressure is in millimeters and L_0 is the Loschmidt number (2.6868×10^{19} cm^3). This gives the cross section in centimeters^2. For convenience, the cross sections in the figures are reported in megabarns (Mb = 10^{-18} cm^{-2}). Spectral intensities are often expressed in terms of absorbancy index (A) and this is related to the cross section by

$$A = 257.80 \times 10^{18}\,\sigma_\nu$$

A comparison of our observed cross sections with those reported for oxygen[16] and ethylene[17] indicated an uncertainty of about ±20%. The spectra were plotted using a Complot incremental plotter driven by the PDP-12. This allowed any desired section of the spectra to be plotted using any desired plot size.

The MO energy levels and wave functions were calculated using GAUSSIAN-70[18] and the experimental geometry. The wave functions were plotted using the program written by Jorgensen.[19]

References and Notes

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Electronic States of Organic Molecules. 5. High-Resolution Spectrum of the Ã State of Bicyclo[1.1.0]butane[1]

Kenneth B. Wiberg,*[3a] Kevin S. Peters,[2a,3a] G. Barney Ellison,[2b,3a] and F. Alberti[3b]

Contribution from the Department of Chemistry, Yale University,
New Haven, Connecticut 06520, and the National Research Council,
Ottawa, Canada.

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Abstract: The Ã state of bicyclo[1.1.0]butane was examined with a resolution of 0.3 cm^{-1}, permitting the rotational band contours for the vibronic components to be observed. The geometry change accompanying this electronic transition was deduced by an analysis of the band contours. The band origin was located (39 477 cm^{-1}) and was found to be at lower energy than the first transition of ethylene (43 769 cm^{-1}).

In the preceding paper,[4] we presented survey spectra for bicyclobutane and made an initial set of assignments for the observed electronic states of this saturated hydrocarbon. The lowest state (Ã) and the C̃ state were characterized by extensive vibronic activity. The system of bands in the C̃ state was labeled the "δ" series while the components with alternating intensity in the Ã state were referred to as the "α,β" bands. Both of these states were considered to be optically forbidden under one-photon dipole selection rules because they are so weak and were assigned as A_2 under the point group C_{2v}.

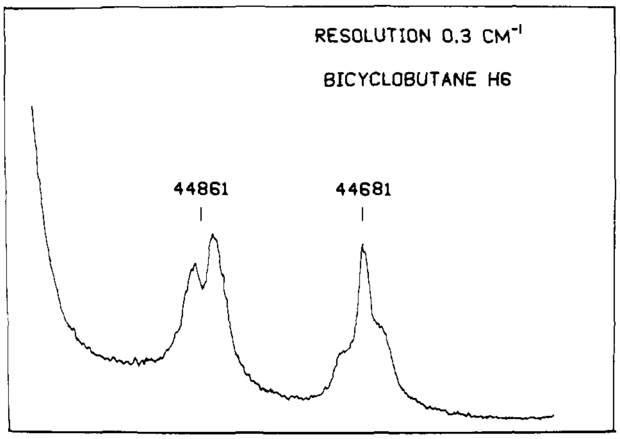


Figure 1. The α_4 and β_3 bands of bicyclobutane-d_0 (from left to right).

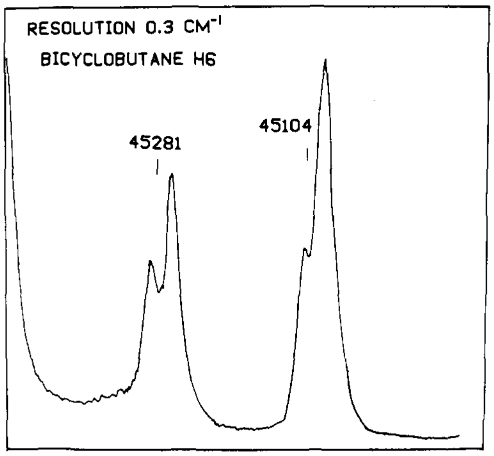


Figure 2. The α_5 and β_4 bands of bicyclobutane-d_0.

A transition to an optically forbidden state may be observed if intensity is borrowed from a nearby allowed transition. This borrowing of intensity results from mixing of the two states by a vibration. In vibronic coupling, the transition moment has the same symmetry as the state from which the intensity is borrowed.[5]

In this paper we examine the individual vibronic bands of the $\tilde{A}$ state under high resolution. From an analysis of the band contours via calculation of the rotational envelopes, we are able to establish the symmetry of the active vibrations that couple the $\tilde{A}$ state and the symmetry of the strong optical state that donates intensity.

