Organic and Biological Chemistry

Theoretical Studies of Bicyclobutane

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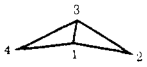
Abstract: The electronic structure of bicyclobutane has been treated by molecular orbital theory within the LCAO approximation. Hybridizations inferred through the use of localized orbitals show the methylenes to be similar to those in cyclopropane, while the central bond is formed from hybrid orbitals with 96% p character (sp^{24}), directed at an angle of 31° with respect to the bond vector. Experimental values for directly bonded spin–spin coupling constants are correlated with calculated hybridization, and INDO finite perturbation calculations lead to the prediction of a zero or slightly negative J_{CC} value for the central bond. Several features of the *ab initio* potential energy surface have been examined, including the calculated equilibrium geometry of the ground state, and the 1,2- and 1,3-diradical states studied as well. The *ab initio* energy yields a reasonable value for the strain energy.

The electronic structure of strained-ring hydrocarbons has been a subject of increasing interest since Baeyer[2] first studied deviations of carbon from tetrahedral valency. Early attention focused on cyclopropane, and for a number of years lively discussion dealt with an apparent contradiction between the "olefinic" and bent-bond models of Walsh[3a] and Coulson–Moffitt,[3b] respectively. However, Coulson and Moffitt have pointed out that their hybrid orbitals, and the different set used by Walsh, both lead to the same invariant total molecular orbital (MO) electron density, provided that the full molecular orbital problem is solved.[4] The two treatments differ merely in the choice of hybrid orbital basis set, and should lead to the same values for any observables.

It is often useful in MO studies of molecular bonding to transform the usual set of delocalized MO's to a set of maximally localized ones, according to some reasonable physical criterion.[5] Such a procedure furnishes a particularly convenient model for making connections with various static and dynamic chemical properties as we shall do here, and still preserves the invariance of the total electron density.

The recent development of *ab initio* molecular orbital techniques for large molecules and the availability of highly efficient basis sets in the form of contracted Gaussian-type orbitals[6] make it feasible to carry out intensive studies of polycyclic strained-ring compounds at a high level of accuracy. It is the purpose of the present series of papers to deal with the electronic structure of a number of such molecules. In this work we consider bicyclo[1.1.0]butane (I), and elaborate on the previously proposed model of Schulman and Fisanick[7] in which the central bond between bridgehead carbons was shown to be formed from (a) two essentially pure 2p orbitals which are (b) canted toward each other at angles consistent with a bent σ bond picture. Notice that this model extends the previous qualitative description of Pomerantz and Abrahamson,[8] who constructed a Walsh model for bicyclobutane. Again, as with cyclopropane, the CC symmetry orbitals were not allowed to mix with each other or with the CH bonds, and the claim of pure p orbitals was therefore not proven. In the current study we infer quantitatively, through the use of localized orbitals, the percentage s character in the almost pure p hybrids, and assign the relative angle of interaction, or equivalently, the bending angle.



I

Further analysis of the bicyclobutane electronic structure is presented here in terms of charge-density contours, the dipole moment, and the ^{13}CH and ^{13}C–^{13}C nuclear spin–spin coupling constants, the latter computed by INDO finite perturbation theory.[9] Several of these results are new predictions, and they will hopefully encourage test in experiment.

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(2) A. Baeyer, *Ber.*, **18**, 2269, 2277 (1885).

(3) (a) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (b) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(4) We refer here, not to the elegant valence bond treatment given in ref 3, but rather the discussion of molecular orbitals given in the Appendix of ref 3b.

(5) (a) C. Edmiston and K. Reudenberg, *J. Chem. Phys.*, **43**, S97 (1965); (b) M. D. Newton, E. Switkes, and W. N. Lipscomb, *ibid.*, **53**, 2645 (1970); (c) R. Bonaccorsi, E. Scrocco, and J. Tomasi, *ibid.*, **52**, 5270 (1970). (d) It is worth noting that in the case of cyclopropane, different localization criteria[5b,c] have led to the same localized picture of three equivalent bent CC bonds, as opposed to the possible alternative of three-center bonding orbitals suggested by Walsh. Localization of boron hydride molecular orbitals[5e] routinely leads to three-center bonding orbitals. (e) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969); E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

(6) (a) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966); (b) E. Clementi and D. R. Davis, *ibid.*, **45**, 2593 (1966); (c) J. M. Schulman, J. W. Moskowitz, and C. Hollister, *ibid.*, **46**, 2759 (1967); (d) J. M. Schulman, C. J. Hornback, and J. W. Moskowitz, *Chem. Phys. Lett.*, **8**, 361 (1971).

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

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

(9) (a) J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2965 (1968); (b) for previous applications to ring systems see P. D. Ellis and G. E. Maciel, *J. Amer. Chem. Soc.*, **92**, 5829 (1970).

