

Electronic Structures of Bicyclo[1.1.0]butane and Bicyclo[1.1.1]pentane

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Abstract: Mulliken population analyses of *ab initio* SCF calculations for bicyclo[1.1.0]butane and bicyclo[1.1.1]pentane are reported and used to clarify the nature of the bonding in these molecules. The central CC bond of bicyclobutane is found to be describable as partially olefinic, although not strictly of π character. The central carbon atoms of bicyclopentane have strongly antibonding overlap population, consistent with their small separation and the large spin-coupling constant between the bridgehead protons. The bridgehead CH bonds of bicyclobutane are found to be strongly polarized, in explanation of the marked acidity of these bridgehead protons.

Bicyclo[1.1.0]butane and bicyclo[1.1.1]pentane have striking properties which make examination and comparison of their electronic structures of interest. The central bond of bicyclobutane exhibits both olefinic¹ and nonolefinic² properties, and its bridgehead proton is distinctly acidic,¹ with a very large ¹³C-H spin coupling constant (205 Hz).³ Bicyclopentane has the shortest nonbonded carbon-carbon distance on record,⁴ and a surprisingly large long-range spin coupling constant between bridgehead protons (18 Hz).¹

The electronic structure of bicyclobutane has been the subject of several apparently conflicting investigations. To explain the olefinic properties of the central bond Pomerantz and Abrahamson⁵ proposed two largely qualitative models, one attributing ethylenic character and the other acetylene-like character to this bond. Wiberg⁶ has performed CNDO calculations on bicyclobutane with the conclusion that the central bond has appreciable p character, and most recently Schulman and Fisanick⁷ have reported the results of *ab initio* SCF calculations which indicate that the central bond is nearly pure p character. The nature of the bonding orbitals in bicyclopentane has also been the subject of speculation. Chiang and Bauer⁴ suggest that the bridgehead carbon-hydrogen bond involves a carbon orbital that is nearly pure p character and that substantially pure p orbitals on the methylene carbons are involved in bonding to the bridgehead carbons.

The present *ab initio* SCF calculations with Mulliken population analyses are intended to identify the similarities and differences of the electronic structures of these two bicyclic molecules and to select among the proposed descriptions of their bonding.

Ab Initio SCF Calculations. A modified form of the IBMOL program⁸ has been used for the calculations reported here. The basis functions for the molecular

orbital expansions were atomic-optimized⁹ Gaussian type functions

$$\chi = Nr^l \exp(-\alpha r^2) Y_l^m(\theta, \phi)$$

where the $Y_l^m(\theta, \phi)$ are normalized spherical harmonics and α is the optimized orbital exponent. Such functions have proved useful and near optimal for other molecular calculations.^{10,11} The uncontracted bases used for carbon (3s, 1p) and hydrogen are listed in Table I.

Table I. Gaussian Type Functions Optimized Orbital Exponents

Atom	Exponents	
	s	p
C	46.5100	
	6.7170	
	0.3117	
H	1.6150	0.3545
	0.2521	

The total bases consist of 36 functions for bicyclobutane and 46 functions for bicyclopentane. While these bases are by no means sufficient to approach the Hartree-Fock limit, nevertheless they are well balanced and thus can be expected to yield reasonably reliable bonding and antibonding properties in Mulliken population analyses.¹²

The geometry of bicyclobutane determined by microwave spectroscopy¹³ and the electron diffraction geometry of bicyclopentane⁴ were assumed for these calculations. The numbering and coordinate systems are identified in Figure 1. Symmetry orbitals were not predetermined in either calculation, and thus the electron

(1) K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(2) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 496 (1966).

(3) K. Wüthrich, S. Meiboom, and L. C. Snyder, *J. Chem. Phys.*, **52**, 230 (1970).

(4) J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 1614 (1970).

(5) M. Pomerantz and E. W. Abrahamson, *ibid.*, **88**, 3970 (1966).

(6) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(7) J. M. Schulman and G. J. Fisanick, *J. Amer. Chem. Soc.*, **92**, 6653 (1970).

(8) E. Clementi and D. R. Davis, *J. Comput. Phys.*, **1**, 223 (1966).

(9) D. R. Whitman and C. J. Hornback, *J. Chem. Phys.*, **51**, 398 (1969).

(10) C. J. Hornback, Ph.D. Thesis, Case Institute of Technology, 1967.

(11) L. M. Sachs, M. Geller, and J. J. Kaufman, *J. Chem. Phys.*, **51**, 2771 (1969); L. C. Snyder, R. G. Shulman, and D. B. Neumann, *ibid.*, **53**, 256 (1970); J. F. Chiang and D. R. Whitman, *Theor. Chim. Acta*, **17**, 155 (1970); J. R. Sabin, R. E. Harris, T. W. Archibald, P. A. Kollman, and L. C. Allen, *ibid.*, **18**, 235 (1970); D. R. Armstrong and D. T. Clark, *Chem. Commun.*, 99 (1970); D. T. Clark and D. M. Lilley, *ibid.*, 549, 603 (1970).