Experimental Section

The vacuum spectrometer used for recording the spectra is a 10 m Eagle with a 600 line/mm grating yielding a dispersion of 0.75 Å/mm in first order. The resolving power is 200 000 which results in a resolution of 0.25 cm^{-1} at 50 000 cm^{-1}. The spectra were taken in the gas phase in a 1-m cell with pressures from 0.03 to 100 Torr. A 600-W Xenon continuum lamp was used with detection by Ilford type Q2 photographic plates.

Results

For bicyclobutane-d_0 (H6) the first fourteen members of the δ,β series were examined. The frequencies were measured directly from the photographic plate, using Cu emission lines as a standard with an accuracy of 1 cm^{-1}. Since the vibrations are broad, it was only possible to assign the band positions within 3 cm^{-1}. Densitometer tracings of a few of the vibrations are shown in Figures 1-4. With more accurate data it is found that the α,β bands are two distinct series with even a third progression starting at higher frequencies. The progressions are listed in Table I. There are also at least two more vibrations to the red of 44 259 cm^{-1} (β_2) which fit into the first two series but are too weak to be measured accurately.

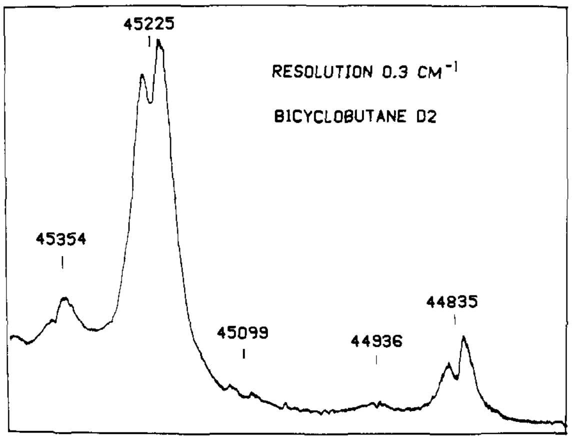


Figure 3. The B4, A4, C3, B3, and A3 bands of bicyclobutane-d_2.

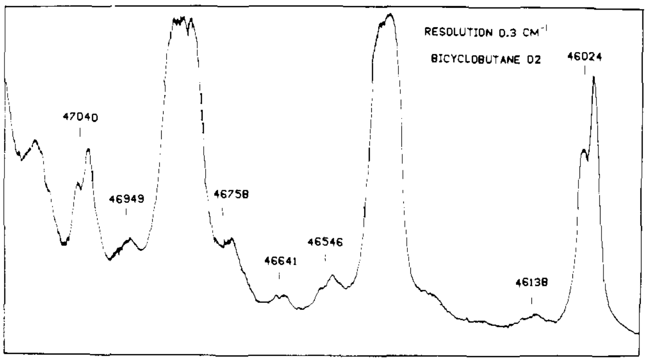


Figure 4. The ultraviolet spectrum of bicyclobutane-d_2 from 46 000 to 47 100 cm^{-1}.

Table I. Frequencies (cm^{-1}) for High-Resolution Spectrum of Bicyclobutane H6

First series (β)		Second series (α)		Third series	
44 259	$18^1_0 9^{10}_0$	44 437	$17^1_0 9^{10}_0$	45 745	$18^3_0 9^{11}_0$
44 681	$18^1_0 9^{11}_0$	44 861	$17^1_0 9^{11}_0$	46 161	$18^3_0 9^{12}_0$
45 104	$18^1_0 9^{12}_0$	45 281	$17^1_0 9^{12}_0$	46 587	$18^3_0 9^{13}_0$
45 519	$18^1_0 9^{13}_0$	45 707	$17^1_0 9^{13}_0$	47 018	$18^3_0 9^{14}_0$
45 944	$18^1_0 9^{14}_0$	46 132	$17^1_0 9^{14}_0$		
46 363	$18^1_0 9^{15}_0$				
46 787	$18^1_0 9^{16}_0$				

The first vibrations in series one and two display a very pronounced P, Q, R structure indicating an "A" type band,[6] but the second member of the first series (β_3) (44 681 cm^{-1}) begins to lose the sharp P, Q, R and the second vibration (α_4) (44 861 cm^{-1}) of the second series has a doublet structure. This is shown in Figure 1. These band contours will be discussed in greater detail later.

Bicyclobutane-d_2 (D2) has four observed series which are listed in Table II. The first band is so weak that a contour cannot be observed. The first observed contour, Figure 3, is at 44 835 cm^{-1} which has the same doublet type band as the 44 861 band in H6. No triplet "A" type bands are observed.

