Consistent with the above interpretation, the isopropyl resonance at −172.3 °C is accurately simulated using two superimposed doublet resonances one at δ 1.16 and 0.80 and the other at δ 1.08 and 0.88 with respective relative populations of 0.46 and 0.54.

It is obvious of course that *rotation* of **2** to **4** or **5** to **7** involves C–N rotation for *both* the ethyl and isopropyl groups. Only one of these processes need have a barrier within the limits of the DNMR method to produce the observed spectral changes (Figure 1). Based on steric arguments only, the rate-controlling process is most likely isopropyl C–N rotation with the ethyl group rotating in concert with the isopropyl group or in a separate rotation (after isopropyl rotation) to the appropriate optimized geometry. The nature of the DNMR spectra do not allow a stereodynamical distinction between ethyl or isopropyl rotation being rate-controlling. *However, it is clear that although multiple in character, C–N rotation has been observed under conditions of static nitrogen inversion in an acyclic trialkylamine.*

Complete ^{1}H DNMR line shape analyses for both the methylene and isopropyl resonances were performed using a locally revised version of computer program DNMR3[9] and employing four molecular configurations (eq 1: **2, 4, 5, 7**). The exact correlation between the k_i or k_r values (Figure 1) used separately for the methylene and isopropyl resonances speaks strongly for the stereodynamical model described above. Rate constants in Figure 1 which are either very large (>10 000) or very small (<0.5) have been extrapolated from values obtained for a particular rate process in the intermediate exchange region. Activation parameters for nitrogen inversion are $\Delta H^{\ddagger} = 8.3 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = 5.5 \pm 4.0$ gibbs, and $\Delta G^{\ddagger} = 7.5 \pm 0.2$ kcal/mol at −121.3 °C. For C–N rotation, they are $\Delta H^{\ddagger} = 5.3 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -3 \pm 2$ gibbs, and $\Delta G^{\ddagger} = 5.6 \pm 0.2$ kcal/mol at −157.8 °C.

It should be pointed out that in a formal sense separate DNMR coalescence phenomena for rotation and inversion have been observed in the *cyclic* system *N,N′,N″*-trimethyl-1,3,5-triazane[8] in which the barrier to ring reversal is observed to be much higher than that for nitrogen inversion. The ring reversal process does indeed involve rotation about C–N bonds but the transition state for ring reversal possesses a significant amount of angle strain which is not present in an acyclic case such as **1**.

The results reported here reveal that it is possible to observe separate and distinct DNMR coalescence phenomena for inversion and rotation rate processes in relatively unhindered acyclic trialkylamines and we are pursuing research aimed at assessing the effect of structural modifications on the relative rates of the two processes.

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(2) Alfred P. Sloan Research Fellow; Camille and Henry Dreyfus Teacher-Scholar.

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Electronic States of Organic Molecules. 4. Ultraviolet Spectrum of Bicyclobutane[1]

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Abstract: The ultraviolet spectrum of bicyclo[1.1.0]butane has been examined from 43 000 to 77 000 cm^{-1}. The first band (~45 000 cm^{-1}) is low in intensity, but has marked vibronic structure. The second band (~50 000 cm^{-1}) is broad, relatively intense, and has little structure. It probably results from a transition between the bonding and antibonding "π-like" central C–C bond orbitals. Another weak band (~58 000 cm^{-1}) follows which has a vibronic structure quite similar to that found in the first band. The remainder of the spectrum is relatively broad with little structure.