We have also studied various aspects of the energetics of bicyclobutane, including its strain energy and important features of the potential energy surface. In particular, we have investigated the ability of an *ab initio* basis to predict the correct equilibrium geometry. A knowledge of such behavior is necessary, if we are to have confidence in predicted distortion energies. A case in point is the degree of "softness" of the $H_1C_1C_3$ angle of bicyclobutane to enlargement, which may be of importance in understanding its metal-catalyzed rearrangements and inability to undergo Diels–Alder reaction.

Finally, we compare the energetics and localized orbitals of INDO theory with the *ab initio* results. This tests the applicability of a semiempirical method, used mainly for normal hydrocarbons, to the unusual systems which will be the subject of future papers of this series.

Computational Methods

The *ab initio* and INDO–SCF calculations performed here for singlet states are based on the closed-shell single-determinant Roothaan formulation.[10] For the triplet states a single determinant is also used (*i.e.*, the $M_s = 1$ component), based on the Pople–Nesbet open-shell procedure.[11] It is well known that for large distortions from equilibrium corresponding to bond cleavage, the restricted closed-shell single determinant[10] is not a reliable approximation to the ground state singlet and should, in principle, be replaced by an appropriate superposition of determinants. In this study, we will make the plausible assumption that the energies of such distorted singlets are close to those of their related triplets, both states being loosely referred to as diradicals. That this is a reasonable approach can be seen by consideration of a simplified example, the minimal basis set representation of H_2. The triplet MO wave function is easily shown to be equivalent to the triplet valence-bond or Heitler–London wave function. For large interatomic distances the latter function differs little in energy from the VB or H–L singlet, which leads to the correct ground state dissociation products.

For the semiempirical studies we have chosen the INDO over the CNDO method, since the presence of one-center exchange integrals leads to significantly better nuclear spin–spin coupling constants.[9] The energetics and hybridizations are generally similar in the two methods.

The *ab initio* treatments require a careful choice of basis set. For studying electronic structure, we have employed a minimal contracted Gaussian set optimized for ethylene[5d] with p_x, p_y, and p_z orbitals identical with each other (but different from the 2s) so as not to bias the relative extents of π and σ character in the results. Coefficients and exponents of this minimal-basis molecule optimized (MBMO) set are given in Table I. Since it was also of interest to compute accurate strain energies, the extended basis (4-31 G) of Pople and coworkers,[12] developed and tested for computing accurate heats of reaction, has been employed as well. This set uses two contracted basis functions for each occupied valence atomic orbital and will be denoted in the following discussion as the EBMO basis (extended-basis molecule optimized), for easy comparison with the MBMO notation.

Table I. Coefficients and Exponents of the MBMO Basis Set[a]

Atom	Orbital	Coefficients (exponents)
C	2s	0.3153853 (0.5500315), 0.3859611 (0.3858485), 0.3522476 (0.1432262)
	2p	0.0230551 (14.871573), 0.1568288 (3.1741450), 0.4871830 (0.7491988), 0.5498280 (0.1927036)
H	1s	0.0193609 (22.87791), 0.1362125 (3.44643), 0.4763110 (0.778612), 0.5050215 (0.212822)

[a] Coefficients are those of the optimized basis of ref 6d, in which the carbon 1s function may be found.

Both *ab initio* and INDO orbitals were localized using the Edmiston–Ruedenberg[5a] procedure for minimizing the total exchange energy or, equivalently, maximizing the total intraorbital coulomb energy. The deviation of a given localized MO (LMO) from perfect localization on a given number of atomic centers (generally two) can be conveniently expressed in terms of the rms deviation of the LMO from its truncated counterpart, the latter being obtained by excluding all contributions from unwanted atoms, and renormalizing. According to this criterion,[5b] all the LMO's of bicyclobutane were found to be at least 90% localized, unless noted otherwise.

Electronic Structure of Bicyclobutane

The molecular orbital energies of bicyclobutane in the MBMO and EBMO bases are displayed in Table II, and the Mulliken population analysis for the MBMO set is given in Table III. All calculations mentioned in this section are based on the experimental microwave geometry.[13] Since there is significant mixing of CC and CH symmetry orbitals, the delocalized MO's cannot be simply identified with particular CC or CH

Table II. Orbital Energies of Bicyclobutane in the Extended Basis[a–c]

Orbital	Energy, au	Orbital	Energy
$1a_1$	−11.2230 (−11.2734)	$5a_1$	−0.6957 (−0.7084)
$1b_2$	−11.2230 (−11.2734)	$3b_2$	−0.5833 (−0.6017)
$2a_1$	−11.2195 (−11.2724)	$6a_1$	−0.5800 (−0.5948)
$1b_1$	11.2191 (−11.2721)	$4b_2$	−0.5151 (−0.5325)
$3a_1$	−1.2311 (−1.2522)	$3b_1$	−0.4627 (−0.4871)
$2b_2$	−0.9308 (−0.9393)	$1a_2$	−0.4359 (−0.4623)
$4a_1$	−0.7861 (−0.7949)	$7a_1$	−0.3465 (−0.3727)
$2b_1$	−0.7837 (−0.7922)		

[a] Values in parentheses are orbital energies in the MBMO calculation. The MBMO and EBMO total energies are −154.5417 and −154.6219 au, respectively. [b] The coordinate system chosen places the *x* and *z* axes parallel to the C_2 and central bond axes, respectively. b_2 orbitals are antisymmetric in the *xz* plane. In the nomenclature of Pomerantz and Abrahamson the names b_1 and b_2 are interchanged, with respect to this work. [c] The three lowest unoccupied orbitals are of energy: 0.2492($8a_1$), 0.2644($4b_1$), and 0.2762($9a_1$).