In an effort to determine whether hot bands were present, spectra were recorded at 90 °C but it was found that bicyclobutane begins to rearrange thermally to butadiene and the broad structure of butadiene swamps out the vibrational

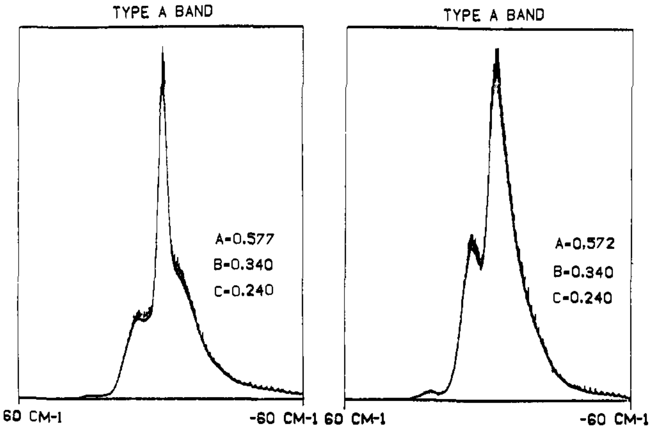


Figure 5. Calculated rotational band contours for the vibronic bands of bicyclobutane-d_0.

Table II. Frequencies (cm^{-1}) for High-Resolution Spectrum of Bicyclobutane D2

First series		Second series		Third series		Fourth series	
44 432	$18_0^1 9_0^{11}$	44 936	$17_0^1 9_0^{12}$	45 099	$18_0^3 9_0^{10}$	46 248	$16_0^1 9_0^{15}$
44 835	$18_0^1 9_0^{12}$	45 353	$17_0^1 9_0^{13}$	45 927	$18_0^3 9_0^{12}$	46 640	$16_0^1 9_0^{16}$
45 225	$18_0^1 9_0^{13}$	45 727	$17_0^1 9_0^{14}$	46 333	$18_0^3 9_0^{13}$	47 040	$16_0^1 9_0^{17}$
45 618	$18_0^1 9_0^{14}$	46 140	$17_0^1 9_0^{15}$	46 758	$18_0^3 9_0^{14}$	47 446	$16_0^1 9_0^{18}$
46 024	$18_0^1 9_0^{15}$	46 546	$17_0^1 9_0^{16}$			47 854	$16_0^1 9_0^{19}$
46 429	$18_0 9_0^{16}$	46 949	$17_0^1 9_0^{17}$				
46 842	$18_0 9_0^{17}$						

structure of bicyclobutane. Also, spectra were taken at −78 °C which resulted in a vapor pressure of 5 Torr making the first four bands unobservable in the H6 compound. However, the remaining intensities were insensitive to the low temperature thus indicating the presence of only vibrational bands originating in the ground state with $v'' = 0$.

Rotational Band Contour Analysis. By far the most intriguing aspect of the vacuum ultraviolet spectrum of bicyclobutane is the first five vibrations observed in the α and β bands. As mentioned above, the first three members display an "A" type band contour with a P, Q, R structure, and the next two bands, along with the rest of the α,β bands, show a "B" type or doublet band. Mixed polarization of the transition moment must be ruled out for this would manifest itself by alternating band contours. This implies that a change in rotational band contour must occur from a vibrational level dependence of the rotational constants. An example of this can be found in glyoxal.[7]

In an asymmetric rotor such as bicyclobutane where the three moments of inertia are not equal, the rotational energy levels within an isolated molecule are given by

$$E(A,B,C) = (A + C)J(J + 1) + (A - C)E_\tau(K)$$

where $A = h/4\pi c I_a$ with A in units of cm^{-1} and I in g cm^2 and $E_\tau(K)$ is defined in ref 8. It is found[8] that A is not constant but has a vibrational dependence of the form

$$A_v = A_e + \alpha_i(v_i + d_i/2)$$

where A_v is the effective rotational constant, A_e is the equilibrium rotational constant, d_i is the degeneracy of the ith normal mode, and α_i is the constant representing the change in rotational constant per quantum of vibration. Contributions to α_i come from anharmonicity of the vibrational potential function and from Coriolis perturbation.

