Tetrahedron, 1963, Vol. 19, pp. 1539 to 1546. Pergamon Press Ltd. Printed in Northern Ireland

THE MO THEORY OF BENT BONDS IN STRAINED CYCLIC HYDROCARBONS

DAVID PETERS
Royal Holloway College, Englefield Green, Surrey, England

Abstract—It is shown that it is possible to describe both the CC and the CH bonds of strained cyclic hydrocarbons in terms of localized orthogonal MOs which are built from low principal quantum number AOs of the atoms. The results agree surprisingly well with Coulson and Moffitt's VB calculation. The CC bonds of cyclopropane are extensively bent and their carbon hybrid AOs contain very little of the 2s AO. The CH bonds of cyclopropane resemble those of ethylene. The CC bonds of cyclobutane are also slightly bent and their carbon hybrid AOs contain less of the 2s AO than do those of an unstrained paraffin.

The results support Walsh's general contention that the electrons of the CC bonds of cyclopropane are responsible for the olefin-like properties because these electrons are similar to the π electrons of olefins in that they inhibit AOs which are much closer to pure 2p AOs than are the 2s containing hybrid AOs which carbon uses in unstrained CC bonds.

INTRODUCTION

SOME years ago, Coulson and Moffitt[1] discussed the nature of the bonding in the strained saturated cyclic hydrocarbons cyclopropane and cyclobutane. They used Valence Bond (VB) Theory and the approximation of perfect pairing. As a result of these assumptions, it is possible to write the total energy of a cyclic saturated hydrocarbon in terms of one hybridization parameter, h or h^2, and a number of integrals whose values may be taken from analogous calculations on simpler systems. Then, by minimizing the total energy with respect to the parameter, it is possible to get an estimate of the total energy of the system, of the value of the hybridization parameter and of the degree of bond bending. The method is rather complicated, and even now there is little numerical evidence as to the reliability of the assumptions which were used, but their results seemed sensible. Work of this kind rests directly on the assumption that the hybrid AOs(HAOs) which the carbon atom uses in the molecule are orthogonal. This was (and is) a common assumption, but it is now realized[2] that it may be less safe than was once thought. The details of Coulson and Moffitt's results are discussed in the main body of this text.

It is natural to ask whether it is possible to give an analogous discussion in terms of the visually simpler and now much better understood MO Theory. Straightforward energy minimization calculations for such molecules are not yet possible because they are too big to be handled in the detailed SCF LCAOMO theory and because there are no analogous molecules on which to base parameter choices in a more empirical theory.* Some preliminary progress can be made if the methods used in a

---

* Handler and Anderson earlier[3] suggested that the two HAOs of one carbon atom, which are used to form two CC bonds from this atom, are non-orthogonal. In the case of cyclopropane, these two HAOs are then so far from orthogonal (overlap integral of $\frac{5}{8}$) that serious and presently unresolved questions and difficulties about the internal energy of the atom in the molecule are raised. By an apparently lucky chance, the present method avoids this difficulty. Handler and Anderson also require a value of the MO parameter β in an unusual situation. It is quite impossible to say what the value of this parameter will be in the situation they envisage.

[1] C. A. Coulson and W. E. Moffitt, *Phil. Mag.* **40,** 1 (1949).

[2] D. Peters, Symposium on the Status of Quantum Chemistry in the Interpretation of Organic Chemistry, *Tetrahedron* **19,** Suppl. 2, 143 (1963).

[3] G. S. Handler and J. A. Anderson, *Tetrahedron* **2,** 345 (1958).

previous paper[2] to deal with unstrained hydrocarbons can be extended to handle the bent bond situation in strained cyclic hydrocarbons. The general method, which is essentially a stop-gap measure until SCF LCAOMO wave functions can be obtained, is an MO parallel to Pauling's idea[4] in VB theory that the HAOs of an atom should be taken orthogonal. It is now assumed that the σ electrons can be represented by localized two electron bonds and that these in turn can be represented by localized, orthogonal, MOs (BMOs) which are built from low principal quantum number AOs of the constituent atoms of the molecule.* Then the orthogonality condition on the localized MOs, together with some simple electronegativity arguments where necessary, is often sufficient to determine completely the localized MOs.[2] An analysis of some Slater AO SCF LCAOMO wave functions for some small molecules originally suggested these assumptions[5] and so may be said to provide some justification for them.