Bicyclo[1.1.0]butane, cyclobutene, and butadiene form an interesting triad of molecules which may be interconverted. Thermolysis of the first two leads to butadiene,[4] whereas irradiation of butadiene leads to both bicyclobutane and cyclobutene.[5] Our interest in these compounds and their interconversions has led us to examine their spectra in some detail. We have presented a vibrational analysis for the ground state of bicyclobutane,[6] and we now report the ultraviolet spectrum from 43 000 to 76 000 cm^{-1}. The spectra have been obtained for bicyclobutane-d_0, *-1,3*-d_2, and *-2,2,4,4*-d_4. The preparation of the labeled compounds has been given previously.[6]

Results

The ultraviolet spectrum of bicyclobutane-d_0 (H6) from 43 000 to 76 000 cm^{-1} is shown in Figures 1–4 and in Table I. The spectra of bicyclobutane-d_2 and -d_4 are similar. The lowest energy transition, Figure 2a, extends from 44 000 to 48 100 cm^{-1} and is not included in Figure 1. It is characterized

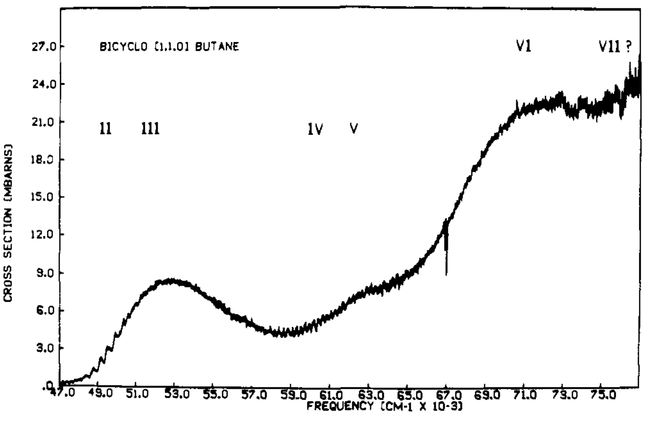

Figure 1.

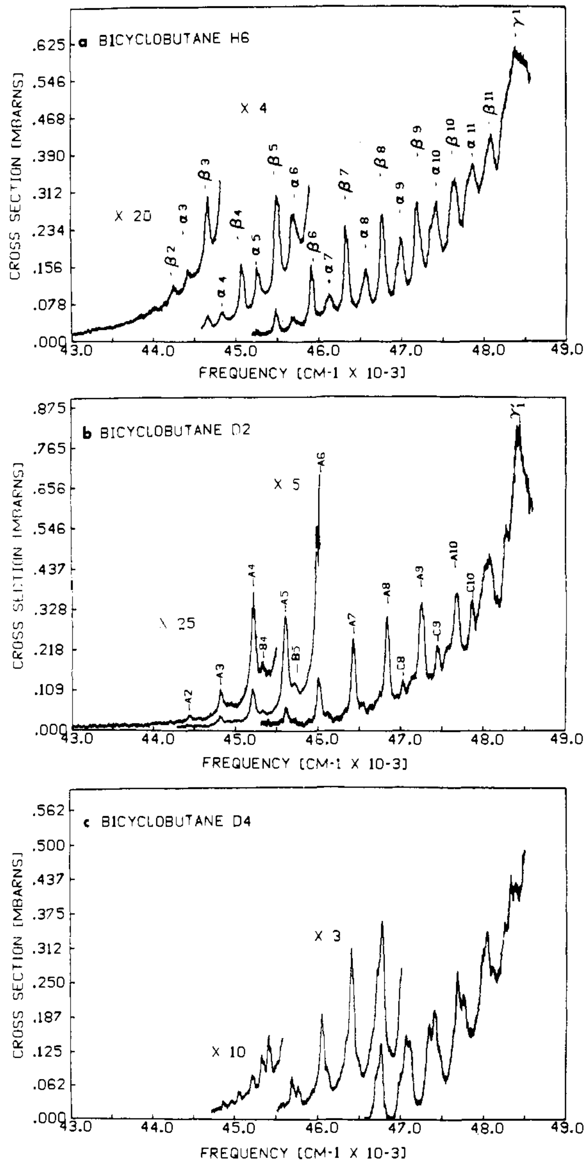

Figure 2.

by low intensity and a long vibrational progression. This is followed by less well resolved vibrational structure which rides on a broad relatively intense band from 48 000 to 55 000 cm^{-1}. This band probably represents the first allowed transition.