To find the rotational constants that would match the band contours of the β's at 44 681 cm^{-1} (β_3) and 45 104 cm^{-1} (β_4) a search was carried out using an asymmetric rotor computer program described previously.[9] A computed band contour was synthesized using the rotational constants for the ground state held constant at the observed experimental values of $A'' = 0.580\,149$ cm^{-1}, $B'' = 0.311\,649$ cm^{-1}, and $C'' = 0.280\,94$ cm^{-1}.[10]

From the calculations it was found that only an A band could be changed from a triplet to a doublet with just a small change in rotational constants. Furthermore, only one combination of rotational constants allowed a triplet to go to a doublet. Here A' and C' decreased and B' increased from the ground state equilibrium values. The best set of constants are $A' = 0.577$, $B' = 0.340$, and $C' = 0.240$ which resulted in a triplet shown in Figure 5. By changing A' by 0.9% to $A' = 0.572$ and holding $B' = 0.340$ and $C' = 0.240$, a doublet resulted (Figure 5). Both of these spectra were calculated for $J = 0$ to 80 and convoluted with a triangular slit with a fwhm of 5.0 cm^{-1}. The shapes of the calculated bands are in very good agreement with the experimentally observed bands.

As a result of these calculations, we now have the rotational constants and moments of inertia of the excited state. It is not possible with just three moments of inertia to calculate a unique excited state geometry. We can, however, make some qualitative statements from the fact that A' and C' decrease while B' increases. If the dihedral angle between the two three-membered rings in bicyclobutane is allowed to increase from the equilibrium value of 122° while still retaining overall C_{2v} symmetry, it is found that A' increases. Also, if the dihedral angle increases and the bond between C_1 and C_3 is allowed to increase, retaining C_{2v} symmetry, A' again increases. The only molecular motion of the carbon framework that allows a decrease of A' while increasing the dihedral angle is one in which its C_{2v} symmetry is lost by moving C_2 and C_4. There are two possible distortion modes. The first, which remains symmetric with respect to the plane of symmetry which passes through C_1 and C_3, corresponds to b_1 symmetry whereas the second, which is antisymmetric with respect to the above plane, corresponds to b_2 symmetry.

It may be noted that whereas the resolution of the spectrometer was 0.3 cm^{-1}, it was necessary to convolute each rotational line with a slit width of 5 cm^{-1} to reproduce the observed spectrum. The broadening of the band presumably results from the short lifetime of the state. Using the relationship $\Delta E \Delta t \approx h$, the lifetime is about 6×10^{-12} s.

Vibrational Analysis. α,β Bands. From the rotational band contour analysis it was established that α and β bands had A type band contours which, under C_{2v} symmetry, correspond to B_2 polarization of the transition moment. Therefore the state from which the α and β bands, being of A_2 symmetry, borrow their intensity has B_2 symmetry. The vibration involved in the mixing of A_2 with B_2 state must then have b_1 symmetry for $A_2 \times B_2 = b_1$. Thus, the inducing modes in the α,β series have b_1 symmetry and all vibrations built on top of these b_1 modes must retain an overall symmetry of b_1. As established in the previous paper[4] the vibration built on top of these b_1 false origins is ν_9 which has a_1 symmetry thus preserving the overall b_1 symmetry.

Let us now identify the b_1 vibrational modes which are responsible for inducing the electronic transition to the state containing the α,β bands. The vibrations of b_1 symmetry for the ground state of H6 and D2 are as follows:[11]

	H6	D2		H6	D2
ν_{15}	1268	1205	ν_{17}	983	835
ν_{16}	1113	1109	ν_{18}	735	695

We will initially assume that the β vibrations in H6 correspond to the A vibrations in D2, based on similarity of intensities. The next vibrations of higher frequency are the α bands, with a typical splitting from the β bands of 44 861 − 44 681 = 180

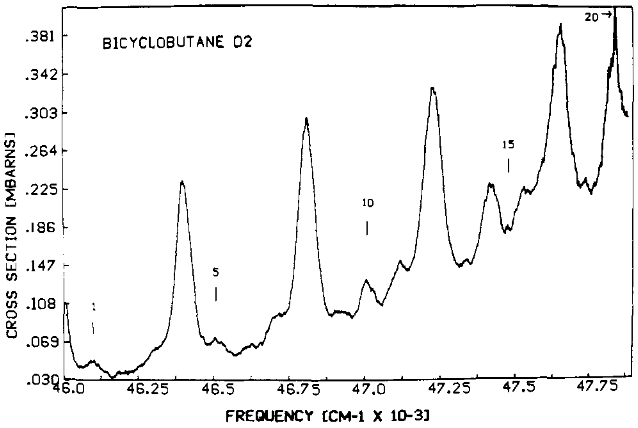


Figure 6. The ultraviolet spectrum of bicyclobutane-d_2 from 46 000 to 48 000 cm^{-1}.