Method. The earlier work[2] showed that, if the bonds are taken to be straight, it is not possible to deal with internuclear angles of less than 100°. It is a question then of whether this approach can be used for bent bonds. There seems to be no *a priori* reason why it should not and the point is explored numerically in this paper. As an example, if we think of the CC bonds of cyclopropane, all three are equivalent and they are to be represented by localized orthogonal MOs. These bonding MOs(BMOs) between atoms a and b, say, are written

$$\mu_{ab} = hy_a'(b) + hy_b'(a) = N[h(2s_a) + (1 - h^2)^{1/2}\{2p\sigma_a'(b)\} + h(2s_b) + (1 - h^2)^{1/2}\{2p\sigma_b'(a)\}]$$

where N is a normalizing constant and symbols such as $2p\sigma_a'(b)$ denote a $2p\sigma$ AO on atom a pointing in the *general direction* of atom b. The AO does *not* in general have its angular maximum along the ab internuclear line. This is the distinction from the usual $2p\sigma$ AO which is conveyed by the prime.

If the internuclear distance and the internuclear angle (2θ) are taken as fixed, there remains undetermined only the interhybrid angle ($2\theta + 2\alpha$) and the hybridization parameter, h^2. The orthogonality condition between adjacent CC bonds then provides a relationship between these two unknowns. Then if either of the unknowns can be fixed by another argument, the form of the BMOs becomes fixed, and the wave function is determined, in part at least, without appeal to energy minimization. When the BMOs are not homopolar (CH bonds, for example) an additional parameter enters and three unknown parameters would arise. Fortunately, there is no reason to suspect that CH bonds are bent so the problem does not arise with hydrocarbons. Only the 2s and the 2p AOs of the carbon atoms are considered and these are

---

* It is usually supposed that there is some small interaction between localized bonds to account for the departures from additivity of such physical properties as the bond strengths. This idea is intuitively attractive, but it is very difficult to provide a firmer justification for it. The real difficulty is that we do not know what the localized bonds themselves are, and in particular, we do not know that ostensibly identical bonds do not vary appreciably from molecule to molecule. It may be possible to account for the departures from additivity by supposing that the bonds do vary somewhat in different molecules.

[4] L. Pauling, *The Nature of the Chemical Bond* Chap. IV. Cornell University Press, New York (1960).

[5] D. Peters, *J. Chem. Soc.* In press.

represented by Slated AOs.* The geometrical situation for the equivalent CC bonds of a cyclic paraffin is shown in Fig. 1.

The results appear in the form of a relationship between the bending angle, α, and the hybridization parameter, h^2, which must be satisfied if orthogonal localized BMOs are to exist. The results for various internuclear distances and angles are shown in Figs 2, 3 and 4 and it is easy to interpolate for any other distance or angle which is likely to be required. As a rough working rule, it may be said that the amount of 2s character (h^2) in the HAOs of the CC bonds increases by 1 to 2% for a 2° increase in the interhybrid angle (increase of 1° in α). There is also shown on the Figs the overlap integral between the two HAOs which together form a CC bond (to the right of the lines) and the non-orthogonality integral between the two HAOs of one carbon atom (to the left of the lines). Using these Figs as a starting point, some individual compounds can be examined.

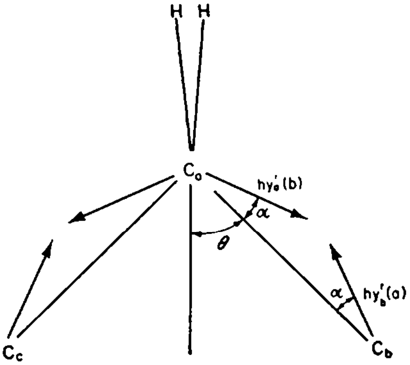

FIG. 1[a]. Geometry of equivalent CC bonds in a cyclic hydrocarbon
[a] cf. equations in text. The arrows denote the lines of maximum value of the angular factors of the hybrid AOs.

Cyclopropane

(a) *The* CC *and* CH *Bonds*. The CC bond length in chloro- and cyano-cyclopropanes is variously estimated[8] at 1·51 to 1·53 Å so Fig. 4 will be sufficiently accurate. It is clear from this Fig that the CC bonds must be bent by at least 21° ($\alpha = +21°$) before it is possible to construct the required BMOs. It seems unlikely that the bond bending will exceed 25° since this gives the tetrahedral angle between the two HAOs of a carbon atom, so the degree of bond bending is fixed at 21 to 25°. This in turn fixes the amount of 2s character in the carbon HAOs(h^2) at 0 to 4%. Coulson and

---

* It is likely that the use of Slater AOs, rather than the true (but unknown) AOs which the atom uses in the molecule, is the weak point of the method. The use of Hartree Fock AOs[6] or, better still, a splitting of the basis functions into a linear combination of Slater type AOs[7] would be an improvement.