(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

(13) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *ibid.*, **50**, 1976 (1969).

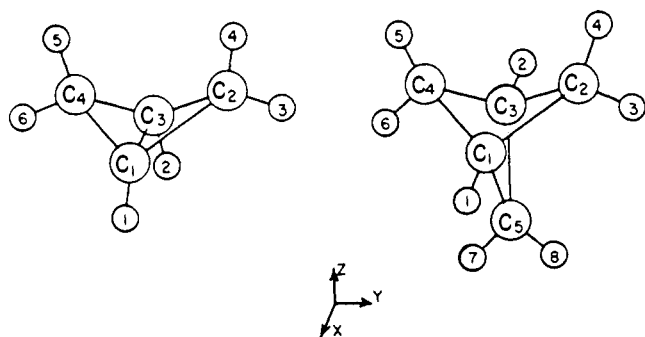


Figure 1. Bicyclobutane and bicyclopentane numbering and coordinate systems.

configurations of the molecules are predictions of the *ab initio* treatment, not assumptions within it.

Bicyclobutane. The 30 electrons of bicyclobutane occupy 15 molecular orbitals, each consisting of a linear combination of the 36 basis functions. Many of these occupied molecular orbitals are substantially delocalized throughout the molecule such that they cannot be unambiguously categorized as associated with particular C-C or C-H bonds, nor even identified as of σ or π character. However, a Mulliken population analysis does provide insight into the nature of the electronic structure and bonding in this molecule.

Looking first at total carbon-carbon overlap populations, Table II contains the present results along with

Table II. Bicyclobutane Bond Populations

	2s-2s	2s-2p	2p-2p	Total
Bond indices ^a				
C ₁ -C ₃	0.037	0.168	0.688	
C ₁ -C ₂	0.050	0.327	0.596	
Bond orders ^b				
C ₁ -C ₃	-0.0712	0.0332	0.3844	0.3464
C ₁ -C ₂	0.0254	0.3090	0.3026	0.6330
Overlap populations				
	s-s	s-p	p-p	
C ₁ -C ₃	-0.1782	0.0088	0.4708	0.3014
C ₁ -C ₂	-0.0170	0.2780	0.3788	0.6398

^a Reference 6. ^b Reference 7.

those of the two previous quantitative treatments. The bond indices and bond orders are not strictly comparable with the present overlap populations, but the similar relative magnitudes support similar conclusions. Thus, the low s-p values for the central bond relative to those for the side bond suggest that the central bond is of nearly pure p character. In addition, the high $p\sigma$ to $p\pi$ ratio alluded to by Schulman and Fisanick indicates little π character in the central bond. Thus, this bond could be interpreted as largely a p-p σ bond, with some increased electron density between and above the bridgehead carbons.

Closer examination of the details of the *ab initio* overlap populations, however, reveals that this σ interpretation for the central bond is somewhat misleading. Table III lists, for each occupied molecular orbital in order of increasing energy, its overlap populations, major bonding character, and symmetry type. Only overlap populations of magnitude greater than 0.01 are included, in order to emphasize major bonding charac-

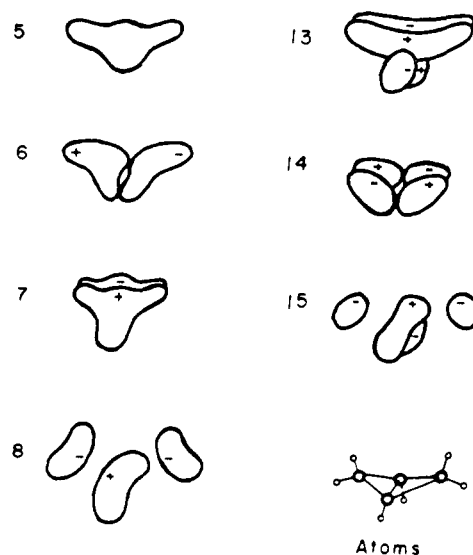


Figure 2. Representations of molecular orbitals of bicyclobutane with major carbon-carbon overlap populations.

teristics without the distractions of ubiquitous small overlaps.