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(10) C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

(11) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, 22, 571 (1954).

(12) (a) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, 54, 724 (1971); (b) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 4796 (1970); L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, 93, 2189 (1971).

(13) (a) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, 50, 1976 (1969); (b) the dihedral angle (α) listed in Table IV of ref 13a should read 121°40′ ± 30′, instead of the misprinted value of 122°40′ ± 30′.

Table III. Mulliken Population Analysis of Bicyclobutane (MBMO Basis)

Atoms	Overlap population	Atom	Charge
C_1–C_2	0.607	C_1	−0.245
C_1–C_3	0.335	C_2	−0.335
C_1–H_{brbd}	0.819	H_1	+0.202
C_2–H_{exo}	0.806	H_{exo}	+0.193
C_2–H_{endo}	0.808	H_{endo}	+0.185

bonds. For this same reason, the degeneracies predicted by Pomerantz and Abrahamson[8] in their models I and II are not found. There are two near degeneracies (pairs $4a_1$–$2b_1$ and $3b_2$–$6a_1$), but these are accidental.

The overlap populations for the side and central bonds are 0.607 and 0.335, respectively. Their relation to "bond strength," always somewhat unclear, is particularly so in the case of bicyclobutane where the side and central bonds are strongly coupled. Moreover, the overlap populations (and the protonic charges, as well) fail to reveal either the relatively high bridgehead-hydrogen acidity or the important differences in ^{13}CH spin–spin coupling constants.

Thus, to uncover these important consequences of the electronic structure, it is useful to employ the localized-orbital description, the hybridizations of which are given in Table IV, along with the values for ethane and cyclopropane in the same basis for comparison. The most striking feature seen is the confirmation of negligible s content in the $sp^{24.3}$ hybrids, ϕ, which comprise the central bond, equivalent to 96% p character.

$$\phi = 0.2084(2ps)_C + 0.8405C(2p\sigma)_C + 0.5001(2\pi)_C$$

Table IV. Localized Molecular Orbitals (LMO's) for Bicyclobutane Generated From MBMO and INDO Molecular Orbitals

Molecule	Bond	Hydridizations MBMO	Hydridizations INDO
Ethane	CC	$sp^{4.01}$	$sp^{2.67}$
	CH	$sp^{3.02}$	$sp^{2.81}$
Cyclopropane	CC	$sp^{5.69}$	$sp^{4.16}$
	CH	$sp^{2.27}$	$sp^{2.20}$
Bicyclobutane	C_1–C_3	$sp^{24.3}$	$sp^{18.0}$ [a]
	C_1–C_2	$sp^{2.97}$–$sp^{5.10}$	$sp^{2.65}$–$sp^{4.10}$
	C_1H_{brhd}	$sp^{1.58}$	$sp^{1.58}$
	C_2H_{endo}	$sp^{2.23}$	$sp^{2.06}$
	C_2H_{exo}	$sp^{2.26}$	$sp^{2.19}$

[a] The C_1C_3 LMO as determined by the INDO method was ~19% delocalized (see Section II), as compared with values of $\lesssim$10% for all other LMO's obtained in this work.

The orientation of these almost pure p hybrids is such as to give a bond bent by 30.8°, only 4° more bent than cyclopropane in this basis. Alternatively, the coefficients of the localized central bond hybrid may be used to obtain the amount of π character as

$$\frac{(0.5001)^2 \times 100}{(0.5001)^2 + (0.8405)^2} = 26.1\%$$

Thus, the previously reported model of Schulman and Fisanick,[7] of an essentially pure p–p bent σ bond, is fully validated. By σ bond we mean merely that the bending angle is significantly less than 45°.

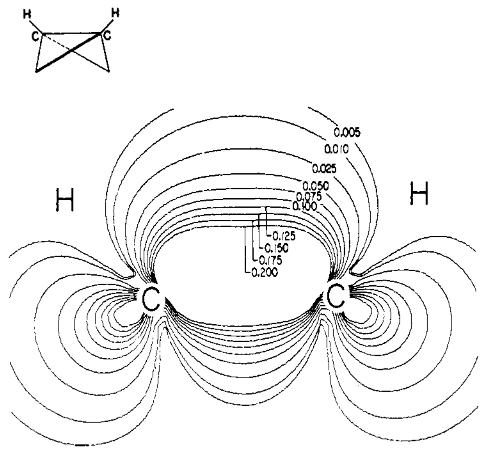

Figure 1. Electron density (au) from double occupancy of the localized MO associated with the C_1–C_3 bond in bicyclobutane.

