

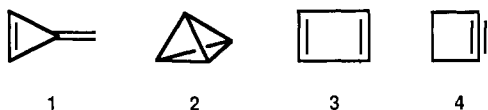
An ab Initio Study of the Vibrational Spectrum of Bicyclo[1.1.0]but-1(3)-ene

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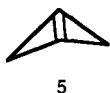
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Abstract: Vibrational force constants, frequencies, and IR intensities calculated with several basis sets at the SCF level and with inclusion of electron correlation are reported for bicyclo[1.1.0]but-1(3)-ene. Bicyclobutene (**5**) is predicted to have a singlet ground state with a nonplanar carbon skeleton. Its IR spectrum should consist of two absorptions in the C-H stretch region, a series of weak bands between 600 and 1800 cm⁻¹, and at lower frequencies a very intense and a quite weak absorption. Its computed energy relative to other known C₄H₄ isomers suggests that it will be stable only at very low temperatures in a matrix. The barrier to ring inversion is predicted to be 12 kcal/mol. Finally, geometrical structures, adiabatic and vertical excitation energies, and vibrational frequencies are reported for the lowest triplet state (³B₁) of bicyclobutene (**5**).

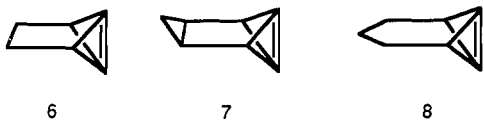
The continued theoretical and synthetic interest in unusual molecules on the C₄H₄ potential surface [e.g., methylenecyclopropene (**1**),¹⁻⁵ tetrahedrane (**2**),⁶⁻⁹ cyclobutadiene (**3**),¹⁰⁻²⁰ and



cyclobutene (**4**)²¹] has led us to carry out an ab initio theoretical vibrational analysis of bicyclo[1.1.0]but-1(3)-ene (**5**). Both



cyclobutadiene and methylenecyclopropene have been prepared, but tetrahedrane, cyclobutene, and bicyclobutene are as yet unknown, although Szeimies has shown that three tricyclic bicyclobutene derivatives (**6-8**) may exist as transient species.²² For



the two known systems (**1** and **3**) computed ab initio IR spectra played an important role in the confirmation of their synthesis. Cyclobutadiene was initially reported^{11,12} to have a square structure, but later^{13,16-19} observed and computed IR spectra showed it to be a rectangular molecule. The synthesis of methylenecyclopropene was also in part confirmed by the computation of its IR spectrum.^{1,4,5} We have recently reported the computed vibrational spectra of tetrahedrane⁶ and cyclobutene²¹ in order that these spectra might be useful in their eventual identification. Similarly we report here the vibrational spectrum of bicyclo[1.1.0]but-1(3)-ene (**5**).

Hehre and Pople²³ reported the first calculation on **5** in 1975 with the STO-3G basis set, and surprisingly it was predicted to have a nonplanar carbon skeleton (C_{2v}) with the double bond carbons significantly pyramidalized. More recent theoretical studies on highly strained cycloalkenes have shown that pyramidalization of double bond carbons is likely to be a common phenomenon in such systems.²⁴ On the basis of model calculations on ethylene, Schleyer, Pople, and co-workers²⁵ have suggested that when the R-C=C angle is constrained to be less than 100°,

pyramidalization of the double bond carbons should occur. In contrast to these ab initio results, Dewar²⁶ found that a MINDO/3

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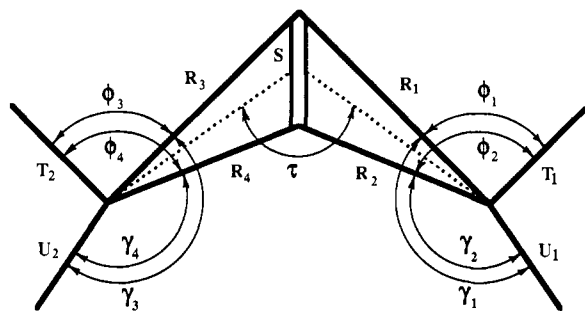
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Table I. Optimized Geometry of Bicyclobutene^a

parameter ^b	basis set							
	MINDO/3 ^c	STO-3G ^{d,e}	4-31G ^{d,f}	6-31G ^{*g}	MP2 6-31G ^{*g}	TCSCF 6-31G ^{*g}	TCSCF DZP ^g	2R CISD 6-31G ^{*g}
<i>R</i>	1.46	1.535	1.505	1.481	1.489	1.479	1.487	1.483
<i>S</i>	1.53	1.343	1.353	1.344	1.412	1.375	1.383	1.385
<i>T</i>	1.12	1.086	1.068	1.073	1.086	1.074	1.077	1.081
<i>U</i>	1.12	1.092	1.077	1.084	1.096	1.083	1.086	1.091
α		117.7	117.6	118.0	118.2	118.5	118.1	118.4
β		128.7	127.6	127.8	127.6	127.4	127.3	127.5
τ	180.0	128.3	132.4	135.2	138.1	133.5	133.2	134.9
energy		-151.65018	-153.30584	-153.58020 ^h	-154.10804	-153.62050	-153.64546	-154.07006

^aBond distances in Å, angles in deg. ^bAs defined in Figure 1, except α is the angle made by a C-H bond of length *T* and the bisector of the three-membered ring and β is the angle made by a C-H bond of length *U* and the same bisector. ^cReference 26. ^dReference 23. ^eThese in fact do not correspond to minima (see text). ^fReference 24c. ^gThis work. ^hThis value is in good agreement with that reported by Wiberg (ref 24c).

**Figure 1.** Definition of internal coordinates of bicyclobutene (**5**).

calculation predicts a planar carbon skeleton for **5**. However, ab initio calculations with larger basis sets (4-31G and 6-31G^{*})^{24c,25} have confirmed the prediction of the earlier ab initio work that the double bond carbons in **5** should be significantly pyramidalized. The computed ab initio IR spectrum should therefore be of use not only in helping to identify **5** but also in confirming its geometry, since planar and puckered carbon skeletons would be expected to yield very different IR spectra.