The four lowest energy orbitals are essentially atomic 1s orbitals associated with the four carbon atoms, as expected. Comparing the total CH and CC overlaps of the other 11 orbitals, we may identify numbers 5, 6, 13, 14, and 15 as predominantly C-C bonding orbitals, while the remaining six contain the major C-H bonding components. The five predominantly C-C bonding orbitals consist of two low-energy A₁ and B₁ orbitals, and a group of three high-energy orbitals of symmetries B₂, A₂, and A₁. The electronic structure of model I proposed by Pomerantz and Abrahamson⁵ is

$$\sigma_{1a_1}^2 \sigma_{1b_1}^2 \pi_{1b_2}^2 \pi_{1a_1}^2 \pi_{1a_2}^2$$

This also consists of two lower energy orbitals and three of higher energy, and except for the interchange of the two highest energy orbitals, the symmetry types agree precisely with the present *ab initio* MO results. The *ab initio* results do not yield degeneracy of the two low-energy orbitals as does the PA model, nor an antibonding a₂ orbital, but this is expected since the *ab initio* method avoids simplifying approximations invoked in the PA energy calculations.

Still more insight into the nature of the central bond in bicyclobutane is available by examining the individual molecular orbitals contributing substantially to this bond. In fact, both the strongest bonding and the largest antibonding overlaps throughout the molecule are associated with the central bond. This point is illustrated in Figure 2, which contains representations of all the molecular orbitals which make the largest contributions to carbon-carbon overlap populations. While each of these orbitals possesses overall C-C bonding character, nevertheless only numbers 5, 6, 8, and 15 contribute positive C₁-C₃ overlap populations, while numbers 7, 13, and 14 are distinctly antibonding with respect to the central bond. Thus the low total overlap population of this bond is due not to the absence of electron density in the interatomic vicinity but rather to the considerable cancellation of positive and negative overlaps. This aspect is completely con-

Table III. Bicyclobutane Molecular Orbital Properties

MO	Overlap populations					Major bonding	Symmetry
	C ₁ -C ₃	C ₁ -C ₂	C ₁ -H ₁	C ₂ -H ₃	C ₂ -H ₄		
1	0.01	-0.01				C(1s)	A ₁
2		-0.01				C(1s)	B ₁
3	-0.04					C(1s)	B ₂
4	0.01	-0.01				C(1s)	A ₁
5	0.29	0.17	0.02	0.01	0.01	C-C	A ₁
6	0.02	0.09		0.12	0.09	C-C	B ₁
7	-0.20	0.07	0.24			C-H	B ₂
8	0.13	-0.04	0.09	0.11	0.17	C-H	A ₁
9	0.09	0.05	0.15	0.17		C-H	A ₁
10	0.06	-0.02	0.13	0.11	0.14	C-H	A ₁
11	0.03	0.07		0.01	0.31	C-H	B ₁
12	0.04	0.07		0.26	0.03	C-H	B ₁
13	-0.39	0.11	0.14			C-C	B ₂
14	-0.17	0.19				C-C	A ₂
15	0.42	-0.08		0.02	0.01	C-C	A ₁

cealed when only total overlap populations are considered.

The electron density associated with the central bond of bicyclobutane is neither concentrated near the axis as in a σ bond nor distributed symmetrically above and below the axis as in a conventional π bond. Thus any classical description is distinctly inadequate. However, considering orbital 15, which contributes by far the largest positive C₁-C₃ overlap population, the total of 0.42 consists of 0.22 p_x - p_x overlap and 0.20 p_z - p_z . Thus a major component of the central bond arises from p orbitals making an angle near 45° with the central axis. This description corresponds closely with the bonding π orbital of PA model I. However, because of the "folded" nature of bicyclobutane, electron density above and between the central carbon atoms can simultaneously contribute substantial overlap populations to the peripheral carbon bonds as well as to the central one. This is particularly evident in orbitals 5 and 13, one bonding and the other antibonding with respect to the central carbons. As in all molecules, the total electron distribution in bicyclobutane occupies a minimum energy configuration; yet in this type of molecule the distribution does not conform to a convenient classical description.

The carbon-hydrogen overlap populations in bicyclobutane contain no unexpected features. However, the strong polarization of the bridgehead C-H bond is apparent in Table IV, where total gross atomic popula-

Table IV. Total Population Analyses for Bicyclobutane and Bicyclopentane

	Net atomic charges				
	C ₁	C ₂	H ₁	H ₃	H ₄
Bicyclobutane	-0.227	-0.140	0.153	0.113	0.100
Bicyclopentane	-0.102	-0.145	0.092	0.076	0.076
	Total overlap populations				
	C ₁ -C ₃	C ₁ -C ₂	C ₁ -H ₁	C ₂ -H ₃	C ₂ -H ₄
Bicyclobutane	0.301	0.639	0.772	0.785	0.750
Bicyclopentane	-0.554	0.746	0.753	0.764	0.764

tions and total overlap populations of bicyclobutane and bicyclopentane are compared. The negative carbon and positive proton of bicyclobutane correlate well with the distinct acidity of the bridgehead protons.