The region from 57 000 to 62 000 cm^{-1} is again rich in vibrational structure (Figure 4a). This appears to be followed by a structureless band centered at about 63 000 cm^{-1}. The most intense band in the spectrum appears at about 69 000-71 000 cm^{-1}, and may be followed by another band.

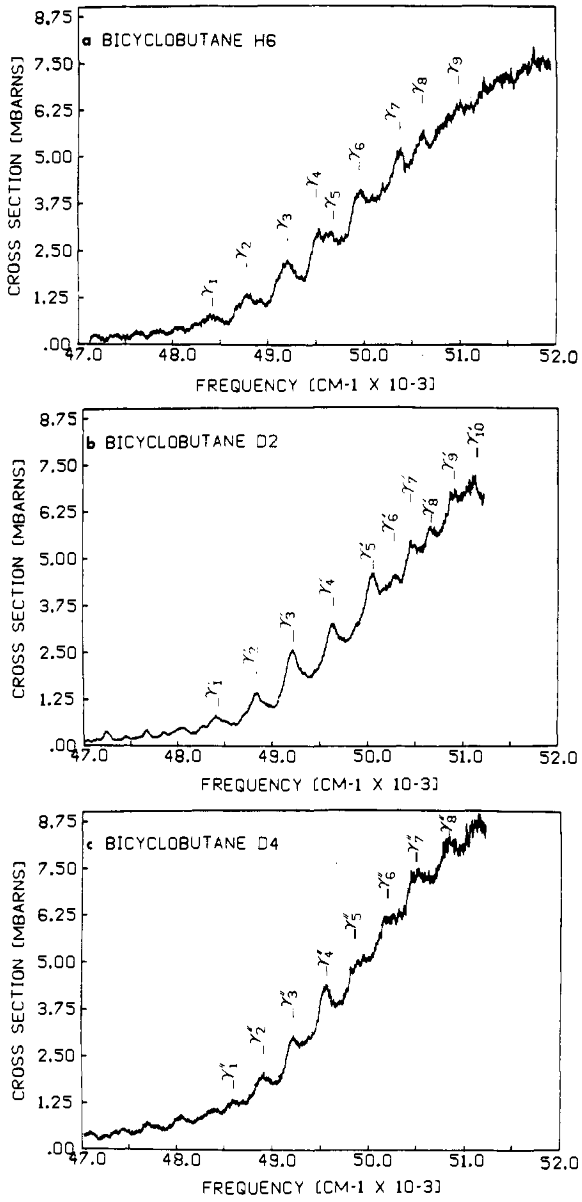

Figure 3.

At least five transitions are easily recognized in the region which was examined, and there may be several others. Unlike most saturated hydrocarbons, some of the bands show vibrational structure and are candidates for vibronic analysis. It is reasonable to assign all of the bands showing vibrational structure to valence transitions rather than Rydberg transitions. The first band in the photoelectron spectrum of bicyclobutane shows no vibrational structure. The Rydberg transitions, if any, would be expected to have similar Franck-Condon factors and also be structureless.

H6. The lowest energy transition for H6 (Figure 2a) consists of at least 20 members which alternate in intensity. These bands are designated as the α and β bands with the β's being the more intense. If assumed to be one series, the bands can be fitted to a harmonic potential with $\Delta\nu = 210 \pm 26$ cm^{-1}. If, however, it is assumed that every other vibration is a member of the same series, then $\Delta\nu = 424 \pm 18$ cm^{-1} for the α's and $\Delta\nu = 416 \pm 28$ cm^{-1} for the β's. With a resolution of 12 cm^{-1} it cannot be determined whether this is one or two series of vibrations. The oscillator strength of these bonds is $f = 5.3 \times 10^{-4}$.