Computational Methods

SCF. The (RHF) SCF calculations were performed with GAUSSIAN 80²⁷ with use of the internally stored 6-31G^{*} basis set. Beginning with the optimized geometry (Figure 1 and Table I), each symmetry adapted internal coordinate in Table II was distorted by 0.01 Å for bond lengths and 3° for angles. Plus and minus distortions were done for coordinates of A₁ symmetry and single distortions for the remainder. The Cartesian coordinates of these distorted structures were obtained with use of the BMAT link of Pulay's program TEXAS.^{28,29} From these coordinates GAUSSIAN 80 input was computed, and the analytic gradient and dipole moment were calculated and transformed to the original Cartesian coordinates generated by BMAT. The Cartesian gradient for each structure was converted to forces with respect to each internal symmetry coordinate. After computation of the force constants (Table III) from these internal forces, a standard Wilson GF analysis gave vibrational frequencies (Table IV) and their normal modes. Intensities of the A₁, B₁, and B₂ blocks were obtained from dipole moment derivatives and the normal mode eigenvectors.³⁰ SCF frequencies were obtained analytically with the program GAUSSIAN 82³¹ with the STO-3G, 4-31G, and, as a check of the above numerical frequencies, 6-31G^{*} basis sets.

MP2. The geometry of **5** was reoptimized (Table I) with the 6-31G^{*} basis set with the inclusion of electron correlation (RHF MP2).³² The carbon 1s orbitals were frozen. For evaluation of

Table II. Symmetry Coordinates for Bicyclobutene^a

species	coordinate
A ₁	$S_1 = 1/2(R_1 + R_2 + R_3 + R_4)$
	$S_2 = (2)^{-1/2}(T_1 + T_2)$
	$S_3 = (2)^{-1/2}(U_1 + U_2)$
	$S_4 = S$
	$S_5 = 1/2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$
	$S_6 = 1/2(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)$
	$S_7 = \tau$
A ₂	$S_8 = 1/2(R_1 - R_2 - R_3 + R_4)$
	$S_9 = 1/2(\phi_1 - \phi_2 - \phi_3 + \phi_4)$
B ₁	$S_{10} = 1/2(\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4)$
	$S_{11} = 1/2(R_1 - R_2 + R_3 - R_4)$
	$S_{12} = 1/2(\phi_1 - \phi_2 + \phi_3 - \phi_4)$
B ₂	$S_{13} = 1/2(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4)$
	$S_{14} = 1/2(R_1 + R_2 - R_3 - R_4)$
	$S_{15} = (2)^{-1/2}(T_1 - T_2)$
	$S_{16} = (2)^{-1/2}(U_1 - U_2)$
	$S_{17} = 1/2(\phi_1 + \phi_2 - \phi_3 - \phi_4)$
	$S_{18} = 1/2(\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4)$

^aThe symmetry species referred to in this paper correspond to the C_{2v} and D_{2h} character tables in ref 43 assuming the C₂ and z axes are coincident and the x axis lies along the C-C double bond.

the MP2 force constants (Table III), the second derivatives of the energy were computed numerically. Plus and minus distortions were made for the diagonal force constants and appropriate combination distortions for the off-diagonal force constants. Diagonalization of this force constant matrix in a GF analysis gave MP2 frequencies (Table IV). No MP2 intensities were computed.

TCSCF. With use of methods developed at Berkeley,^{21b} two-configuration SCF (TCSCF) computations were performed with two basis sets (6-31G^{*} and DZP³³) for bicyclobutene (**5**). A single-reference CISD (6-31G^{*}) calculation at the optimum 6-31G^{*} geometry (with carbon 1s orbitals frozen) gave $E(\text{CISD}) = -154.05192$ hartree with $C_1 = 0.928$, $C_2 = -0.082$, and $C_3 = 0.034$. The relatively large value of C_2 suggests that **5** might possess significant diradical character, and as a consequence a single-reference wave function might be inadequate. The TCSCF method was then used ($\Psi = C_1 \det |(\text{core})(4b_2)^2(1a_2)^2(6a_1)^2(7a_1)^2| + C_2 \det |(\text{core})(4b_2)^2(1a_2)^2(6a_1)^2(3b_1)^2|$) with the 6-31G^{*} basis set to optimize the geometry (Table I) and to obtain frequencies and intensities (Table IV) with analytic second derivatives. At the optimal geometry the TCSCF coefficients were $C_1 = 0.957$ and $C_2 = -0.290$. The geometry of **5** was also optimized with the DZP basis ($C_1 = 0.958$ and $C_2 = -0.288$) and frequencies and intensities computed. The large values of the TCSCF coefficients C₂ confirm the likely diradical character of **5**.

The optimal planar bicyclobutene structure (D_{2h}) was obtained with the 6-31G^{*} basis set. The optimized parameters found for

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Table III. Calculated Force Constants for Bicyclobutene^a