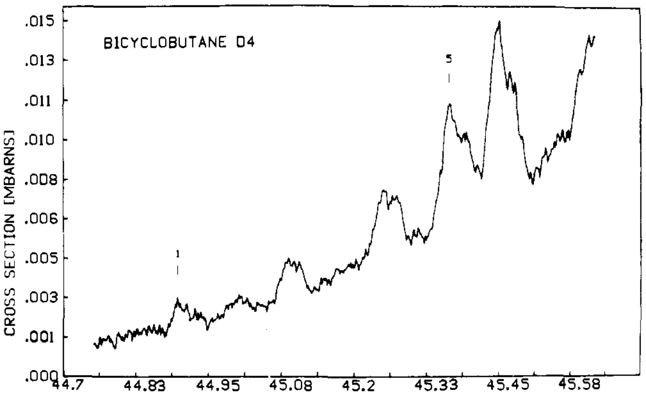


Figure 7. The ultraviolet spectrum of bicyclobutane-d_4 from 45 000 to 45 500 cm^{-1}.

cm^{-1}. In D2 the next vibrations of higher frequency are the B bands which are typically split from the A bands by 44 936 − 44 835 = 101 cm^{-1}. In order to identify the ground vibrations that correspond to β and α, a pair of vibrations must be found which differ by at least 180 cm^{-1} in H6 and at least 101 cm^{-1} in D2. Vibrational frequencies generally decrease on going to an excited state; hence the excited state vibrational frequency differences are less than those in the ground state.

An examination of the b_1 frequencies suggests that the β bands are induced by ν_{18} (735 cm^{-1} in the ground state) and the α bands are induced by ν_{17} (983 cm^{-1}). The ratio of the excited state difference to the ground state difference is 180/248 = 0.725. In D2, the ground state frequency for ν_{18} is 695 cm^{-1} whereas that for ν_{17} is 835 cm^{-1}, yielding a ratio of 101/140 = 0.721 which is in excellent agreement with H6. An additional requirement is that the intensity of the α bands decreases markedly on deuteration. This indicates a significant change in the nature of the vibrational mode so as to cause a change in the Franck-Condon factors. The vibration ν_{17} has been found to have a change in the contribution from various internal coordinates on deuteration.[11]

To assign the remaining vibrations in the ABCD series let us turn our attention to Figure 6. Again we have the set of four vibrations repeating itself every 400 cm^{-1} where the intense vibration of the set is A and the remaining three are BCD. A has been assigned 18^1_0 and B as 17^1_0. One notable aspect of this spectrum is that while the intensities of the ABD progression remain in constant proportion relative to one another, C markedly increases its intensity relative to A, B, D for each additional quantum of vibration. This indicates that C is not a member of the ABD series but is an overtone.

The difference between D, which is yet to be assigned, and A is 311 cm^{-1}. If D were to be equated to ν_{16} in the ground state then the ratio of ν_{16}–ν_{18} in going from the ground state to the excited state is 311/414 = 0.75 which is consistent with all other vibrational frequency changes in both H6 and D2.

If C is to be assigned making the assumption that it is an overtone of a fundamental series in the excited state one must assume that C is an overtone of A, based upon an intensity consideration, for only A is strong enough to have observable overtones. Let us assume that all vibrations in the excited state drop to 72% of their ground state frequency. Then 18^1_0 would have a frequency shift of 500 cm^{-1} from the origin in D2. The selection rules of vibronic coupling theory require that only odd overtones will be observed. The first overtone, 18^3_0, would have a frequency shift of 1500 cm^{-1} from the origin. Since we do not know the origin of the transition, the only means of identifying the 18^3_0 would be its expected displacement from 18^1_0. By building quanta of 9^n_0 upon 18^1_0 we would have $18^1_0 9^2_0$ = 1300 cm^{-1} and $18^1_0 9^3_0$ = 1700 cm^{-1}. Therefore the displacement of 18^3_0 from the $18^1_0 9^n_0$ series is approximately 200 cm^{-1}. Experimentally it is found that the displacement of C from A is 201 cm^{-1}. Consequently, the following assignments are made:

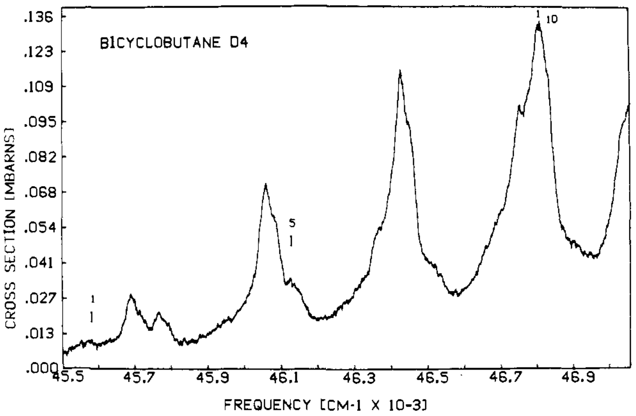


Figure 8. The ultraviolet spectrum of bicyclobutane-d_4 from 45 500 to 47 000 cm^{-1}.