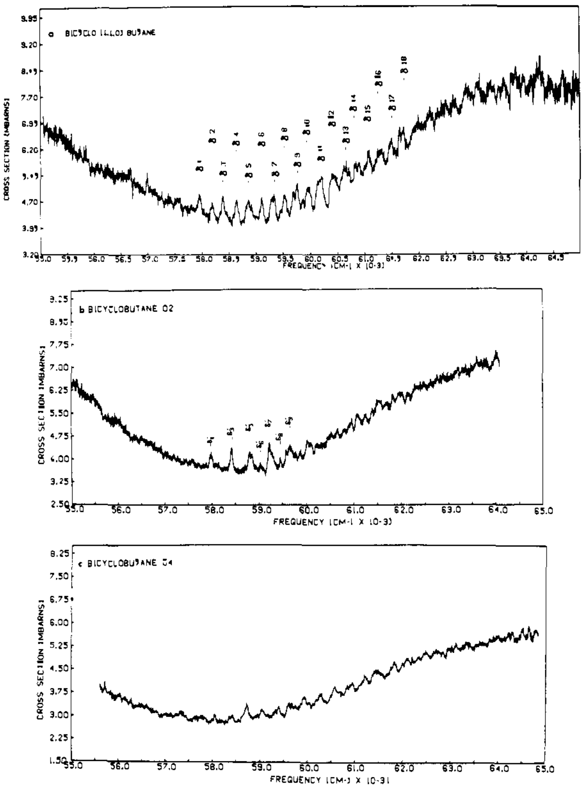

Figure 4.

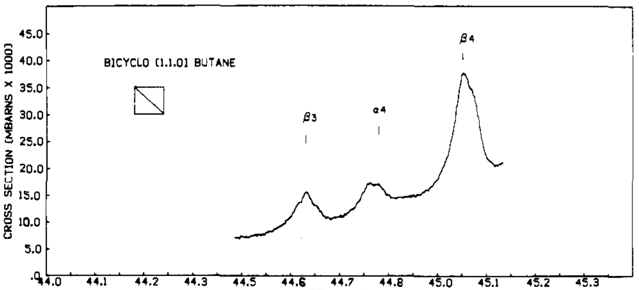

Figure 5.

Table I. Bicyclobutane-d_0

	Frequency, cm^{-1}	Cross section, Mb
α_1	43 674	0.002
β_1	43 861	0.003
α_2	43 995	0.004
β_2	44 249	0.006
α_3	44 433	0.008
β_3	44 665	0.015
α_4	44 851	0.017
β_4	45 071	0.044
α_5	45 277	0.038
β_5	45 492	0.083
α_6	45 708	0.072
β_6	45 909	0.214
α_7	46 124	0.134
β_7	46 326	0.321
α_8	46 566	0.203
β_8	46 768	0.352
α_9	46 989	0.288
β_9	47 192	0.388
α_{10}	47 405	0.374
β_{10}	47 617	0.441
α_{11}	47 865	0.493
β_{11}	48 086	0.573
γ_1	48 431	0.817
γ_2	48 810	1.459
γ_3	49 200	2.297
γ_4	49 523	3.192
γ_5	49 630	3.100
γ_6	49 943	4.271
γ_7	50 371	5.393
γ_8	50 610	5.779
γ_9	50 990	6.611
γ_{10}	51 243	7.302
γ_{11}	51 635	7.943
δ_1	57 960	4.909
δ_2	58 201	4.680
δ_3	58 401	4.867
δ_4	58 647	4.755
δ_5	58 866	4.738
δ_6	59 108	4.800
δ_7	59 336	4.906
δ_8	59 528	4.869
δ_9	59 768	5.207
δ_{10}	59 949	5.084
δ_{11}	60 195	5.419
δ_{12}	60 392	5.492
δ_{13}	60 656	5.850
δ_{14}	60 822	5.765
δ_{15}	61 083	6.150
δ_{16}	61 240	6.191
δ_{17}	61 498	6.484
δ_{18}	61 718	6.798

The bands β_3 and α_4 are of particular interest as shown in Figure 5. β_3 appears to have a parallel type band contour with a P, Q, R structure, while α_4 has a more doublet nature, hinting at a perpendicular band. This band contour can result from mixed polarization of the transition moment or a change in the moments of inertia with increasing quanta of vibration.[7]

The next set of bands, the γ bands, as shown in Figure 3a, extends from 48 430 to 51 000 cm^{-1}. The splitting between the different bands varies between 250 and 450 cm^{-1}. Since these bands are so diffuse, with each component 100 cm^{-1} in width, no progression in a single mode can be assigned. The oscillator strength for γ bands and the continuum on which they ride is $f = 7.4 \times 10^{-2}$.