species	constants	6-31G*	6-31G* MP2	DZP TCSCF	6-31G* 2R CISD
A ₁	F ₁₁	5.276	5.120	5.375	5.283
	F ₂₂	6.316	5.783	6.221	5.998
	F ₃₃	5.842	5.398	5.829	5.599
	F ₄₄	8.592	5.337	6.841	6.617
	F ₅₅	0.872	0.830	0.849	0.832
	F ₆₆	0.857	0.810	0.828	0.808
	F ₇₇	0.994	0.763	1.059	0.925
	F ₁₂	0.178	0.152	0.151	0.165
	F ₁₃	0.291	0.254	0.253	0.265
	F ₁₄	-1.041	-0.832	-0.892	-0.879
	F ₁₅	0.348	0.344	0.308	0.319
	F ₁₆	0.080	0.089	0.081	0.083
	F ₁₇	-0.607	-0.525	-0.534	-0.546
	F ₂₃	0.065	0.042	0.051	0.057
	F ₂₄	-0.158	-0.188	-0.168	-0.177
	F ₂₅	-0.048	-0.049	-0.029	-0.035
	F ₂₆	-0.121	-0.128	-0.122	-0.126
	F ₂₇	-0.012	0.000	-0.031	-0.019
	F ₃₄	-0.279	-0.223	-0.192	-0.215
	F ₃₅	-0.127	-0.126	-0.124	-0.124
	F ₃₆	-0.020	-0.034	-0.027	-0.024
	F ₃₇	0.037	0.021	0.026	0.031
	F ₄₅	-0.015	-0.037	-0.046	-0.029
	F ₄₆	0.067	0.135	0.126	0.120
	F ₄₇	0.555	0.612	0.620	0.574
	F ₅₆	0.387	0.369	0.378	0.369
	F ₅₇	-0.064	-0.041	-0.097	-0.070
F ₆₇	0.072	0.052	0.077	0.073	
A ₂	F ₈₈	3.962	4.208	4.172	4.216
	F ₉₉	1.485	1.223	1.366	1.292
	F _{10,10}	1.452	1.245	1.378	1.307
	F ₈₉	0.976	0.654	0.773	0.732
	F _{8,10}	-0.006	0.033	0.090	0.055
B ₁	F _{9,10}	0.052	0.011	0.042	0.024
	F _{11,11}	1.035	3.058	2.244	2.383
	F _{12,12}	1.562	1.283	1.500	1.379
	F _{13,13}	1.037	1.098	1.159	1.063
	F _{11,12}	1.014	0.578	0.654	0.665
B ₂	F _{11,13}	0.424	0.170	0.532	0.410
	F _{12,13}	0.245	0.119	0.133	0.135
	F _{14,14}	5.367	5.034	5.365	5.224
	F _{15,15}	6.311	5.785	6.215	5.992
	F _{16,16}	5.825	5.385	5.819	5.586
	F _{17,17}	0.849	0.810	0.815	0.805
	F _{18,18}	0.876	0.835	0.848	0.830
	F _{14,15}	0.163	0.123	0.124	0.135
	F _{14,16}	0.212	0.189	0.177	0.192
	F _{14,17}	0.200	0.182	0.159	0.170
	F _{14,18}	0.197	0.207	0.197	0.202
	F _{15,16}	0.061	0.039	0.047	0.051
	F _{15,17}	-0.063	-0.062	-0.048	-0.050
F _{15,18}	-0.126	-0.136	-0.121	-0.129	
F _{16,17}	-0.139	-0.137	-0.132	-0.133	
F _{16,18}	-0.077	-0.084	-0.076	-0.076	
F _{17,18}	0.361	0.339	0.360	0.346	

^aStretching force constants are in $\text{myn} \text{Å}^{-1}$ and bending force constants in $\text{myn} \text{Å} \text{rad}^{-2}$.

the planar form were the following: $R_{\text{C-C}} = 1.457 \text{ Å}$, $R_{\text{C=C}} = 1.434 \text{ Å}$, $R_{\text{C-H}} = 1.082 \text{ Å}$, and the angle made by the C-H bond with the plane of the ring = 123.8° . A vibrational analysis confirmed this geometry to be a transition structure since one imaginary frequency was obtained ($988i \text{ cm}^{-1}$).

2R CISD. Two-reference CISD (2R CISD) computations were carried out on puckered and planar bicyclobutene with analytic gradient methods newly developed at Berkeley.³⁴ The carbon 1s orbitals were kept doubly occupied, but no virtual orbitals were frozen. Geometries were optimized for both the puckered (Table I) and planar forms ($R_{\text{C-C}} = 1.461 \text{ Å}$, $R_{\text{C=C}} = 1.439 \text{ Å}$, $R_{\text{C-H}} = 1.090 \text{ Å}$, C-H bond to ring-plane angle = 123.9°). Force constants of **5** (Table III), frequencies, and intensities (Table IV) were computed by taking finite differences of analytic gradients

and dipole moments. The four types of displacements required for the frequency calculation (A_1 , A_2 , B_1 , and B_2) gave 74 576, 145 588, 145 767, and 148 462 configuration state functions (CSFs), respectively. Completely symmetrized internal coordinates (Table II) were displaced by $\pm 0.01 \text{ Å}$ and ± 0.01 radians. All cubic contaminations were eliminated by appropriately using positive and negative displacements. CISD dipole moments were computed as expectation values rather than as derivatives with respect to an electric field.³⁵

Results and Discussion

Optimized Geometry. In Table I are given the optimized geometries of bicyclobutene for various methods of calculation. However, we have determined that the previously reported STO-3G²³ and 4-31G^{24c} structures are *not* minima on their respective potential surfaces since a single imaginary frequency was obtained in the vibrational analyses with both basis sets (see Table IV). Apparently polarization functions on carbon (6-31G*) are required in order to make bicyclobutene an energy minimum. The normal mode of the B_1 imaginary frequency in both cases corresponds to a ring deformation in which only a single plane of symmetry is preserved (see below).

As seen from Table I the trends from increasing the size of the basis set and the inclusion of electron correlation are those normally expected. However, it is apparent from the MP2 geometry that the carbon-carbon double bond length is significantly overestimated ($S = 1.412 \text{ Å}$) when this value is compared with the other correlated values ($S = 1.375\text{--}1.385 \text{ Å}$). The increase in the value of this bond distance on going from the 6-31G* basis set at the SCF level to the MP2 level is in fact quite large ($1.344 \rightarrow 1.412 \text{ Å}$). While an increase in the bond length is to be expected, this increase is much larger than any we have encountered in the past. This result suggests that a one-reference method for computing electron correlation (MP2) might not be suitable for bicyclobutene (see below). All the ab initio methods do predict that bicyclobutene should have a strongly puckered structure ($\tau = 128.3\text{--}138.1^\circ$). This is in strong contrast to the MINDO/3 result²⁶ which predicts a planar carbon skeleton for bicyclobutene.