$$A = 18^1_0 9^n_0$$

$$B = 17^1_0 9^n_0$$

$$C = 18^3_0 9^n_0$$

$$D = 16^1_0 9^n_0$$

Under high resolution, the spectrum of H6 displays a third series that appears as a broadening of the α bands at medium resolution beginning with α_6 (45 745 cm^{-1}). Using the same argument as for the overtone C band in D2, this third series is assigned as an overtone of the β's. The resulting assignments of the α,β bands are as follows:

$$\beta = 18^1_0 9^n_0$$

$$\alpha = 17^1_0 9^n_0$$

$$\text{third} = 18^3_0 9^n_0$$

In light of the assignment of the α,β bands in both H6 and D2, let us turn our attention to the same sequence of bands in the medium resolution spectrum of D4. The lack of a simple progression built upon two or three fundamentals as in D2 and H6 is immediately apparent. Instead, on close examination of Figures 7, 8, and 9 at least six different progressions, each with an average of 352 cm^{-1}, can be assigned and are listed in Table III. There is one feature in the D4 progression that is not similar to H6 and D2. The first and third series, Table III, are initially as intense as the second series but by the third observed

Table III. Frequencies (cm^{-1}) for the Low-Resolution Spectrum of Bicyclobutane-d_4

First series		Second series		Third series		Fourth series		Fifth series		Sixth series	
44 895	$17^1_0 9^{13}_0$	45 010	$18^3_0 9^{11}_0$	45 085	$18^1_0 9^{14}_0$	46 007	$18^5_0 9^{11}_0$	46 630	$18^7_0 9^{10}_0$	47 288	$18^9_0 9^{10}_0$
45 251	$17^1_0 9^{14}_0$	45 383	$18^3_0 9^{12}_0$	45 447	$18^1_0 9^{15}_0$	46 365	$18^5_0 9^{12}_0$	46 982	$18^7_0 9^{11}_0$	47 639	$18^9_0 9^{11}_0$
45 597	$17^1_0 9^{15}_0$	45 727	$18^3_0 9^{13}_0$	45 797	$18^1_0 9^{16}_0$	46 723	$18^5_0 9^{13}_0$	47 340	$18^7_0 9^{12}_0$	47 977	$18^9_0 9^{12}_0$
		46 074	$18^3_0 9^{14}_0$	46 136	$18^1_0 9^{17}_0$	47 062	$18^5_0 9^{14}_0$	47 678	$18^7_0 9^{13}_0$	48 327	$18^9_0 9^{13}_0$
		46 417	$18^3_0 9^{15}_0$	46 504	$18^1_0 9^{18}_0$	47 404	$18^5_0 9^{15}_0$	48 039	$18^7_0 9^{14}_0$		
		46 775	$18^3_0 9^{16}_0$	46 866	$18^1_0 9^{19}_0$	47 775	$18^5_0 9^{16}_0$	48 383	$18^7_0 9^{15}_0$		
		47 109	$18^3_0 9^{17}_0$			48 108	$18^5_0 9^{17}_0$				
		47 460	$18^3_0 9^{18}_0$								
		47 860	$18^3_0 9^{19}_0$								
		48 172	$18^3_0 9^{20}_0$								

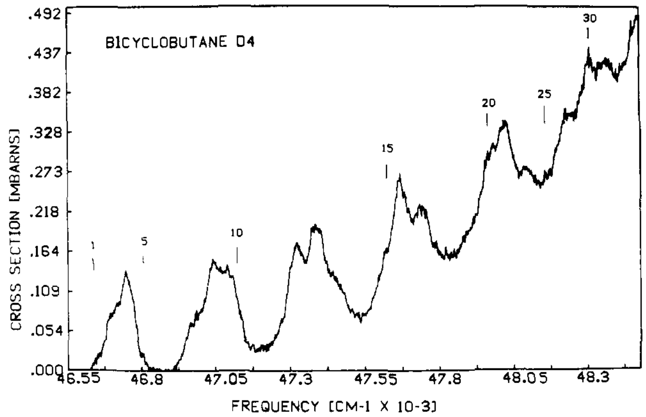


Figure 9. The ultraviolet spectrum of bicyclobutane-d_4 from 46 500 to 48 500 cm^{-1}.

quantum of excitation of the series, the second series is much more intense than the first and third. By the time the second progression has reached 47 109 cm^{-1}, there are now a fourth and fifth series and going up one more quantum in the progression, the fourth and fifth are more intense than the second.