It is interesting to view charge-density contours of the central bond LMO, and these are given in Figure 1. The large external lobe, lying below and behind the central bond (more pronounced than its cyclopropane counterpart), is clearly seen. It is a consequence of the relatively small s content of its hybrids. A total charge-density plot is given in Figure 2, using the same contours as in Figure 1. Though the external lobes are less apparent, close inspection reveals that they contribute nearly all of the outermost total density in their regions of importance.

The bicyclobutane side bonds are formed from carbon bridgehead and methylene orbitals which are hybridized $sp^{3.0}$ and $sp^{5.1}$, respectively, the latter being close to the cyclopropane value, $sp^{5.7}$. The side bonds are also bent outward by 33° from their C–C bond vectors and are rotated downward into the region between the two cyclopropane planes. The out-of-plane distortion of the side bond arises mainly from the bridgehead hybrids (~10° out of plane), while the methylene hybrids are within 2° of planarity.

The bridgehead CH bonds are constructed from $sp^{1.6}$ hybrids, essentially the same value previously inferred from population analysis,[7] and consistent with the acidic nature of the bridgehead proton. In contrast, the methylene hybrids to the endo and exo protons are $sp^{2.2}$ and $sp^{2.3}$, respectively (cyclopropane is $sp^{2.2}$), again confirming that the methylenes of bicyclobutane and cyclopropane are quite similar.

The MBMO wave function furnishes a dipole moment of 0.69 D, in excellent agreement with experiment, 0.70 D,[13] and it is interesting to examine the contributions made by each LMO. These may be made origin independent by (arbitrarily) assigning a unit positive charge to both nuclei of each LMO.[5b] The results are given in Table V and show that the net dipole moment stems from partial cancellations among several LMO values larger in size than the total. The resultant of the six CH bond moments (−0.60 D) is more than offset by the sum of the CC moments, which we note arise mainly from the distortion of the CC LMO densities perpendicular to the CC bond vectors, rather than from any significant polarization of the LMO's along the bonds. The total dipole, along the C_2 axis, has its positive end exocyclic to the central bond.

Experimental connection with the predicted hybridizations of localized molecular orbital theory can be

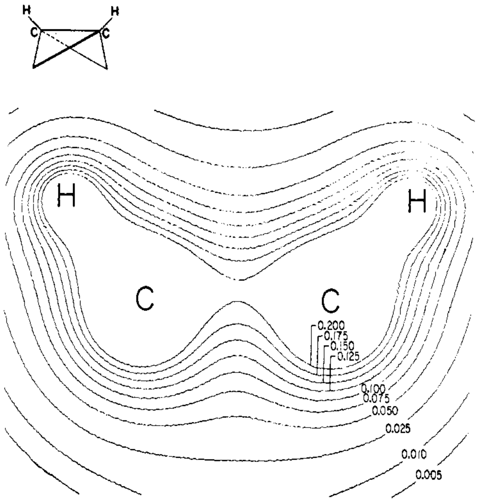

Figure 2. Total electron density (au) of bicyclobutane.

made through nuclear spin–spin coupling constants between directly bonded atoms. A linear relationship has been shown[14] to exist between $J_{^{13}CH}$ values and nominal hybridizations (ethylene: sp^2; ethane: sp^3; etc.). There is similar relationship between $J_{^{13}CH}$ and the *ab initio* (MBMO) per cent s character, as shown in Table VI for cyclopropane, ethane, and bicyclobutane. The ratio of J to the fraction of s character is found to be 522 ± 23 Hz, and though this value is probably somewhat basis dependent, the linearity is clearly indicated. A more sophisticated treatment of ^{13}CH spin–spin coupling constants has been performed here, using the INDO finite perturbation method,[9] the results of which are given in Table VI. The $J_{^{13}CH}$ values obtained are in good agreement with experiment, and though they lie consistently several hertz below the latter, there is a definite one-to-one correspondence between theory and experiment. In particular, the finite perturbation method clearly distinguishes the exo and endo coupling constants of bicyclobutane confirming the relative assignments of Wüthrich, *et al.*[15]

Table V. Dipole Moment (Debye) Partitioned Over Localized Molecular Orbitals (LMO's)

Bond[a]	Bond moment[b]	Contributions to the total z component[c]
C_1C_3(central)	1.87	−1.81 (1)
C_1C_2(side)	2.26	+3.10 (4)
C_1H_{brhd}	1.74	−2.51 (2)
C_1H_{endo}	1.76	+3.50 (2)
C_1H_{exo}	1.75	−1.60 (2)
		Total = +0.69[d,e]

[a] The contribution from inner shell (1s) orbitals is negligible. [b] Obtained as the sum of the LMO electronic contribution and a nuclear term obtained by adding one positive charge to each center. See, for example reference 5b. [c] The number of equivalent bonds contributing to these values is given in parentheses. [d] The dipole points with positive end exocyclic to the central bond. [e] A somewhat larger total moment, 0.89 D, is obtained from the EBMO basis.