Force Constants, Frequencies, and Intensities. Calculated force constants for the various basis sets are given in Table III for the symmetry coordinates in Table II. In all cases force constants were obtained at the optimized geometry for the basis set used. Force constants are often computed at experimental or corrected ab initio geometries.³⁶ However we have found that this is not necessary^{37,38} since the pattern obtained when both IR frequencies and intensities are computed normally compares quite favorably with the experimental pattern. Computed frequencies and IR intensities (the A_2 block is Raman active only) are given in Table IV. The SCF 6-31G* frequencies were obtained both numerically and analytically. The latter were computed with GAUSSIAN 82. It is reassuring to see that the largest difference between the frequencies obtained from a numerical evaluation of the second derivatives of the energy and those from analytical second derivatives is only 5 cm^{-1} .

Examination of the normal modes led to the assignments given in Table IV. These assignments are consistent for all theoretical methods with the exception of the B_1 block for 6-31G*/MP2. This discrepancy is another indication of the possible inadequacy of

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Table IV. Calculated Frequencies and IR Intensities of Bicyclobutene^a

symmetry species	STO-3G	4-31G	6-31G* numerical ^b	6-31G* analytical ^b	6-31G* MP2	6-31G* TCSCF	DZP TCSCF	6-31G* 2R CISD	assignment ^c
A ₁	3768	3422	3402 (0.05)	3401	3259	3393 (0.07)	3380 (0.05)	3316 (0.06)	C-H sym str
	3602	3271	3244 (0.38)	3244	3155	3254 (0.41)	3239 (0.34)	3175 (0.41)	C-H sym str
	1822	1692	1715 (0.01)	1714	1606	1697 (0.01)	1672 (0.01)	1638 (0.00)	CH ₂ sym scissoring
	1595	1490	1563 (0.01)	1562	1337	1471 (0.01)	1459 (0.01)	1435 (0.01)	C=C str
	1300	1243	1240 (0.02)	1239	1165	1237 (0.00)	1218 (0.00)	1193 (0.00)	CH ₂ sym rocking
	1138	978	1030 (0.09)	1029	921	1011 (0.08)	1003 (0.07)	986 (0.09)	ring breathing
	468	434	405 (0.02)	405	355	411 (0.01)	409 (0.01)	387 (0.01)	ring puckering
A ₂	1396	1265	1272	1271	1209	1250	1233	1223	CH ₂ twisting + ring def
	1289	1238	1232	1227	1143	1228	1208	1171	CH ₂ wagging
	867	665	757	756	829	830	813	814	ring def + CH ₂ twist
B ₁	1259	1209	1182 (0.08)	1177	1158 ^d	1200 (0.05)	1180 (0.05)	1140 (0.09)	CH ₂ wagging
	1069	1012	988 (0.06)	986	820 ^e	1117 (0.00)	1100 (0.00)	1042 (0.00)	CH ₂ twisting
	288i	253i	210 (1.00)	206	512 ^f	521 (1.00)	505 (1.00)	530 (1.00)	ring def
B ₂	3765	3420	3400 (0.04)	3399	3258	3392 (0.05)	3378 (0.04)	3314 (0.03)	C-H asym str
	3599	3274	3244 (0.38)	3244	3116	3254 (0.40)	3240 (0.37)	3176 (0.43)	C-H asym str
	1777	1663	1669 (0.10)	1667	1578	1664 (0.07)	1636 (0.03)	1603 (0.07)	CH ₂ asym scissoring
	1519	1369	1452 (0.24)	1452	1397	1441 (0.14)	1430 (0.11)	1417 (0.16)	ring def
	1159	1137	1161 (0.00)	1160	1114	1141 (0.02)	1118 (0.01)	1112 (0.01)	CH ₂ asym rocking

^aFrequencies in cm⁻¹; relative IR intensities given in parentheses. ^bSee text. ^cWhile the four hydrogens are not equivalent due to symmetry, their vibrations are strongly coupled. Scissoring, wagging, rocking, and twisting modes of the CH₂ groups are described with respect to the HCH plane. ^dRing def + CH₂ wag. ^eCH₂ def(γ). ^fCH₂ def(φ).

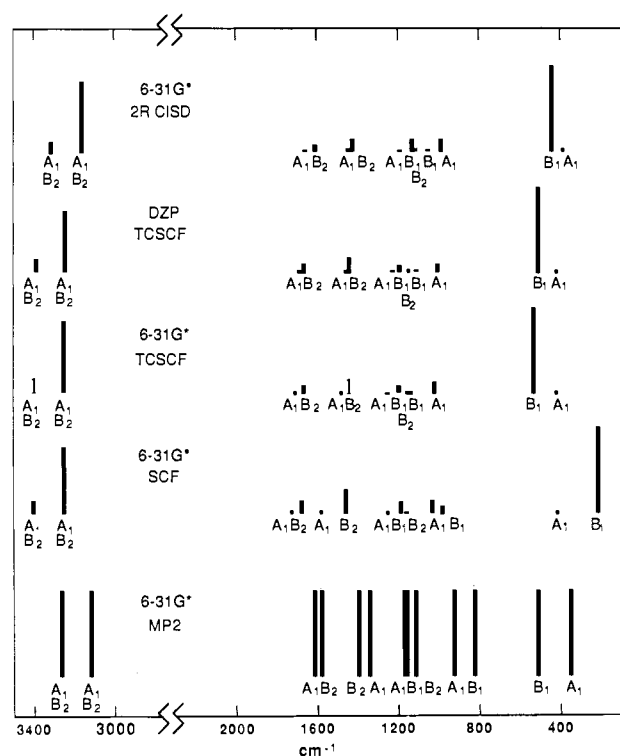
the MP2 method for bicyclobutene. It is interesting that even the SCF (6-31G*) assignments are in agreement with the other correlated results.

There are two notable differences between the 6-31G* SCF and MP2 frequencies. The A₁ C=C stretch is shifted more than 200 wavenumbers to lower frequency, and the lowest frequency B₁ absorption is shifted more than 300 wavenumbers to *higher* frequency by the MP2 computation. Both of these shifts are much larger than those we have observed previously when using the MP2 method.^{5,6,19} These frequency shifts and the large change in geometry mentioned above prompted us to pursue methods based on multireference wave functions. It is reassuring (see Table IV and Figure 2) that the two methods chosen (TCSCF and 2R CISD) gave results consistent with one another. Since it was found that bicyclobutene is likely to have significant diradical character, it is surprising that the 6-31G* SCF computed spectrum (when both frequencies and intensities are compared) agrees as well as it does with the two-reference results. The only major differences are in the two lower B₁ frequencies, which are too low in the SCF computation, although the SCF intensities are in reasonable agreement with those of the TCSCF and 2R CISD methods.

