The Electronic Structure and Reactivity of Small Ring Compounds. I. Bicyclobutane

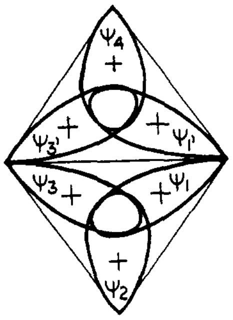
Martin Pomerantz and E. W. Abrahamson

Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106. *Received April 28, 1966*

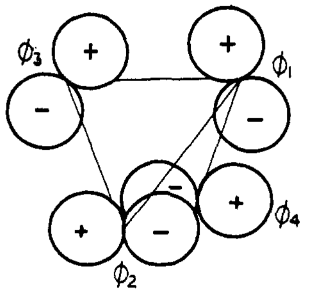
Abstract: Two models for the electronic structure of the bicyclobutane ring system are suggested and correlated with known chemical and physical properties. Both models introduce π character into the peripheral and bridgehead bonds, employing sp^2-hydridized carbon for the methylene groups. One model uses sp^2- and the other sp-hybridized bridgehead carbon atoms.

Many small ring compounds have chemical and physical properties which make their description by the sp^3 "bent bond" model questionable. Some years ago Walsh[1] offered an alternate molecular orbital description for cyclopropane which in large measure accounted for its "ethylenic" chemistry. But it is only recently that substantial support for the Walsh model has been provided by measurements of C_{13}–H spin–spin coupling constants and their correlation with s character of C–H bonds.[2] This raises the question of whether adequate molecular descriptions of a host of similar strained ring compounds such as bicyclobutane, tetrahedrane, and cubane might be similarly given. In this paper we shall confine our attention to bicyclobutane. An examination of its reported physical and chemical properties[3,4] suggests that a proper electronic description might lie somewhere between the two limiting molecular orbital descriptions, here designated as models I and II. The models suggest other chemical properties which we have correlated with those given in the literature.

Electronic Structure. On the basis of infrared and Raman spectral data, Haller and Srinivasan[3] conclude that bicyclobutane has C_{2v} symmetry with essentially equilateral triangular rings having one common edge. The interplanar angle they reckon as 126 ± 3° and the bridgehead $\mathrm{H}\diagdown_{\mathrm{C-C}}$ angle as 163 ± 3°. With this picture in mind model I is constructed in the following way: σ molecular orbitals are formed by a three-center overlap of carbon sp^2 hybrid orbitals at the center of the plane of each three-membered ring, the bridgehead carbons each providing two such orbitals, one for each plane, and the methylene carbons providing one (model Ia). A set of six composite orbitals results, of which only two have a net bonding character.



Ia



Ib

Degenerate bonding

$$\sigma_{1a_1} = \sqrt{{}^1/_6}(\psi_1 + \psi_2 + \psi_3 + \psi_1' + \psi_3' + \psi_4)$$

$$\sigma_{1b_1} = \sqrt{{}^1/_6}(\psi_1 + \psi_2 + \psi_3 - \psi_1' - \psi_3' - \psi_4)$$

Degenerate antibonding

$$\sigma_{2a_1} = \sqrt{{}^1/_{12}}(\psi_1 - 2\psi_2 + \psi_3 + \psi_1' + \psi_3' - 2\psi_4)$$

$$\sigma_{2b_1} = \sqrt{{}^1/_{12}}(\psi_1 - 2\psi_2 + \psi_3 - \psi_1' - \psi_3' - 2\psi_4)$$

$$\sigma_{1a_2} = {}^1/_2(\psi_1 - \psi_3 - \psi_1' + \psi_3')$$

$$\sigma_{1b_2} = {}^1/_2(\psi_1 - \psi_3 + \psi_1' - \psi_3')$$

Like the Walsh model for cyclopropane, the regions of maximum σ-electron density lie at the centers of the two rings.

In a similar way four orbitals, largely π in character, can be constructed from the unhybridized carbon 2p orbitals (Ib). If we assume that the adjacent carbon overlap integrals are all equal, then two of these π orbitals will have a net bonding character; one will be nonbonding and one antibonding.

Bonding

$$\pi_{1b_2} = 0.557(\phi_2 - \phi_4) + 0.435(\phi_1 - \phi_3)$$

$$\pi_{1a_1} = \sqrt{{}^1/_2}(\phi_1 + \phi_3)$$

Nonbonding

$$\pi_{1a_2} = \sqrt{{}^1/_2}(\phi_2 + \phi_4)$$

Antibonding

$$\pi_{2b_2} = 0.435(\phi_2 - \phi_4) - 0.557(\phi_1 - \phi_3)$$

In contrast to the σ case, the π-electron density is largely distributed in the peripheral regions and between the bridgehead carbons. The electronic structure of the ground state of model I is then logically given as

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

A second model (II) can be formulated which gives a much more pronounced π character to the bridgehead carbon–carbon bond. In this case a set of σ orbitals are constructed from the four-center overlap of one sp^2 orbital from each methylenic carbon and an sp orbital

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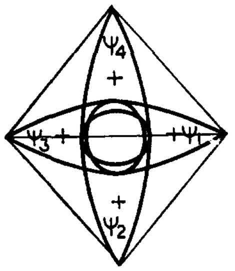
[1] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

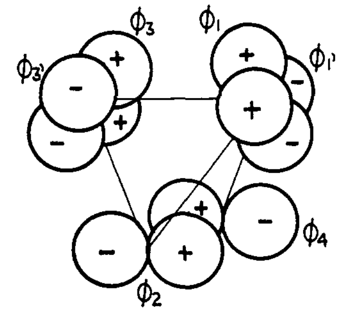
[2] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

[3] I. Haller and R. Srinivasan, *ibid.*, **41**, 2745 (1964).