Table VI. ^{13}CH Nuclear Spin-Spin Coupling Constants of Bicyclobutane, Cyclopropane, and Ethane (Hz)

Molecule	Bond	Fraction s character[a] in carbon hybrid, f	$J_{^{13}C-H}$ (expt)	$J_{^{13}C-H}$[b] (expt)/f	$J_{^{13}C-H}$ (INDO)
Ethane	CH	0.249	125[c]	503	122[d]
Cyclopropane	CH	0.306	162[e]	529	156[f]
Bicyclobutane	CH_{brhd}	0.387	205[g]	530	190[f]
	CH_{endo}	0.310	169[g]	545	165[f]
	CH_{exo}	0.307	153[g]	499	148[f]

[a] Computed from the MBMO hybridizations (sp^λ) given in Table IV as $f = 1/(1 + \lambda)$. [b] The ratio is found to be $J_{^{13}C-H}/f$ = 522 ± 23 Hz. [c] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962). [d] Given previously in reference 9. [e] L. C. Snyder and S. Meiboom, *J. Chem. Phys.*, **47**, 1480 (1967). [f] Very similar calculated values were previously given by Ellis and Maciel.[9b] [g] Reference 15.

The INDO method can also be used to compute $J_{^{13}C-^{13}C}$ values, a few of which have now been measured. The results for cyclopropane, ethane, and bicyclobutane, given in Table VII, suggest that theory will now overestimate experimental values. A thorough investigation of this method is now in progress. What is most interesting is the slightly *negative J* value for the central bond. To a first approximation $J_{^{13}C-^{13}C}$ is proportional to the product of the fraction s character in each of the bonded hybrids.[16] For the bicyclobutane central bond the latter is 0.0016, essentially zero compared with the cyclopropane value of 0.075 (J = 13–15 Hz). Thus, if a linear relationship analogous to that for ^{13}CH coupling is found, bicyclobutane would be the zero intercept. Of course it also may be that the bicyclobutane C_1–C_3 spin–spin coupling is, in fact, negative, but in any case it is certain to be one of the smallest J_{CC}'s to be found.

Table VII. ^{13}C–^{13}C Nuclear Spin–Spin Coupling Constants of Bicyclobutane, Cyclopropane, and Ethane (Hz)

Molecule	Bond	$J_{^{13}C-^{13}C}$ (INDO)	$J_{^{13}C-^{13}C}$ (expt)
Ethane	CC	41.5[a]	35[b]
Cyclopropane	CC	21.0	13–15[c]
Bicyclobutane	Side CC	32.6	
	Central CC	−1.85	

[a] Previously given in ref 9. [b] Footnote *c*, Table VI. [c] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 5962 (1967).

We have seen that both the *ab initio* and INDO results can be successfully correlated with the experimental $J_{^{13}CH}$ values, thus suggesting at least qualitative similarities in the two methods. That this is true can be seen from the similar LMO hybridizations in each case, given in Table IV. Also, an approximately linear dependence of $J_{^{13}CH}$ on per cent INDO s character can be found, as can a linear relationship between the $J_{^{13}C-^{13}C}$ values of INDO perturbation theory and the product of INDO fractional s character in the bonded hybrids. The importance of the latter, however, is not clear, since it may merely reflect an internal consistency in the INDO theory.

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(14) J. N. Schoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(15) K. Wüthrich, S. Meiboom, and L. C. Snyder, *ibid.*, **52**, 230 (1970).

(16) Such a relationship was previously suggested by K. Frei and H. J. Bernstein, *ibid.*, **38**, 1216 (1963).

While the INDO method is quite useful in predicting spin–spin coupling constants and generally useful for dipole moments (though in this case it gives 1.2 D), it is unreliable in thermochemistry. For this reason we use the *ab initio* level of theory to compute strain and distortion energies in the next section.

Energetics of the Bicyclobutane Ring System

An adequate model for a strained ring system should give quantitative account of its strain energy. Thus, we turn to the EBMO basis set total energies (for equilibrium geometries) of methane, ethane, cyclopropane, and bicyclobutane given in Table VIII. The zero-point energies also included in the table are based on experimental vibrational frequencies, and their addition to the SCF energies (approximate within the limited LCAO treatment) give, in turn, energies which may be compared with experimental enthalpies corrected to 0°K. In employing *ab initio* molecular energies to estimate reaction enthalpies, it has been found that despite omission of correlation energies, results within a few kcalories per mole can be obtained for reactions in which the same number of electron pairs and bond types appear in both reactants and products.[12b] With the EBMO basis, it is also possible to give good account of the relative energetics of saturated and unsaturated, or strained and unstrained systems.[12b]

Table VIII. Molecular Energies for Methane, Ethane, Cyclopropane, and Bicyclobutane (EBMO Basis)[a]

Molecule	Total energy, au	Zero-point energy, au
Methane	−40.1394	0.0432
Ethane	−79.1156	0.0721
Cyclopropane	−116.8803	0.0788
Bicyclobutane	−154.6219[b]	0.0831[c]

[a] Values for methane, ethane, and cyclopropane were given previously in ref 12. [b] Based on the experimental geometry of ref 13. [c] Obtained from experimental frequencies given by I. Haller and R. Srinivasan, *J. Chem. Phys.*, **41**, 2745 (1964).