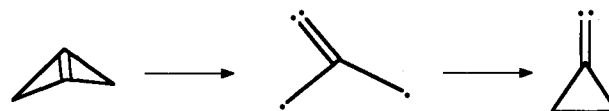
While there are four C-H stretching vibrations predicted in the IR spectrum of **5**, in all cases the calculated symmetric and antisymmetric stretching vibrations of each pair of equivalent hydrogens have almost the same frequency. Therefore in the infrared spectrum of **5** one is likely to observe only two (C-H) bands with each band corresponding to two closely spaced (C-H) modes of A₁ and B₂ symmetry. The plotted intensity of each C-H band in Figure 2 is the sum of intensities of individual components.

The C=C stretching vibration (A₁) corresponds to a very weak band in the IR spectrum, and its position might very well be obscured by the presence of the close-lying B₂ mode associated with ring deformation (see Table IV). Bending motions of the two pairs of nonequivalent hydrogen atoms were found to be strongly coupled; however, these motions are easily interpreted as CH₂ scissoring, rocking, twisting, and wagging modes by taking linear combinations of the symmetrized internal coordinates in each symmetry block (Table II) and appropriately transforming the normal mode eigenvectors.

Of note also is the very intense band (B₁) predicted to appear at quite low wavenumber. The unusually high intensity of this band indicates the increase of polarity in the molecule during this particular normal vibration. From the examination of the B₁ normal mode obtained, it is seen that this band corresponds to the deformation of the carbon skeleton in which displacement of the carbon atoms does produce a large change in the dipole moment. The force constant associated with this normal mode

Figure 2. Computed IR spectra of bicyclobutene (**5**).

($F_{11,11}$) is much smaller than F_{11} , F_{88} , and $F_{14,14}$, which correspond to the deformations of the carbon skeleton of A₁, A₂, and B₂ symmetry, respectively. Distortion of the molecule along this B₁ normal mode will eventually break the two carbon-carbon bonds according to the scheme

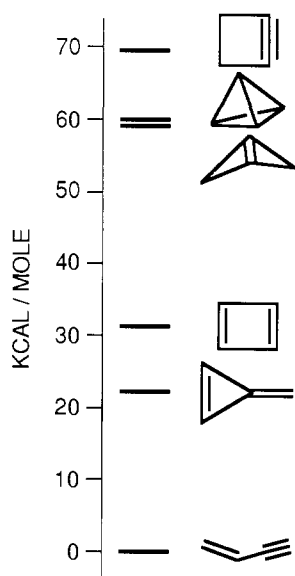


This distortion has an imaginary frequency with the STO-3G and 4-31G basis sets. It is seen that as the size of the basis set is increased, the frequency of this B₁ distortion changes from imaginary to real; and inclusion of electron correlation increases the value even further. This is additional evidence that one must exercise caution in the choice of the method of calculation in

Table V. Energy of Planar Bicyclobutene (D_{2h}) and Barrier to Inversion of the C_{2v} Form

molecule	method ^a	energy (hartree)	classical barrier ^d (kcal/mol)
bicyclobutene (D_{2h})	6-31G* SCF//6-31G* SCF	-153.55949	13.0 ^b
	6-31G* MP2//6-31G* MP2	-154.09596	7.6
	DZP TCSCF//6-31G* 2R CISD	-153.61600	18.4
	DZP 2R CISD//6-31G* 2R CISD ^c	-154.08570	14.1
	DZP 2R CIDVD//6-31G* 2R CISD	-154.15040	12.5

^a Abbreviations: // = at the geometry of; CIDVD = Davidson-corrected CISD. See footnote *a* of Table VI. ^b Reference 24c. ^c 56773 CSFs. ^d The following harmonic frequencies (in cm^{-1}) were obtained at the 6-31G* TCSCF level of theory for D_{2h} bicyclobutene: 3235, 1738, 1288, 936 (A_g); 1314, 1064 (B_{1g}); 841 (B_{2g}); 3285, 1296 (B_{3g}); 1120 (A_u); 3288, 1021, 988 (B_{1u}); 3229, 1719, 1598 (B_{2u}); and 1263, 454 (B_{3u}). Thus, the 6-31G* TCSCF zero-point correction to the barrier is $-422 \text{ cm}^{-1} = -1.21 \text{ kcal/mol}$.

**Figure 3.** CIDVD (Davidson-corrected CISD) energies of C_4H_4 isomers relative to that of vinylacetylene.

dealing with such highly unusual and strained systems.

Barrier to Ring Inversion of Bicyclobutene. As shown by our 6-31G* TCSCF vibrational analysis, a likely transition structure for the ring inversion of bicyclobutene is the structure with all carbon atoms in a plane (D_{2h}). Wiberg has computed the energy of this barrier and found a value of 19 kcal/mol with the 4-31G basis set and 13 kcal/mol with the 6-31G* basis set.^{24c} In Table V are given current energies of the D_{2h} structure and the barrier to inversion for the various methods of calculation. From these values it is concluded that if bicyclobutene were prepared at the temperature of an argon or nitrogen matrix, ring inversion would not occur.