Bicyclopentane. Reference to Table IV shows that the bonding in bicyclobutane and in bicyclopentane is quite similar at every position except the bridgeheads. There is antibonding overlap between the bridgehead carbons in bicyclopentane, reinforcing the conventional assumption of an absence of bonding. Further, the large magnitude of this overlap explains the surprisingly large long-range spin coupling constant between the bridgehead protons. Once again, the negative overlap population correlates with antibonding characteristics but does not imply an absence of internuclear electron density.

Yonezawa, *et al.*,¹⁴ have proposed that the value of the ratio of the bond populations, $(p\sigma_{c-h})/(s_{c-h})$, may represent a measure of the state of hybridization of the carbon orbitals involved in a C-H bond. The values of these ratios for the present calculations on bicyclobutane and bicyclopentane are presented in Table V.

These data show that the per cent s character of the carbon orbitals involved in C-H bonding is uniformly greater in bicyclobutane than in bicyclopentane. This is particularly true of the bridgehead C-H bond and supports the suggestion of Chiang and Bauer that in bicyclopentane the bridgehead C-H carbon orbitals are predominantly of p character.

The correlation originally proposed by Muller and Pritchard,¹⁵ $\rho_{C-H} = 0.20J_{C-H}$ between per cent s character of carbon orbitals involved in a C-H bond and carbon-hydrogen spin coupling constant is not followed by the data of Table V. The deviations may be attributed to any or all of several significant factors.

1. The technique of Yonezawa, *et al.*, for estimating s character is not without ambiguities and inadequacies. It does not generally lead to a total of one s and three p occupied orbitals on each carbon. Also, negative hybridizations can result, as in the central bond of bicyclobutane with both the present calculations and with those of Schulman and Fisanick.

2. The correlation of spin coupling constants with per cent s character alone also is questionable. The original work of Muller and Pritchard¹⁵ identifies a dependence of J values upon C-H bond lengths, $r(C-H) = 1.159 - 4.17 \times 10^{-4}J$. The greater bridgehead C-H length in bicyclopentane (1.10 Å)⁴

(14) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

(15) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).

Table V. Carbon Orbital Hybridizations^a

Bond	Bicyclobutane			Bicyclopentane		
	Hybridization	% s	$J^{13}\text{C-H}$	Hybridization	% s	$J^{13}\text{C-H}$
C ₁ -H ₁	sp ^{2.62}	28	205 ^b	sp ^{4.87}	17	164 ^c
C ₂ -H ₃	sp ^{2.76}	27	170 ^c	sp ^{3.84}	21	144 ^c
C ₂ -H ₄	sp ^{3.17}	24	152 ^c	sp ^{3.84}	21	144 ^c
C ₁ -C ₃	sp ^{-2.73}				(antibonding)	
C ₁ -C ₂	sp ^{4.24}			sp ^{3.69}		

^a Calculated by the method of ref 14. ^b Reference 3. ^c Reference 1.

than in bicyclobutane (1.071 Å)¹³ alone accounts for nearly all of the difference in these spin coupling constants without reference to s character. Thus, as pointed out by Wiberg,¹ simple correlations of s character with spin coupling constants may not always be entirely valid, particularly between different types of molecules.

3. As in all *ab initio* calculations on larger molecules, the basis functions for the present work are not complete, with consequent possible distortion of the true p to s ratios. This problem is not easily solved. The use of contracted bases does not necessarily improve the situation, since contraction can involve a larger set of basis functions, but at the expense of a reduced total number of variational parameters.

Conclusions

The *ab initio* SCF results indicate that in bicyclobutane there is significant electron density between and above the central carbon atoms, distributed in such a way as to explain the partial olefinic properties of the central bond. The electron distribution is, however, not such that it can be correctly described solely as part of a central π bond. The density in some regions

resides in molecular orbitals which are simultaneously bonding for peripheral carbon atoms and antibonding between the central carbons. Although no classical description of the central bond of bicyclobutane can be entirely adequate, the Pomerantz and Abrahamson model I appears to be the best classical approximation.

In bicyclopentane, the central carbon atoms are found to be strongly antibonding, yet with appreciable internuclear electron density, as expected with the very short nonbonded carbon distance. This internal electron density explains the unexpectedly large long-range spin coupling constant between the bridgehead protons.

The C-H bonds of the methylene groups of both molecules are found to be quite similar and ordinary, with somewhat more p character observed for the carbon orbitals in the bicyclopentane bonds. However, the bridgehead C-H bond of bicyclobutane is far more strongly polarized than in bicyclopentane, explaining the acidity of the bicyclobutane protons.

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