[6] H. Kaplan, *J. Chem. Phys.* **26**, 1704 (1957): A. M. Karo and L. C. Allen, *Ibid.* **31**, 968 (1959): L. C. Allen, *Ibid.* **37**, 200 (1962).

[7] E. Clementi, *J. Chem. Phys.* **36**, 33 (1962): R. K. Nesbet, *Ibid.* **36**, 1518 (1-62).

[8a] J. P. Friend and B. P. Dailey, *J. Chem. Phys.* **29**, 577 (1958): [b] Hs. H. Gunther, R. C. Lord and T. K. McGubbin, *Ibid.* **25**, 768 (1956): [c] W. H. Flygarde, A. Narath and W. D. Gwinn, *Ibid.* **36**, 200 (1962).

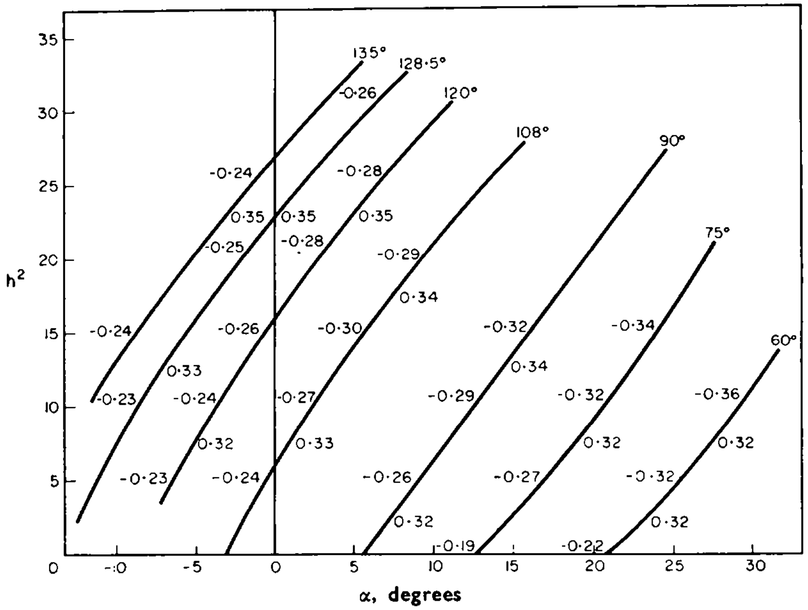

FIG. 2 (1·30 Å). Relationship between the bending angle (α) and the hybridization parameter (h^2) for adjacent, equivalent CC bonds of length 1·30 Å in a cyclic hydrocarbon. The internuclear angle (2θ) is given at the top of the lines.

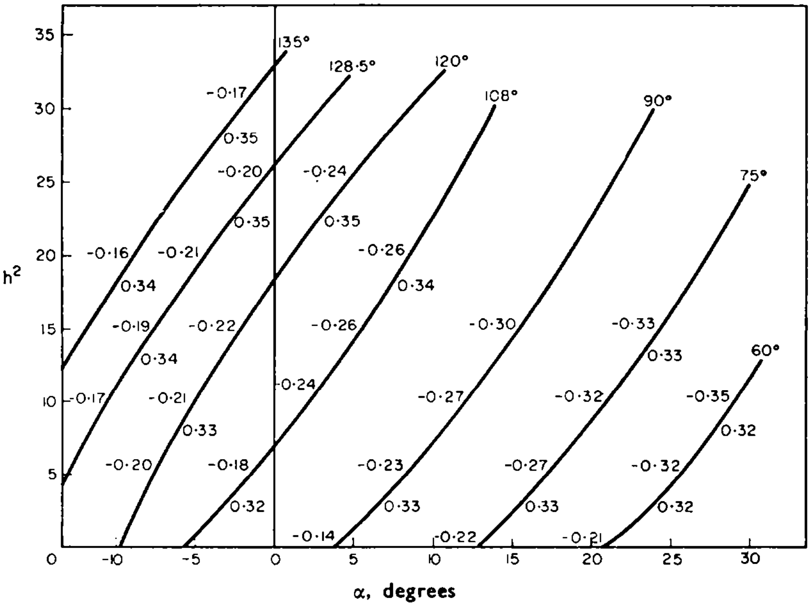

FIG. 3 (1·40 Å).[a]

[a] cf. heading of Fig. 2 with CC bond length of 1·40 Å.