One hint at an interpretation comes from the A, C series in D2. It is observed that with each additional quantum within the progression, the C series becomes more intense than the A series. Let us assume that the intense vibrations are the overtones in D4 and are the same as those involved in H6 and D2, that is overtones in ν_{18}. In the ground state $\nu_{18} = 623$ cm^{-1} for D4. Assuming that in D4 there is a decrease to 80%, then for the fundamentals and overtones of ν_{18}, $18^1_0 = 498$ cm^{-1}, $18^3_0 = 1494$, and $18^5_0 = 2490$. As in D2 and H6, we have yet to assign an origin, therefore the only means of identifying overtones is by their displacement from one another. Let us assign the peak at 45 085 cm^{-1} as a member of a progression in $18^1_0 9^n_0$ and assign the peak at 45 447 cm^{-1} is a member of the progression $18^1_0 9^{n+1}_0$. Next we assign the peak at 45 383 cm^{-1} as a member of the $18^3_0 9^n_0$ progression. There is actually a peak approximately 360 cm^{-1} to the red of 45 383 cm^{-1} which is a member of this progression but because it is so broad and weak we shall use 45 383 as representative of the progression. Based on a drop to 80% in fundamental vibrational frequency on going to the excited state we have $18^1_0 9^3_0 = 1554$ cm^{-1} and $18^3_0 = 1494$. The displacement of the series would be $18^1_0 9^3_0 - 18^3_0 = 60$ cm^{-1}. The observed displacement is 64 cm^{-1} which is in good agreement with this interpretation. By similar arguments it can be shown that the fourth series is a progression in 18^5_0, the fifth series in 18^7_0, and the sixth series in 18^9_0.

All the observed series have been assigned as a fundamental or overtone of ν_{18} except the first series which cannot be put into this scheme. It must therefore be another fundamental. Consider the peaks at 45 085 cm^{-1} and 45 251 cm^{-1} with an energy difference of 166 cm^{-1}. As in H6 and D2 this mode is assigned as derived from ν_{17}. In the ground state $\nu_{17} - \nu_{18} = 227$ cm^{-1} and the ratio of the excited state drop to the ground state drop is $166/227 = 0.73$ which is in excellent agreement with H6 and D2.

δ Bands. In the previous paper we presented the argument that since the inducing vibrations of the δ bands are not of a_1 symmetry, the state symmetry is A_2 which is consistent with the observed oscillator strength of $f = 6.6 \times 10^{-4}$. We were not able to obtain high-resolution spectra of the δ bands from which to identify the symmetry of the active vibrations obtained through the polarization of the transition moment. However, there is a striking similarity between α, β, and δ bands vibrational patterns in terms of frequencies and the change in intensities upon deuteration thus suggesting vibrational symmetries of b_1. As in the α,β bands, δ_1 and δ_1' are assigned as 18^1_0. δ_2 in H6 is assigned as 17^1_0 which in D2 cannot be observed. This same effect occurs upon deuteration of the α bands. δ_6' in D2 corresponds to the C band series which is an overtone of ν_{18}, 18^3_0.

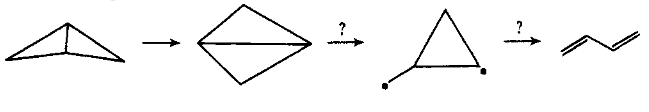
Origin of the α–β Bands. The question of where the origin of the α,β series is in all three compounds is yet to be answered. A method similar to Innes'[12] treatment of the n-ν transition of ethylene will be used in determining the origin. For the δ bands we cannot observe the origin, but the displacement of ν_{18} upon deuteration can be observed. In H6 18^1_0 is at 57 960 cm^{-1}, while in D2 18^1_0 is at 57 977 cm^{-1} and in D4 18^1_0 is at 58 054 cm^{-1}, which gives blue shifts relative to H6 of 17 cm^{-1} for D2 and 94 cm^{-1} for D4. Assuming comparable force fields for the two $^1A_2$ states, the extrapolated false origins 18^1_0 for the α,β bands of H6, D2, and D4 respectively are 40 006, 40 023, and 40 167 cm^{-1}. In the extrapolation the repeating frequency in the progression for H6 was 422 cm^{-1}, for D2 it was 400 cm^{-1}, and for D4 it was 352 cm^{-1}. This approximation does not allow for anharmonicity in vibrational functions in the excited state. The resulting blue shifts of 18^1_0 from H6 are 15 cm^{-1} for D2 and 188 cm^{-1} for D4.