The last set of observed vibrations in H6 are the δ bands shown in Figure 4a. They appear to be somewhat broadened as compared to the α, β bands. However, in this region a xenon lamp is used, which has a much lower intensity than the deuterium lamp used for the α and β bands. Therefore, larger slits, 40 μm, were used as compared to 20 μm used for the deuterium lamp. The resolution for the δ bands is 30 cm^{-1}. Fitting the bands to a harmonic potential function results in a series of 18 members with $\Delta\nu = 223 \pm 42$ cm^{-1}. For both the α, β, and δ bands the anharmonicity constant appears to be small.

D2. The portion of the spectrum of bicyclobutane-d_2 (D2) corresponding to the α's and the β's is shown in Figure 2b and in Table II. It is apparent that a progression in the same vibration, 405 cm^{-1}, is present as in H6 except that the α series is missing. A closer examination of a portion of this spectrum (Figure 6) shows there are now four vibrations, each a member of a progression of 405 cm^{-1}. The four progressions will be referred to as A, B, C, and D with the most intense vibration as A, and the weak vibrations as B, C, and D in order of increasing energy.

Unlike bicyclobutane-d_0, the γ bands in the D2 compound (Figure 3b) form a fairly harmonic progression beginning at 48 406 with $\Delta\nu = 407 \pm 12$ cm^{-1}. When compared to the ABCD bands they are noticeably broadened with a half-width of approximately 100 cm^{-1}. The structure terminates at 51 000 cm^{-1}.

The final series for bicyclobutane-d_2, the δ bands, is shown in Figure 4b. There initially is one set of bands beginning at

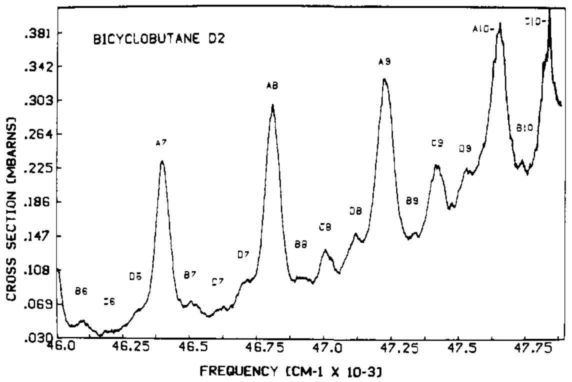

Figure 6.

57 977 cm^{-1} which forms a progression of at least six members with $\Delta\nu = 410 \pm 23$ cm^{-1}. There is a second series beginning at 59 027 cm^{-1} forming a progression with $\Delta\nu = 400$ cm^{-1}. From the many scans taken in this region, 57 977 cm^{-1} is the first observed vibration for the δ bands in bicyclobutane-d_2, while 57 960 cm^{-1} is the first observed band for the δ bands in bicyclobutane-d_0.

D4. The spectrum of bicyclobutane-d_4 is shown in Figures 2c-4c. The α-β region, Figure 2c, is much more complex than in D2 and H6, and at least six different progressions are found with an average $\Delta\nu = 351$ cm^{-1}. The first observed bands (Figure 2c) begin at 44 895 cm^{-1}. Experimentally, it might have been possible to observe bands at lower frequency. However, only 500 mm of pressure was available for the D4 compound, whereas 760 mm was available for H6 and D2.

From Figure 3c, the origin of the γ bands is assigned at 48 586 cm^{-1}. A diffuse progression of vibrations with an interval of 345 cm^{-1} is built on this origin.