Relative Energies of C_4H_4 Isomers. Table VI lists the energies computed at various levels of theory for six C_4H_4 isomers. Their energies relative to that of vinylacetylene are also given in the table and depicted in Figure 3. Of the isomers considered, vinylacetylene is the most stable in all basis sets, followed by methylenecyclopropene and cyclobutadiene. The three remaining isomers, bicyclobutene, tetrahedrane, and cyclobutynes, are all predicted to be of considerably lower stability, although their ordering is seen to be dependent upon the method of calculation used. At the highest level (DZP CIDVD) bicyclobutene and tetrahedrane are both predicted to be approximately 30 kcal/mol less stable than cyclobutadiene with cyclobutynes being about 40 kcal/mol less stable than cyclobutadiene. These results suggest that the

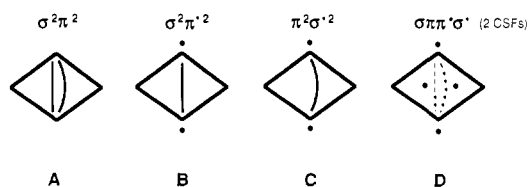
Table VI. Energies of C_4H_4 Isomers

molecule/method ^a	energy (hartree)	relative energy ^g (kcal/mol)
vinylacetylene ^b		
6-31G* SCF//6-31G* SCF	-153.70787	0.0
6-31G* MP2//6-31G* MP2	-154.20420	0.0
DZP CISD//3-21G SCF (117751 CSFs)	-154.19960	0.0
DZP CIDVD//3-21G SCF	-154.26399	0.0
methylenecyclopropene		
6-31G* SCF//6-31G* SCF ^c	-153.66978	23.9
6-31G* MP2//6-31G* MP2 ^c	-154.16682	23.5
DZP SCF//6-31G* MP2	-153.69410	25.1
DZP CISD//6-31G* MP2 (59177 CSFs)	-154.16472	21.9
DZP CIDVD//6-31G* MP2	-154.22936	21.7
cyclobutadiene		
6-31G* SCF//6-31G* SCF ^d	-153.64112	41.9
6-31G* MP2//6-31G* MP2	-154.14520	37.0
DZP SCF//6-31G* MP2	-153.66843	41.2
DZP CISD//6-31G* MP2 (29701 CSFs)	-154.14569	33.8
DZP CIDVD//6-31G* MP2	-154.21433	31.2
bicyclobutene (C_{2v})		
6-31G* SCF//6-31G* SCF	-153.58020	80.1
6-31G* MP2//6-31G* MP2	-154.10804	60.3
DZP TCSCF//6-31G* 2R CISD	-153.64529	55.7
DZP 2R CISD//6-31G* 2R CISD (111380 CSFs)	-154.10822	57.3
DZP 2R CIDVD//6-31G* 2R CISD	-154.17032	58.8
tetrahedrane		
6-31G* SCF//6-31G* SCF ^e	-153.5979	69.0
6-31G* MP2//6-31G* MP2 ^e	-154.1009	64.8
DZP SCF//6-31G* MP2	-153.62436	68.8
DZP CISD//6-31G* MP2 (54949 CSFs)	-154.10391	60.0
DZP CIDVD//6-31G* MP2	-154.16844	60.0
cyclobutynes ^f		
DZP TCSCF//DZ+D TCSCF	-153.63205	64.0
DZP 2R CISD//DZ+D TCSCF (110562 CSFs)	-154.09016	68.7
DZP 2R CIDVD//DZ+D	-154.15327	69.5

^a Abbreviations: // = at the geometry of; CIDVD = Davidson-corrected CISD.^{39,40} For TCSCF cases the two-reference Davidson-like correction was computed according to the formula $\Delta E = (1 - C_1^2 - C_2^2)(E_{\text{CISD}} - E_{\text{TCSCF}})$. ^b 3-21G geometry: Carnegie-Mellon Quantum Chemistry Archive. ^c Reference 5. ^d Reference 19. ^e Reference 6. ^f Reference 21a. ^g These are relative energies of the potential minima. They do not include thermodynamic corrections, the largest of which is the zero-point vibrational energy (ZPVE). At the 6-31G* SCF or TC SCF level, the unscaled, harmonic ZPVE corrections to the relative energies of methylenecyclopropene, cyclobutadiene, bicyclobutene, and tetrahedrane are -0.32 , -0.42 , $+0.67$, and -0.70 kcal/mol, respectively.

synthesis of bicyclobutene, tetrahedrane, and cyclobutynes will need to be performed in a low-temperature matrix since even cyclobutadiene is known to be stable only in such an environment.

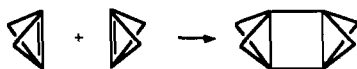
Comments on Bonding in Bicyclobutene. The four most important configurations in the CI wave function for planar (D_{2h}) bicyclobutene can be described by structures A-D. In the planar CI vector the coefficients arising from these electronic structures are $C_1 = 0.910$ (A); $C_2 = -0.192$ (B); $C_3 = -0.064$ and $C_6 = 0.036$ (D); and $C_4 = -0.052$ (C). Hence,



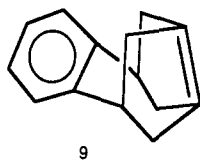
while A and B are dominant, C and D nevertheless make a significant contribution. Examination of the importance of these electronic structures for bent (C_{2v}) bicyclobutene reveals $C_1 = 0.903$ (A); $C_2 = -0.232$ (B); $C_3 = 0.045$ and $C_{19} = -0.018$ (D); and $C_5 = -0.035$ (C). Thus, in the bent form A and B are

significantly more dominant over C and D than in the planar form. Hence the only antibonding orbital in bent bicyclobutene that is of critical importance can be viewed as arising from structure B. However, as the molecule is bent, the σ and π orbitals mix; and this antibonding orbital in fact is a $\pi^*-\sigma^*$ hybrid.

A consequence of the importance of this antibonding orbital is that bent bicyclobutene is likely to have significant diradical character, which of course will add to its chemical reactivity. For example, bicyclobutene might be expected not only to undergo Diels-Alder reactions readily (Szeimies has trapped the bicyclobutene derivative **7** with diphenylisobenzofuran) but also, because of its diradical character, it may very likely undergo Woodward-Hoffmann forbidden [2 + 2] cycloadditions. One possibility is the dimerization



Evidence for this type of reaction has in fact been obtained for the pyramidalized alkene **9** by Borden, who has found that this molecule readily undergoes a [2 + 2] dimerization.⁴¹



9

Because of the likely diradical character of bicyclobutene, a competing reaction to the [2 + 2] dimerization might very well be polymerization. Szeimies has obtained some evidence that the polymerization reaction may be important.^{22b} He found that while the bicyclobutene **8** can be trapped with various dienophiles, an attempt to produce its [2 + 2] dimerization product **10** (no trapping agents were added) gives only a polymeric substance.