[4] K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavnaish, *Tetrahedron*, **21**, 2749 (1965).



IIa



IIb

from each bridgehead carbon atom (IIa). The region of maximum overlap in this case lies between the two planes of the three-membered rings. If we assume the sp and sp^2 coulomb integrals to be equal and all overlap integrals likewise are assumed equal, then four σ orbitals can be constructed of which only one is bonding.

Bonding

$$\sigma_{1a_1} = {}^1/_2(\psi_1 + \psi_2 + \psi_3 + \psi_4)$$

Antibonding

$$\sigma_{2a_1} = {}^1/_2(\psi_1 - \psi_2 + \psi_3 - \psi_4)$$

$$\sigma_{1b_1} = \sqrt{{}^1/_2}(\psi_2 - \psi_4)$$

$$\sigma_{1b_2} = \sqrt{{}^1/_2}(\psi_1 - \psi_3)$$

Similarly π orbitals are constructed from the single 2p orbitals on the methylenic carbons and from the pair of 2p orbitals on each bridgehead carbon (IIb).

Degenerate bonding

$$\pi_{1a_2} = 0.557(\phi_2 + \phi_4) + 0.435(\phi_1' + \phi_3')$$

$$\pi_{1b} = 0.557(\phi_2 - \phi_4) - 0.435(\phi_1 - \phi_3)$$

Degenerate bonding

$$\pi_{1a_1} = \sqrt{{}^1/_2}(\phi_1 + \phi_3)$$

$$\pi_{1b_1} = \sqrt{{}^1/_2}(\phi_1' - \phi_3')$$

Degenerate antibonding

$$\pi_{2a_2} = 0.435(\phi_2 + \phi_4) - 0.557(\phi_1' + \phi_3')$$

$$\pi_{2b_2} = 0.435(\phi_2 - \phi_4) + 0.557(\phi_1 - \phi_3)$$

The probable electronic configuration for the ground state of model II is therefore

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

The distinguishing feature of both models as compared to the bent-bond descrption is the π character which, though delocalized, is particularly manifest in the bridgehead bond. One can describe this bond in model I as essentially "ethylenic" and in model II as "acetylenic," but it has some antibonding character in both descriptions. Significantly, both models I and II predict the bridgehead bond to be stronger than the peripheral carbon bonds.

Physical and Chemical Properties. We shall now examine the extent to which the physical and chemical properties support the above models. First of all, the π character of the bridgehead bond is quite clearly indicated by the ultraviolet spectrum of methyl 3-methylbicyclobutane-1-carboxylate which bears a strong resemblance to that of an α,β-unsaturated ester.[4] Furthermore, bridgehead-substituted diphenyl derivatives have spectra suggesting conjugative interaction between the two phenyl groups.[5–7]

A quite compelling piece of supporting evidence for models I and/or II is the thermal rearrangement of bicyclobutane to butadiene. This occurs with an activation energy of 40.6 kcal/mole.[8] By the bent-bond description, the bridgehead bond would be expected to be thermally the most labile. Both models I and II, on the other hand, show it to be the strongest. Clearly then, thermal lability should lie in the peripheral bonds, consistent with the path of the thermal rearrangement. A number of other examples of this type of rearrangement are known.[9–14]

There are a number of other experimental observations which substantiate the π character of the bicyclobutane ring system. Carbenes, which, for some time, have been known to add to carbon–carbon multiple bonds but not to carbon–carbon single bonds, add to the bridgehead 1,3 bond in bicyclobutanes. In the cases studied, the major products appear to be derived from a diradical intermediate.[4,9] For example, the addition of methylene to bicyclobutane gives a substantial amount of 1,4-pentadiene and a much smaller yield of bicyclo[1.1.1]pentane. Reaction of 1,3-dimethylbicyclobutane with methylene has been shown not to proceed through a bicyclo[1.1.1]pentane. With dideuteriomethylene the product is 2,4-dimethyl-1,4-pentadiene containing all of the deuterium at the 1 and 5 positions.