The location of the true origin can be determined with the assumption of a decrease in excited frequencies relative to the ground state frequencies of 72% for H6 and D2 and 80% for the D4. Using the resulting frequencies calculated for 18^1_0, the origins for H6 and D2 and D4 are 39 477, 39 522, and 39 668 cm^{-1} resulting in blue shifts of 45 cm^{-1} for D2 and 191 cm^{-1} for D4.

Conclusion

Bicyclobutane is a most unique molecule in terms of its chemical and electronic properties. For a saturated hydrocarbon it has an origin for the first electronic transition (39 477 cm^{-1}) lower in energy than ethylene (43 769 cm^{-1}). The first electronic state based upon molecular orbital theory should have B_1 symmetry. Instead the first state has been shown to have A_2 symmetry. Also, in order to observe the A_2 state optically, there is probably a state of B_2 symmetry close in energy to the A_2 state.

From the rotational band contour analysis bicyclobutane was shown to undergo a distortion in the excited state breaking its C_{2v} ground state symmetry. The vibronic coupling involving b_1 vibrations along with a long progression involving the "ring-flapping" mode, ν_9, suggests that the excited species approaches planarity and is distorted in accord with b_1 symmetry. We should like to obtain an approximate geometry for the excited state based on the moments of inertia. The three moments allow only three geometrical variables. These were taken as the central C–C bond length, the change in the outside C–C bond lengths (which were assumed to be equal and opposite), and the dihedral angle between the two three-carbon planes. Local C_{2v} symmetry was assumed at the methylene groups with unchanged bond angles and lengths, and the C–C–H angle at the bridgehead also was assumed to be unchanged. Based on these assumptions, it was necessary to increase the dihedral angle to a value close to 180°. It was set at 180° and the other variables were adjusted. The best fit was found with the central C–C length = 1.647 Å and the outside C–C lengths = 1.778 and 1.218 Å. This gave as moments of inertia $A' = 0.567$ cm^{-1}, $B' = 0.338$ cm^{-1}, and $C' = 0.241$ cm^{-1}, which are in good agreement with the observed values, especially considering the uncertainty in the hydrogen positions. In summary, the experimental data suggest that the equilibrium geometry is planar, and that the molecule becomes "kite" shaped.



The sudden broadening of the vibrational bands at 48 431 cm^{-1} further suggests that the molecule may undergo a photochemical transformation at this energy. One obvious candidate would be a photochemical rearrangement to butadiene, and the observed deformation mode could lead to this product. The photochemical transformations which accompany this electronic transition are being examined.

References and Notes

(1) Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-72-2239.
(2) (a) Taken in part from the Ph.D. thesis of K.S.P., 1975; (b) Taken in part from the Ph.D. thesis of G.B.E., 1974.
(3) (a) Yale University; (b) National Research Council.
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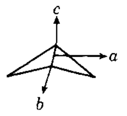
(6) A type "A" band implies polarization of the transition moment along the molecular *a* axis:



(cf. ref 11 for A, B, and C type band shapes for bicyclobutane).
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Ground States of Molecules. 33.[1] MINDO/3 Calculations of NMR Coupling Constants

Michael J. S. Dewar,* David Landman, Sung Ho Suck, and Paul K. Weiner

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received October 24, 1975*

Abstract: MINDO/3 calculations of NMR coupling constants, using finite perturbation theory, for couplings between carbon, hydrogen, and nitrogen are in fair agreement with experiment but somewhat inferior to INDO. The orbital densities calculated by a nonlinear least-squares procedure are close to their theoretical values.

Now that NMR spectroscopy has grown into a major technique for determining molecular structures, the need for a corresponding theory of chemical shifts and coupling constants has become pressing. If such calculations could be carried out with sufficient accuracy and at reasonable cost, the results would be of major practical value in the identification of unknown molecules. However, while a number of approaches to this problem have been reported,[2] none as yet has proved satisfactory. Either the results are too inaccurate, or the calculations are limited by considerations of cost to very small molecules.

Recent work in these laboratories has led to the development of a semiempirical SCF-MO method (MINDO/3[3]) which has met with remarkable success in a number of connections. Although it was parametrized solely to fit the energies and geometries of molecules, it has also given surprisingly good results for a variety of other molecular properties.[4] We therefore decided to see whether the same would be true for calculations of NMR coupling constants partly in the hope that the results might be accurate enough for such calculations to be of practical value and partly to see how well MINDO/3 would cope with yet another molecular property.

This paper reports calculations of coupling constants between carbon, hydrogen, and nitrogen in a variety of organic molecules.

Procedure

The MINDO/3 method has been described in detail.[3] The calculations reported here were carried out using the standard parameters.[3] The geometry of each molecule was first determined by minimizing the energy with respect to all geometrical variables.[3] The calculations of coupling constants were then

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