Moffitt's figures are 22° for the angle and 20% for the value* of $\bar{h}^2$. The perfect angle agreement is no doubt partly fortuitous, but there is good agreement on the two essential points: (1) that the CC bonds are markedly bent and (2) that the carbon HAOs contain less of the 2s AO than do those of unstrained paraffins (20% versus 25% in the VB theory[1] and 0 to 4% versus 13% in the MO theory[2]). In fact, as a first approximation, the localized bent CC bonds of cyclopropane may be thought of as made up from pure 2p AOs. It is also interesting that the non-orthogonality integral between the two HAOs of one carbon atom is —0·21 to —0·26, the same value as was found in unstrained systems.[2] This result may be interpreted to mean that the internal energy of the atom is not affected by the bending and that the strain energy is taken up in the gross bond energy[9] rather than in the energy of the atom in the molecule.

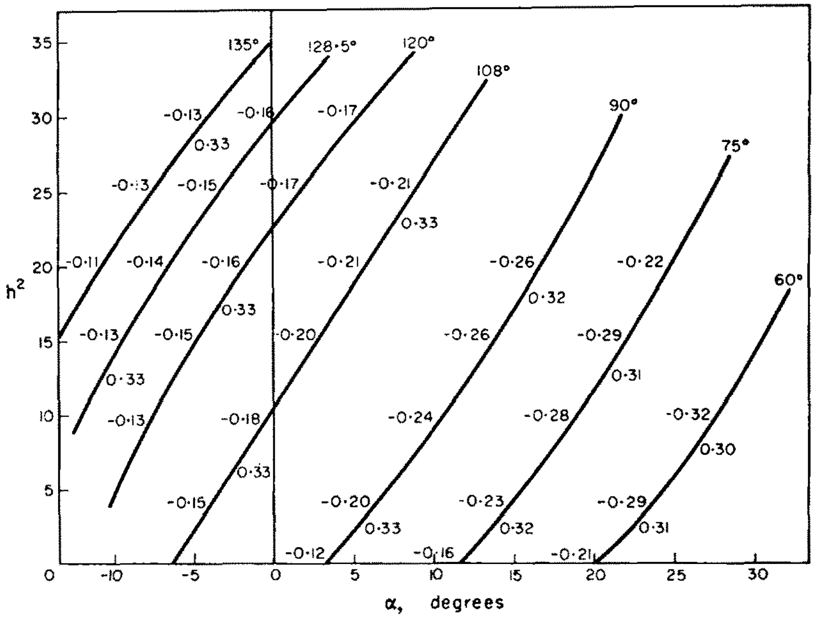

FIG. 4 (1·54 Å).[a]

[a] cf. heading of Fig. 2 with CC bond length of 1·54 Å.

The CH bonds of cyclopropane are more difficult to deal with for two reasons. First, there is some doubt as to the experimental values[8] of their bond lengths (1·085 Å and 1·105 Å have been reported), although there is agreement that the HCH angle is 115° to 116°, very close indeed to that in ethylene.[10] The CH stretching frequencies are also close to those of ethylene[8b,11] and the proton-C^{13} coupling in the CH bonds of cyclopropane can be interpreted[12] as showing that they are like the ethylene CH

---

* $\bar{h}$ or $\bar{h}^2$ refers to the hybridization required in the VB theory. When the bar is omitted, the hybridization refers to the MO theory. There is no reason to suppose that the hybridizations required in the two theories need be the same.

[9] R. S. Mulliken, *J. Phys. Chem.* **56**, 305 (1952).

[10] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **31**, 400, 826 (1959).

[11] J. W. Linnett, *Nature, Lond.* **160**, 162 (1947).