10

The \tilde{a}^3B_1 State of Bicyclobutene. The presence of a low-lying π^* orbital in bicyclobutene not only imparts significant diradical character to the ground electronic state but also provides for the existence of a low-lying triplet excited state ($\sigma^2\pi\pi^*$) of B_1 symmetry. One should consider the possibility that the chemistry exhibited by bicyclobutenes might also involve this triplet diradical state. Thus, additional calculations were undertaken to characterize the 3B_1 state. By using the 6-31G* basis and RHF SCF wave functions, D_{2h} and C_{2v} stationary points for the 3B_1 state were located and characterized at Berkeley with analytic first and second energy derivative methods.^{21b} Vertical and adiabatic excitation energies were then obtained at 6-31G* CISD and Davidson-corrected CISD (CIDVD) levels of theory. The geometrical structures, vibrational frequencies, and excitation energies appear in Table VII.

The 6-31G* SCF structure (C_{2v}) for the 3B_1 state is even more strongly puckered than the analogous structure for the ground state ($\tau = 119.3^\circ$ vs. 133.5°), but the 3B_1 SCF inversion barrier is predicted to be much smaller than the \tilde{X}^1A_1 TCSCF barrier (5.4 vs. 18.3 kcal/mol). The 3B_1 C=C distance in the C_{2v} structure ($S = 1.430 \text{ \AA}$) is 0.055 \AA longer than the \tilde{X}^1A_1 TCSCF value, such a moderate lengthening being expected. However, the $S = 1.758 \text{ \AA}$ distance in the 3B_1 D_{2h} structure is over 0.3 \AA longer than the \tilde{X}^1A_1 distance of $S = 1.434 \text{ \AA}$. Thus, it is evident from the geometrical structures and the inversion barrier that the C-C bond remaining across the ring in the 3B_1 electronic state is quite weak. In fact, the D_{2h} 3B_1 CISD wave function exhibits a relatively large $\sigma^2 \rightarrow \sigma^*2$ CI coefficient ($C_2 = -0.098$). Finally, note in Table VII that the 3B_1 state actually appears to have a D_{2h} minimum at the CISD and CIDVD levels. It is clear that the 3B_1 CISD (or CIDVD) potential energy surface is relatively flat as the molecule puckers and the carbon-carbon distance S

Table VII. Theoretical Data for the \tilde{a}^3B_1 State of Bicyclobutene Predicted with the 6-31G* Basis Set^a

	optimal geometrical parameters and absolute energies ^b			
	C_{2v}	D_{2h}^c		
<i>R</i>	1.501	1.484		
<i>S</i>	1.430	1.758		
<i>T</i>	1.078	1.081		
<i>U</i>	1.083	1.081		
α	119.9	123.9		
β	125.4	123.9		
τ	119.3	180.0		
<i>E</i> (SCF)	-153.54757	-153.53898		
<i>E</i> (CISD) ^d	-153.99138	-153.99145		
<i>E</i> (CIDVD) ^d	-154.04925	-154.05434		
excitation energies ^e (kcal/mol)				
	C_{2v}	D_{2h}		
Adiabatic				
SCF	45.8	32.9		
CISD	49.2	35.8		
CIDVD	49.5	34.8		
Vertical				
SCF	53.6	65.1		
CISD	58.1	68.9		
CIDVD	59.1	69.6		
harmonic vibrational frequencies (cm ⁻¹)				
	symmetry ^f	C_{2v}	D_{2h}	assignment
A_1	(B_{1u})	3357	3320	C-H sym str
A_1	(A_g)	3250	3270	C-H sym str
A_1	(A_g)	1692	1631	CH ₂ sym scissoring
A_1	(A_g)	1461	890	C-C str
A_1	(B_{1u})	1234	975	CH ₂ sym rocking
A_1	(A_g)	1012	1127	ring breathing
A_1	(B_{1u})	465	621 <i>i</i>	ring puckering
A_2	(B_{1g})	1173	1273	CH ₂ wagging
A_2	(A_u)	1131	1035	CH ₂ twisting
A_2	(B_{1g})	739	863	ring def
B_1	(B_{3u})	1233	1288	CH ₂ wagging
B_1	(B_{2g})	1185	956	CH ₂ twisting
B_1	(B_{3u})	814	533	ring def
B_2	(B_{3g})	3356	3326	C-H asym str
B_2	(B_{2u})	3249	3265	C-H asym str
B_2	(B_{2u})	1642	1617	CH ₂ asym scissoring
B_2	(B_{2u})	1294	1357	ring def
B_2	(B_{3g})	1116	987	CH ₂ asym rocking

^aThe designation C_{2v} refers to the puckered conformation (Figure 1), and D_{2h} refers to the conformation in which all carbon atoms lie in a plane. ^bBond distances in \AA , angles in deg, and absolute energies in hartrees. The geometrical parameters are defined in Table I (footnote b). ^c D_{2h} symmetry imposes the following constraints: $T = U$, $\alpha = \beta$, and $\tau = 180^\circ$. ^dObtained at the optimum SCF geometry with the carbon 1s core orbitals frozen. CIDVD = Davidson-corrected CISD. Note that the D_{2h} CISD and CIDVD energies are lower than the C_{2v} values. ^eBased on the 6-31G* TCSCF geometry for the \tilde{X}^1A_1 state and the 6-31G* SCF geometry for the \tilde{a}^3B_1 state. The 6-31G* TCSCF, 2R CISD, and 2R CIDVD (see footnote a of Table VI) energies were used for the \tilde{X}^1A_1 state, and the corresponding one-reference values were employed for the \tilde{a}^3B_1 state. Zero-point vibrational energy (ZPVE) corrections were not included. ^fFor convenience the frequencies are listed in the C_{2v} ordering appearing in Table IV. The D_{2h} symmetry species are given in parentheses.

varies. A CISD or MCSCF geometry optimization would be necessary to establish firmly the point group of the 3B_1 (or $^3B_{3u}$) minimum.