The δ bands, Figure 4c, are much weaker than in the D2 or H6. As a result of the increase in the noise due to the smaller sample pressure, the origin cannot be assigned.

Discussion

In order to analyze the spectrum of bicyclobutane, it is necessary to briefly review its electronic structure. The microwave spectrum has shown the ground state to have C_{2v} symmetry.[8] Therefore, the symmetry of the molecular orbitals will be classified under this point group. Several closed-shell RHF ab initio calculations have been performed, and have been able to describe the ground state properties of the molecule such as its geometry and dipole moment.[9,10] The virtual orbitals derived from these calculations are at best qualitative descriptions, but are useful in considering the symmetries of the excited states. Some of the higher bonding MO's and lower energy virtual orbitals are shown in Figure 7.

The highest occupied molecular orbital, $7a_1$, can be visualized as being centered on the C(1)-C(3) σ bond. The lowest virtual orbital, $4b_1$, corresponds to an antibonding orbital localized on the C(1)-C(3) bond. The first allowed optical transition for bicyclobutane would be to a $^1B_1$ state ($4b_1 \leftarrow 7a_1$), which is a dipole allowed transition. The next three states, in order of increasing calculated energy, are $^1B_2$ ($4b_1 \leftarrow 1a_2$), $^1A_1$ ($4b_1 \leftarrow 3b_1$), and $^1A_2$ ($2a_2 \leftarrow 7a_1$). A transition to the $^1A_2$ excited state is forbidden.

δ Bands. The discussion of the vibronic structure of bicyclobutane will first consider the δ bands in the H6 and D2 compounds. A schematic representation of the delta bands is as follows.

| | | | | | | |

δ_1 δ_2 δ_3 δ_4 δ_5 δ_6 δ_7

| | | | |

δ_1' δ_3' δ_5' δ_6' δ_7'

Table II. Bicyclobutane-d_2

	Frequency, cm^{-1}	Cross section, Mb
A2	44 424	0.002
B2	44 569	0.002
A3	44 828	0.005
B3	44 939	0.004
A4	45 218	0.018
B4	45 331	0.009
A5	45 611	0.064
B5	45 720	0.027
A6	46 005	0.139
B6	46 124	0.045
C6	46 245	0.032
D6	46 332	0.054
A7	46 428	0.244
B7	46 529	0.073
C7	46 643	0.062
D7	46 749	0.098
A8	46 833	0.300
C8	47 027	0.134
D8	47 139	0.147
A9	47 250	0.332
C9	47 448	0.227
D9	47 590	0.226
A10	47 671	0.363
C10	47 863	0.346
γ_1'	48 406	0.789
γ_2'	48 836	1.44
γ_3'	49 217	2.54
γ_4'	49 629	3.21
γ_5'	50 048	4.42
γ_6'	50 288	4.56
γ_7'	50 444	5.48
γ_8'	50 652	5.82
γ_9'	50 861	6.73
γ_{10}'	51 097	7.19
δ_1	57 977	4.26
δ_3	58 401	4.30
δ_5	58 788	4.36
δ_6	59 027	3.98
δ_7	59 207	4.51
δ_8	59 454	4.10
δ_9	59 658	4.44

The first band observed in H6 is δ_1 at 57 960 cm^{-1}, while in D2, the first band observed, δ_1', is at 57 977 cm^{-1}. Therefore, upon deuteration, there is a blue shift of only 17 cm^{-1}. It is improbable that there are bands to the red of δ' and δ' for all the bands in this group have the same relative intensities. Considering H6 alone, the number of vibrational progressions present cannot be determined, but in light of D2, the existence of two vibrational series becomes obvious. The first progression δ_1, δ_3, δ_5, δ_7 has an average spacing of 449 cm^{-1}, which corresponds to δ_1', δ_3', δ_5' in the D2 with an average spacing of 410 cm^{-1}. The second progression δ_2, δ_4, δ_6, with a spacing of 438 cm^{-1}, has no counterpart in D2. Based upon the resolution (30 cm^{-1}) of our spectrometer in this region, the vibrational mode forming these progressions appear to be the same. For further discussion an average frequency of 443 cm^{-1} will be used for the δ bands in H6.