The rapid, uncatalyzed addition of halogens is well known in the chemistry of carbon–carbon multiple bonds but not in the chemistry of saturated compounds. Bicyclobutane and many derivatives have been shown to add halogen molecules, the initial addition being to a bridgehead carbon atom. In most cases the product results from 1,3 addition,[4,5,9,13] but there is an example of 1,2 addition.[4] Bicyclobutane reacts rapidly with iodine and bromine to give 1,3-dihalocyclobutanes, but with chlorine the product is 1-chloromethyl-2-chlorocyclopropane.[4]

Another reaction type characteristic of unsaturated systems is the addition of an acid molecule HX. Bicyclobutane and derivatives react with various acids to give either cyclobutyl compounds, from 1,3 addition, or cyclopropylcarbinyl compounds, from 1,2 addition, and, in one case, an allylcarbinyl derivative. In all cases the proton appears to add first to the bridgehead carbon atom.[4,9,14]

Mild catalytic hydrogenation, again generally associated with unsaturated systems, proceeds smoothly

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(5) S. Masamune, *Tetrahedron Letters*, 945 (1965).

(6) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).

(7) A. M. Small, *ibid.*, **86**, 2091 (1964).

(8) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965).

(9) W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters*, 991 (1965).

(10) J. P. Chesick, *J. Phys. Chem.*, **68**, 2033 (1964).

(11) W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 961 (1964).

(12) A. M. Small, *J. Am. Chem. Soc.*, **86**, 2091 (1964).

(13) W. Mahler, *ibid.*, **84**, 4600 (1962).

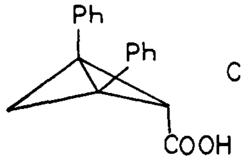
(14) E. P. Blanchard, Jr., and A. Cairncross, *ibid.*, **88**, 487 (1966).

with bicyclobutanes. The products usually result from rupture of one or two bonds.[4,6,9,11,15–18]

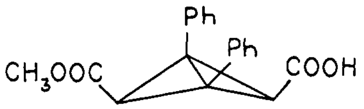
α,β-Unsaturated carbonyl compounds and nitriles have long been known to add nucleophiles to the terminus of the double bond. Once again the unsaturation in bicyclobutane is evidenced by the addition of a number of nucleophiles, such as hydroxide ion, methoxide ion, ammonia, and water, across the central bond in 3-methylbicyclobutanecarbonitrile. The product in these cases is the 3-substituted 3-methylcyclobutanecarbonitrile.[14]

Free radicals have also been shown to add across the 1,3 bond in this compound.[14]

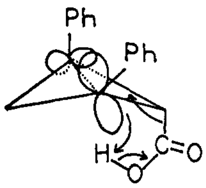
An extremely interesting reaction, reported by Masamune,[5] is the ready decarboxylation of compound III as compared to the relative stability of compound IV, having an *exo*- rather than an *endo*-carboxyl group. Both models I and II contain a p orbital at C-1 in the proper orientation to remove the proton from the *endo*-carboxyl group (V). This type of interaction is precluded for the *exo*-carboxyl group. The observed stereochemistry for the reaction agrees with this scheme.



III



IV



V

Since our models ascribe "olefinic character" to the central bond, it is perhaps surprising that there are no examples of a bicyclobutane reacting with a diene in a "Diels–Alder" type reaction. Instead, "cycloaddition" occurs with 3-methylbicyclobutanecarbonitrile and butadiene and a number of other olefins. It appears that these reactions occur by a two-step process and not by a concerted one since both fumaronitrile and maleonitrile give bicyclo[2.1.1]hexane products which have partially lost stereochemical integrity.[19]

In addition, one of the products of the reaction of benzyne with bicyclobutane appears to be benzobicyclo[2.1.1]hexene, formed by cycloaddition.[20] The similarity to an olefin system is apparent.[21]

It is interesting that the overlap of p orbitals 1 and 3 in both models is net bonding in the ground state and is antibonding in the first excited π^* state, quite similar, once again, to an olefin. Thus, it is not surprising that the 2 + 2 cycloaddition appears not to be concerted.[22]

The question of which model better describes bicyclobutane is, perhaps, best answered by reference to the C_{13}–H spin–spin coupling constants for the bridgehead C–H bond. Forty per cent s character in the carbon hybrid orbital is predicted from the measured constant of 202 cps which places the electronic configuration close to model I.[23] However, the substantial sp-hybrid character of the bridgehead carbon–hydrogen bond, characteristic of model II, is borne out by the acidic nature of the bridgehead hydrogen, a fact demonstrated by its ready removal with methyllithium.[17,25]

The models suggest a number of physical and chemical properties for bicyclobutane and its derivatives which are currently being investigated here.

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(15) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).

(16) D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 3231 (1964).

(17) J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).

(18) A. F. Vellturo and G. W. Griffin, *ibid.*, **87**, 3021 (1965).

(19) E. P. Blanchard, Jr., and A. Cairncross, *ibid.*, **88**, 496 (1966).

(20) M. Pomerantz, results to be published.

(21) See, *e.g.*, H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961); J. A. Berson and M. Pomerantz, *ibid.*, **86**, 3896 (1964).

(22) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(23) The C^{13}–H coupling constant for the bridgehead hydrogen of various bicyclobutanes varies between 200 and 212 cps, 40–42% s character.[4,24,25]

(24) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 2022 (1963).

(25) G. L. Closs and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965).