Our approach for calculating strain energies is to incorporate the molecule in question into an appropriate and generally hypothetical, reaction in which the heats of formation of all other participants are known (*cf.* reference 12b). Thus, for cyclopropane, we consider the reaction

$$3CH_4 + C_3H_6 \longrightarrow 3C_2H_6$$

From the calculated enthalpy of reaction, the zero-point energies of each species, and the experimental enthalpies of formation of methane and ethane we obtain a calculated enthalpy of formation of cyclopropane. Subtraction of the enthalpy of its hypothetical strain-free analog[17] then furnishes the strain energy. The value obtained, 32 kcal/mol, is in moderately good (absolute) agreement with experiment, 25 kcal/mol.[18]

Turning to bicyclobutane and using the reaction, bicyclobutane + ethane → 2 cyclopropane, we obtain for the enthalpy of reaction and strain energy, −12.7 kcal/mol and 70 kcal/mol, respectively, in good agreement with their experimental counterparts,[19] −6.0 and 63 kcal/mol. The absolute errors of 7 kcal/mol are the same as for the cyclopropane case.

These results indicate the ability of the EBMO basis to account for the strain energies of both mono- and polycyclic strained ring systems. Somewhat lesser success is obtained with the MBMO basis, which gives 33 and 79 kcal/mol, for cyclopropane and bicyclobutane, respectively. On the other hand, the INDO method furnishes results which are quite erratic, being in error by 25 kcal/mol for cyclopropane and only 1 kcal/mol for bicyclobutane (essentially the same values are obtained in the CNDO method).

A more reliable semiempirical method for strain energies has been developed by Dewar and Baird.[20] For cyclopropane and bicyclobutane they obtained strain energies of 31 and 66 kcal, 1 and 3 kcal/mol better, respectively, than the *ab initio* results.

The calculations discussed so far have been based on experimental geometries. Since we wish to investigate some aspects of the bicyclobutane potential energy surface, it is of interest to see how well the experimental geometry can be predicted at the MBMO level. Of course, the extended basis would be preferable for a potential energy surface investigation, but we chose the MBMO basis for reasons of economy; it is probably adequate for the general features we wish to examine. Minimization of total energy with respect to geometries of cyclopropane, ethane, and bicyclobutane reveals that the MBMO basis slightly exaggerates CC equilibrium carbon–carbon bond lengths (R_{CC}). For ethane and cyclopropane, the calculated R_{CC} values are 1.59 and 1.55 Å, respectively, whereas the experimental values are 1.531[21] and 1.510.[22] For bicyclobutane we obtained (with microwave results[13] in parentheses): $R_{C_1C_3}$ = 1.53 (1.497), $R_{C_1C_2}$ = 1.55 (1.498), α_{HCC} = 135° (128°22′), ω (dihedral angle between cyclopropane planes) = 118° (121°40′).

The MBMO basis thus picks up relative trends adequately. The bicyclobutane side bonds are correctly found to be the same length as in cyclopropane, though the minute experimental shortening of the central bond is exaggerated. The relative sizes of α and ω are also obtained correctly.

Since a fair amount of steric crowding should be present in 1,3-disubstituted bicyclobutanes, it is of interest to examine the sensitivity of the total bicyclobutane energy to distortions of the HC_1C_3 angles. Opening these angles should not only relieve steric interactions, but would also most likely increase the π-electron character of the central bond. In Table IX we list the energies for a variety of HC_1C_3 angles, and dihedral angles as well. The total and π-electron contributions to the 1–3 overlap populations are also included. Several conclusions are apparent. Distortions of the HC_1C_3 angles, angles cost very little in energy; changes of ± 5° increase the energy by less than 1 kcal/mol and even an opening of 15° requires only 5 kcal/mol, an amount

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(17) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(18) The experimental value is based on the enthalpies, corrected to 0°K, quoted in ref 12b, and the strainless energy of 0°K, based on ref 17.

(19) Obtained for 0°K as described in ref 18, except for bicyclobutane, whose ΔH_f at 0°K (56.0 kcal/mol) was obtained from the 25° value (51.9 kcal/mol) given by K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).

(20) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); N. C. Baird, *Tetrahedron*, **26**, 2185 (1970). This method is based on ΔH_f values at 25°; however, strain energies vary little with temperature.

(21) D. E. Shaw, D. W. Lipard, and H. L. Welsh, *J. Chem. Phys.*, **42**, 3736 (1965).

(22) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, 17, 538 (1964).