As seen in Table VII, the SCF harmonic vibrational frequency for stretching the C-C bond length S is 1461 cm^{-1} in the C_{2v} conformation of 3B_1 bicyclobutene. This frequency is only 10 cm^{-1} below the 6-31G* TCSCF value for the ground state. However, in the D_{2h} conformation this frequency is reduced to 890 cm^{-1} , which is more typical of a bending mode in a carbon ring without

a bridge. Other comparisons between the frequencies of \tilde{a}^3B_1 and \tilde{X}^1A_1 bicyclobutene are instructive too, but the key feature of the vibrational frequencies in Table VII is that there are no imaginary frequencies for ring-breaking modes. Thus, 3B_1 bicyclobutene is predicted to be a relative minimum on the C_4H_4 potential energy surface with either D_{2h} or C_{2v} symmetry.

The adiabatic excitation energy for the transition (C_{2v}) $\tilde{X}^1A_1 \rightarrow (C_{2v}) \tilde{a}^3B_1$ is 45.8 kcal/mol at the SCF level and 49.2 kcal/mol at the CISD level. The corresponding (D_{2h}) $\tilde{X}^1A_1 \rightarrow (D_{2h}) \tilde{a}^3B_1$ results are 32.9 and 35.8 kcal/mol, respectively. The 13-kcal/mol reduction in the latter two values is primarily due to the energy difference between the C_{2v} and D_{2h} conformations of the ground state; thus, regardless of whether the \tilde{a}^3B_1 state actually has a D_{2h} minimum, the (C_{2v}) $\tilde{X}^1A_1 \rightarrow \tilde{a}^3B_1$ adiabatic excitation energy should be near 17500 cm^{-1} , or 50 kcal/mol. Utilizing DZ SCF geometries,⁴² the 6-31G* CISD (D_{2h}) $N(\pi^2) \rightarrow (D_{2h}) T(\pi\pi^*)$ adiabatic excitation energy for ethylene is 78.8 kcal/mol. (The corresponding (D_{2h}) $N(\pi^2) \rightarrow (D_{2d}) T(\pi\pi^*)$ C_2H_4 value of 62.0 kcal/mol is less pertinent since 3B_1 bicyclobutene is not twisted.) Thus, while the singlet-triplet splitting in bicyclobutene is indeed smaller than that in ethylene, the data in Table VII show that the \tilde{a}^3B_1 state of bicyclobutene lies over 30 kcal/mol above the ground state even at the \tilde{X}^1A_1 transition state to inversion. The \tilde{a}^3B_1 state should not be a factor in the chemistry of bicyclobutene unless it is photochemically populated.

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Finally, we find the $\pi^2\sigma\sigma^*$ triplet state to be 80.8 kcal/mol (6-31G* SCF) above the $\sigma^2\pi\pi^*$ (3B_1) triplet state at the $^3B_1 D_{2h}$ optimum geometry. However, the $\sigma\pi\pi^*\sigma^*$ quintet state is much lower in energy. At the 6-31G* SCF level, this quintet state ($^5B_{2g}$) has a D_{2h} optimum geometry of $R = 1.521 \text{ \AA}$, $S = 2.030 \text{ \AA}$, $T = U = 1.087 \text{ \AA}$, and $\alpha = \beta = 125.7^\circ$ (as defined in Table VII). An analytic SCF second derivative calculation shows this D_{2h} stationary point to be a relative minimum. The lowest frequency (301 cm^{-1}) corresponds to ring puckering, and a frequency of 887 cm^{-1} is found for stretching the C-C distance S , a mode which should be considered a ring-bending mode. The $^5B_{2g}$ state can aptly be described as two triplet methylene units high-spin coupled across a four-carbon ring. The $^5B_{2g}$ optimum SCF energy (-153.54177) is only 3.6 kcal/mol above the optimum (C_{2v}) 3B_1 energy, but, as one would expect, the inclusion of electron correlation increases this energy difference to 27.2 kcal/mol [$E(\text{CISD}) = -153.94805$], giving a CISD adiabatic excitation energy of 76.4 kcal/mol for the $\tilde{X}^1A_1 \rightarrow ^5B_{2g}$ transition.

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Registry No. 1, 1120-53-2; 2, 157-39-1; 3, 1120-53-2; 5, 58208-49-4; vinylacetylene, 689-97-4.

Non-Kekulé Acenes. The Dimethylenepolycyclobutadienes, a New Class of $(4n + 2)$ Alternant Hydrocarbons

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Abstract: The dimethylenepolycyclobutadienes (3_n) are the non-Kekulé analogues of the classical acenes. Application of a variety of theoretical methods reveals several novel features of such structures. Most interesting is the emergence of a parity rule. When n is even, 3_n is predicted to be a singlet, with n disjoint NBMO's. When n is odd, theory predicts a triplet ground state with $(n + 1)$ NBMO's that are not fully disjoint.

Interest in new organic materials with unusual optical, magnetic, and electronic properties continues to grow. Polyacetylene (**1**) provides a powerful paradigm for the development of such structures. One starts with a simple monomer with a relatively large HOMO-LUMO energy gap, and builds up highly extended, conjugated π systems. As the chain grows, the HOMO-LUMO energy gap decreases, and when this gap becomes small enough, novel properties must emerge. This approach has led to the development of many new materials such as poly(*p*-phenylene), poly(*p*-phenylene sulfide), polythiophene, etc. Another related example is provided by the classical acenes (**2**) (benzene, naphthalene, anthracene, ...). The smaller acenes are, of course, well-known and extensively studied. Recent theoretical and experimental work on larger acenes with $n > 7$ suggests that such structures could have very intriguing properties.²



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An alternative strategy for building novel structures would be to start with a monomer that has essentially no HOMO-LUMO gap. With this approach, one would expect that the onset of unusual properties would occur for a "polymer" of much shorter chain length. Non-Kekulé molecules provide attractive candidates for such a monomer. A wide variety of non-Kekulé structures has been prepared in recent years,³ including some that are remarkably stable.^{3b} Such structures can be either paramagnetic

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