The above analysis shows that δ_1 and δ_2 are apparent origins for vibrational progressions. There must be a true origin to the red with a low or zero intensity. Since the observed components have essentially constant intensity, this would not be expected for an allowed transition. The low oscillator strength for the δ bands of $f = 6.6 \times 10^{-4}$ (excluding the continuum on which they ride) further suggests a forbidden transition. These considerations lead us to assign A_2 symmetry to the state leading to the δ bands.

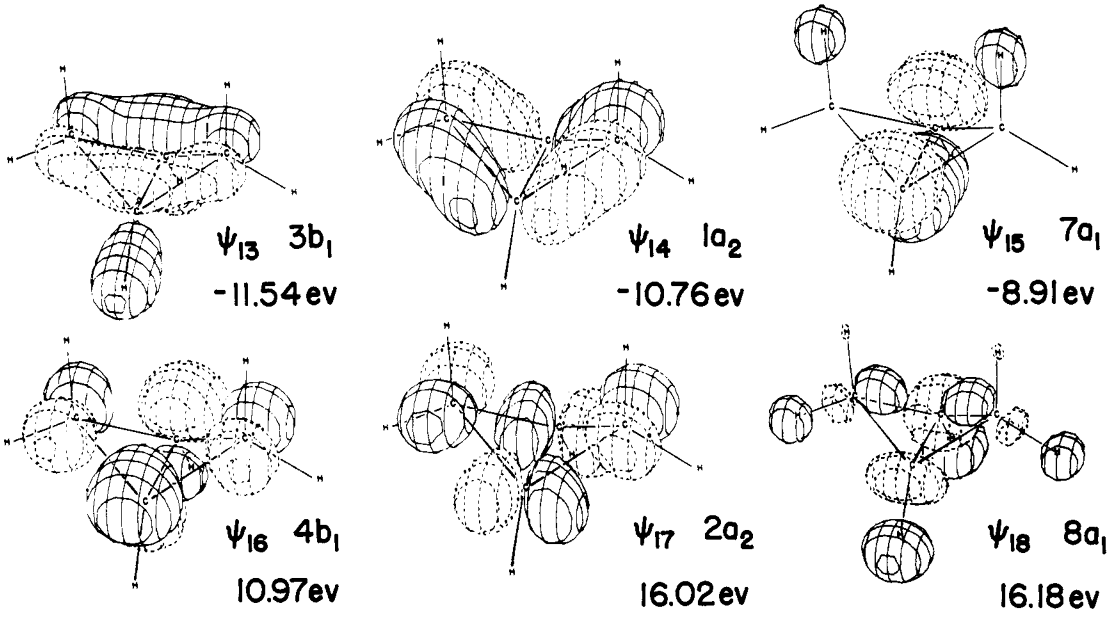

Figure 7.

A characteristic of the vibrational structure of a vibronically induced transition is the appearance of one or more false origins, each of which involves a nontotally symmetric vibration. Series derived from a totally symmetric mode are built on top of the false origins, thus maintaining antisymmetric character and permitting the transition to be observed. For D2, δ_1' constitutes a false origin leading to the series δ_3', δ_5', δ_7' . . . with a 410-cm^{-1} interval. The symmetric vibrational mode which forms this progression is ν_9, the ring flapping mode. For H6, δ_1 and δ_2 are two false origins, leading to series again derived from ν_9. Because of the low resolution it is difficult to make assignments of the vibrational structure in D4. However, it is clear that the progressions are again derived from ν_9.