Table IX. Energetics of Bridgehead Angular Distortion in Bicyclobutane (MBMO basis)[a]

Angles at bridgeheads				
$H_{brhd}C_1C_3$ bond angle (α), deg	Framework dihedral angle (ω),[b] deg	Total energy, kcal[c]	C_1C_3 overlap population Total	π electron[d]
130.4	117.6	0.6	0.363	0.075
135.4	107.6	1.8	0.405	0.078
	117.6	0.0	0.381	0.087
	127.6	4.4	0.355	0.096
140.4	117.6	0.6	0.396	0.099
150.4	107.6	8.9	0.440	0.108
	117.6	5.9	0.416	0.120
	127.6	12.7	0.390	0.134

[a] Based on a value of 1.55 Å for all CC bond lengths. [b] Dihedral angle defined by two C_3 rings. [c] Energies given in kcalories, relative to that for the near-equilibrium values, α = 135.4° and ω = 117.6°. [d] The π-electron contribution is that arising from the bridgehead $2p_x$ orbitals (*i.e.*, those directed parallel to the C_2 axis).

which could be at least partially regained by resonance coupling in the case of unsaturated 1,3 derivatives. Supporting this, the opening of the HCC angles is found to increase the C_1–C_3 π electron (and also total) overlap population. Distortion of the dihedral angle is somewhat more costly, but still the angle is quite soft. Changes of ± 10° require only ~5 kcal/mol.

Another class of distortions of interest in bicyclobutane are those related to its thermal conversion to butadiene.[23] Although a detailed study of the reaction pathway was not our principal concern here, we have examined the process of equal stretching of the C_1C_2 and C_3C_4 bond while maintaining equilibrium values for the other CC bonds and the dihedral angle ω. Increases of 0.2 Å from equilibrium cause the total energy to rise sharply by 27 kcal/mol; however, the effect of simultaneous rotation of the methylene groups is, as yet, unknown.

Let us now consider briefly the energetics of 1,2 and 1,3 diradicals obtained by breaking the side and central bonds, respectively. Employing unrestricted single configuration triplet wave functions (EBMO) as our models for diradical states, we have found that the lowest triplet state ($^3B_1$) at the ground state equilibrium geometry lies 6.3 eV above the ground state. In contrast, for a square planar geometry with the same CC side-bond lengths, the triplet ($^3B_1$) drops to within 19 kcal/mol of the ground state at equilibrium. We have no value for the activation energy for this process, and also note that the value of 19 kcal may be somewhat low, since our basis overestimates strain energies and underestimates the correlation energy of the singlet ground state relative to that of the diradical state. However, an interesting comparison can be made with the energy of a 1,2-diradical which is obtained by expanding the C_1C_2 bond until the $C_1C_3C_2$ bond angle reaches 110°, keeping the dihedral angle ω and the other CC bond lengths fixed and allowing the CCH_2 moiety to become planar. This structure leads to a triplet energy 34 kcal/mol above the ground state at equilibrium. Thus, the 1,2-diradical appears to be less stable than the 1,3. Conclusive verification must await a more thorough study of the bicyclobutane potential energy surface.

Discussion

The most striking feature of the electronic structure of bicyclobutane is the $sp^{24.3}$ hybridization of the central bond, which corresponds to 96% p character. For comparison, the MBMO basis gives for cyclopropane the CC hybrid

$$\phi = 0.3862(2s)_C + 0.8239(2p\sigma)_C + 0.4143(2p\pi)_C$$

equivalent to $sp^{5.69}$ or 86% p character.

It is interesting to compare these MBMO bicyclobutane and cyclopropane results with those of the maximum overlap method.[24,25] For cyclopropane the CC hybrids obtained by the two procedures are quite similar to each other and also to the valence bond values. In the case of bicyclobutane, however, the unconstrained[26] maximum overlap method leads to a model characterized by fairly conventional hybridization values (ranging from $sp^{1.5}$ to $sp^{4.9}$) and almost equal side and central bond orders. This picture is at variance with the results of both the *ab initio* and semiempirical SCF calculations reported here, all of which converged to wave functions exhibiting twisted bonds with very different side and central bond overlap populations, as well as unusual hybridization at the bridgehead carbons. Since our SCF calculations yield reliable values for dipole moment, spin–spin coupling constants, and equilibrium geometry, we view our bonding model as preferable to that obtained from the maximum overlap method. This suggests that the maximum overlap criterion may not always be satisfactory for highly strained rings.

One important difference between the LCAO–MO and maximum overlap methods is that the former does not require hybrids on the same center to be orthogonal, and this allows them to range rather more widely. It is interesting to note that the CH hybridizations are predicted well by either method. Finally, Table IV indicates that the INDO hybrids are in good agreement with the MBMO results, though the CC hybridizations of the former have somewhat less p character and are more akin to the traditional values.

The *ab initio* method is seen capable of providing adequate geometries and strain energies for bicyclobutane. It has also yielded some interesting preliminary results on the potential energy surface. The softness of the $H_1C_1C_3$ angle indicates that steric hindrance to attack of the central bond from above may not be very great and that the inability of bicyclobutane to undergo Diels–Alder addition may be largely electronic.[7] Similarly, the approach from above of metal ions which catalyze skeletal rearrangements appears quite possible. Finally, the ease in opening this angle and the attendant increase in C_1–C_3 π character are also in accord with the

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(23) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(24) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963).

(25) Z. Maksić, L. Klasinc, and M. Randić, *Theor. Chim. Acta*, **4**, 273 (1966).

(26) By constraining the side-bond hybrids to lie in the plane of the cyclopropane rings, Maksić, *et al.*,[25] obtained the hybridizations: C_1–C_3, sp^{10}; C_1–C_2, $sp^{4.78}$–$sp^{5.10}$, which are quite close to those given in Table IV. However, disparate bond orders, 0.4595 and 0.6082 for the central and side bonds, respectively, led them to relax the constraint, with a resulting model which exhibited twisted side bonds, almost equal side and central bond orders, more conventional hybridizations, and a slightly (0.7%) increased overlap.

exo–endo isomerism of a 1,3-diphenylbicyclobutane.[27] The rearrangement need not involve noninteracting phenyl-stabilized radicals, but rather the activation energy might be lowered by the phenyls coupling with each other through a long π bond.

At the level of calculation employed here, the *ab initio* method may be of use in elucidating the mechanisms of bicyclobutane rearrangements. In later papers in this series we shall apply the method to a number of strained systems, and, in particular, to the interesting propellane[28] series.

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(27) R. B. Woodward and D. L. Dalrymple, *J. Amer. Chem. Soc.*, **91**, 4612 (1969).

(28) D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1969).

Theoretical Studies of Tricyclo[1.1.1.$0^{1,3}$]pentane and Bicyclo[1.1.1]pentane[1a]

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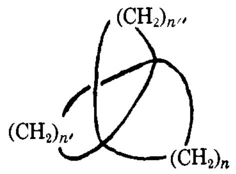
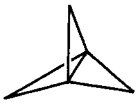
Abstract: We have carried out *ab initio* molecular orbital studies on [1.1.1]propellane and the related system bicyclo[1.1.1]pentane. For the former in D_{3h} symmetry we calculate normal side bond lengths of 1.53 Å and a distance between bridgehead carbons of 1.60 Å. The analogous bridgehead–bridgehead distance in bicyclo[1.1.1]pentane is calculated to be 1.885 Å, in agreement with the X-ray value of its urethane derivative. The [1.1.1]propellane has a negative total overlap population between bridgehead carbons, and its charge density contours in that region resemble those of bicyclopentane. The localized orbital corresponding to the central bond has −0.002 overlap population between centers and is formed from sp^4 hybrids directed *away* from each other. Thus, no evidence for a central bond is found in terms of the charge distribution, although the bond length of 1.60 Å is significantly shorter than the corresponding nonbonded distance of 1.89 Å in bicyclo[1.1.1]pentane. Calculated triplet energies indicate that diradical states lie well above the closed-shell singlet ground state. The long-range spin–spin coupling constant between the two bridgehead protons in bicyclo[1.1.1]pentane, as calculated by the INDO finite perturbation method, is within a few hertz of the unusually large experimental value, 18 Hz (being somewhat dependent on the value chosen for interbridgehead distance), thus suggesting that the phenomenon can be accounted for adequately by the Fermi contact term. The *ab initio* equilibrium HCH angle for the methylene groups in bicyclopentane (111°) lies slightly outside the experimental uncertainty in the electron diffraction value (104 ± 5°), as is also the case for the interbridgehead distance.

The propellanes[2] of general structure I are a set of tricyclic hydrocarbons whose three rings are fused to a common carbon–carbon bond. These molecules, which may be regarded as hexasubstituted ethanes, are probably quite normal hydrocarbons for large $\{n\}$. However, as the three rings are reduced in size to the limiting case $n = n' = n'' = 1$ a number of intriguing, highly strained ring systems are evolved.[3]

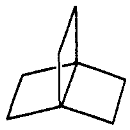


I

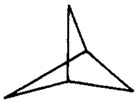
Thus, tricyclo[1.1.1.$0^{1,3}$]pentane (II), known more simply as [1.1.1]propellane,[2] would, with the structural formula taken literally, contain four carbon–carbon bonds to the molecule side of a plane containing the bridgehead carbon. Similarly, [2.2.2]propellane (III) would be anticipated to contain three coplanar carbon–carbon bonds 120° apart (we eschew the term trigonal as it implies sp^2 hydridization) and a fourth axial bond.[4] Although neither of these molecules is known, several



II



III



IV

(1) (a) An initial account of this work is given in the Abstracts of the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 25–30, 1971; (b) Brookhaven National Laboratory; (c) Polytechnic Institute of Brooklyn; Alfred P. Sloan Fellow.

(2) D. Ginsburg, *Accounts Chem. Res.*, 2, 121 (1969).

(3) A general survey of the propellanes has been made by W.-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 778 (1972).

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