α, β Bands. The electronic state giving rise to the α, β bands has an oscillator strength of 5×10^{-4}. Again this is the expected magnitude for a dipole forbidden transition. In H6, D2, and D4 it is not possible to observe the origins giving rise to this series because of the Franck-Condon factors. There is a striking similarity between the α, β, and δ bands in H6 and D2. In H6, progressions in 422 cm^{-1} can be found for the α, β bands and 443 cm^{-1} in the δ bands. Similarly in D2, progressions in 405 cm^{-1} can be found within the δ and α, β bands. Also upon deuteration, the series δ_2, δ_4, δ_6 seemingly disappears or is greatly reduced in intensity on going in D2. The same trend is observed in the α, β bands with the α bands being greatly reduced in intensity upon deuteration.

Therefore the state containing the α, β bands is assigned as having A_2 symmetry and, as in the δ bands, is observed through a vibronic coupling mechanism. In H6, two series (α and β) are observed with a 422-cm^{-1} spacing corresponding to ν_9. These are built on two inducing modes. In D2 there are four series (A, B, C, D) each forming a progression with a 405-cm^{-1} spacing (ν_9) built on four inducing modes.

γ Bands. The vibrations constituting the γ bands are noticeably broadened relative to the α and β bands. Also, there appears to be a discontinuity in the Franck-Condon profile upon going from the α and β bands to the γ bands in H6 and D2 as seen in Figures 2a and 2b. This discontinuity is not apparent in the D4.

Two possibilities exist for an assignment for the γ bands. They may be a continuation of the α and β bands or they may be vibrations belonging to another state. If the γ bands are another state, then γ_1 (48 431 cm^{-1}) for H6 and γ_1' (48 406 cm^{-1}) for D2 would be origins for the transition. This would then be a red shift of the origin upon deuteration, and is opposite to usual blue shift.[12] The other possibility is that the γ bands may be a continuation of the α and β bands. If this is the case, it is clear that some process intervenes at about 48 000 cm^{-1} causing the marked change in appearance of the bands. Similar effects have been observed with formaldehyde[13] as a result of dissociation accompanying high quanta of vibrational excitation.

Both of the states giving rise to the α and β bands and the δ bands are assigned as having A_2 symmetry. In each state progressions in ν_9 are observed. However, the various vibrational modes which induce the transition, i.e., the false origins, have not been assigned. To make an assignment of symmetry of the inducing vibrations, the polarization of the transition must first be determined. The polarization of a transition moment can be determined from the rotational envelope of a vibration.[14] If a high resolution spectrum of β_3 and α_4, Figure 5, were obtained, then a complete vibrational assignment of the α and β bands and δ bands would be possible.

All calculations and models for bicyclobutane agree that the lowest energy transition is from the π-like central C-C bond orbital to the corresponding π^*-like orbital. This will be an allowed transition, and certainly leads to the continuum on which the γ bands ride. A summary of the electronic states of bicyclobutane is given in Table III.

Experimental Section

Bicyclobutane-h_6, -d_2, and -d_4 were synthesized as previously reported.[6]

The spectra were recorded by a 1-m MacPherson 225 scanning double-beam vacuum ultraviolet spectrometer. The grating is a 56 × 96 mm tripartite concave grating blazed at 1500 Å and is ruled at 600 lines/mm with a reciprocal linear dispersion of 16.6 Å/mm. The resolution bandwidth at half-height varies from 12 cm^{-1} at 2000 Å to 50 cm^{-1} at 1300 Å. The continuum light sources were D_2 (2600-1650 Å), Xe (1850-1550 Å), and Kr (1650-1300 Å). Absolute peak positions were calibrated by using the Schumann-Runge bands of molecular oxygen.[15] The uncertainty in the observed line positions was about ±10 cm^{-1}.

The sample cell, 9-cm length, is a Pyrex tube having lithium fluoride windows mounted via Viton O-rings. Pressures from 0.1 to 760 mm were used. The optical signals from the sample and reference beams impinge on sodium salicylate coated plates which abut the front ends of EMI 9035B photomultiplier tubes operating at about 1 kV. The outputs of the two photomultipliers were amplified using PAR Model

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]

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

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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}.