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

[13] J. W. Knowleton and F. D. Rossini, *J. Res. Nat. Bur. Stand.* **43**, 113 (1949).

bonds. These points may be taken as evidence that 1·085 Å is more likely to be correct for the cyclopropane CH bond length, since the ethylene CH bond length is[10] 1·084 Å. Second, there are two different orthogonality requirements which may be imposed on the BMOs of the CH bonds. These are (1) the mutual orthogonality of the two CH BMOs and (2) the orthogonality of the CH BMO to the CC BMO. The first condition leads to a useful relation connecting the hybridization in the carbon HAO with the polarity of the CH BMO. This is shown in Fig. 5. The second condition unfortunately leads to an equation which is not useful because its numerical results are very sensitive to small differences in the assumed geometry of the molecule This is an arithmetical accident similar to the ill conditioning of linear equations.

The best that we can say about the CH bonds of cyclopropane at the moment is that, if they are not bent (the C—Cl bonds of chlorocyclopropanes are straight[8c]), Fig. 5 suggests a hybridization (h^2) of 12 to 14% in the carbon HAO. This is consistent with a sensible choice of the polarity parameter[2] of 0·8 to 1·0 and with the idea that the CH bonds of cyclopropane are like those of ethylene (h^2 = 15% in the MO theory[2]). The VB theory[1] gives the same result ($\bar{h}^2$ = 30% in cyclopropane, $\bar{h}r^2$ = 33% in ethylene). Finally, it is expected that if the HAOs of the CC bonds contain very little of the 2s AO, those of the CH bonds will contain more than usual in an effort to keep the population of the 2s AO of the carbon atom at a reasonable value. This quantity is held fixed at unity in the VB theory but is variable in the MO theory.[2] Were this 2s AO population of the atom in the molecule too low, the energy of the atom in the molecule would be very high because such configurations of the carbon atom as $(1s)^2 (2p)^4$ would make substantial contributions to the atom in the molecule. All of these points do support the idea that the CH bonds of cyclopropane are indeed like those of the ethylene molecule.

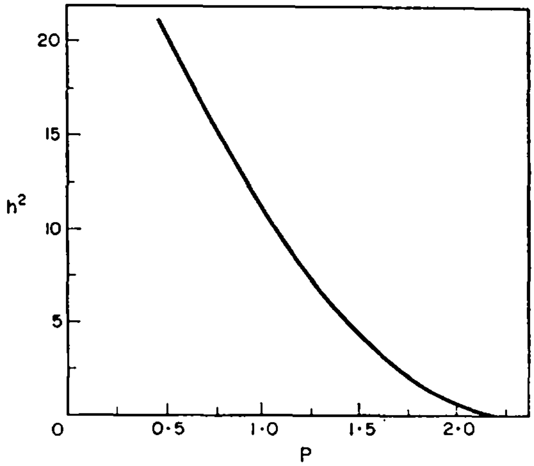

FIG. 5. Relationship between the polarity parameter, p, (cf. ref. 2) and the hybridization parameter (h^2) for the CH bonds of cyclopropane.

(b) *Energy quantities.* The energy of atomization of cyclopropane is 804 Kcals/mole.[13] The value of the so-called strain energy depends on what is taken for the hypothetical unstrained reference molecule.[14] If this is supposed to be made up of

---

[14] T. L. Cottrell, *The Strengths of Chemical Bonds* (2nd Edition) p. 243. Butterworths, London (1958).

three CH_2 units like those in the middle of a long chain paraffin, the strain energy is 36 Kcals/mole (contribution per CH_2 group to the atomization energy = 280·0 Kcals/mole). Alternatively, if the CH bonds of cyclopropane resemble those of ethylene and have much the same strength (~105 Kcals/mole[15]), then the strain energy in the CC bonds will be nearer to 60 Kcals/mole. Then the strengths of the individual CC bonds will be about 60 Kcals/mole, some 20 Kcals/mole smaller than that (~80 K cals/mole[14]) in an unstrained paraffin. It must be emphasized that there is at present no means of deciding what the exact values of these bond strengths are, nor is there any immediate prospect of carrying out computations sufficiently detailed to establish them firmly.

(c) *Unsaturation in cyclopropane.* It is well known[16] that many of the chemical and physical properties of cyclopropane resemble those of an olefin rather than those, of a saturated hydrocarbon. The ionization potential (10·1 eV) is about 1·0 eV lower than that of propane (11·1 eV) but higher than that of propylene (9·7 eV).[17] There is weak U.V. absorption[18] up to 1900 Å, while the unstrained paraffins absorb below about 1700 Å, and there is also evidence[19] of the type of spectral effects in the U.V. spectra of derivatives of cyclopropane which are usually associated with conjugation. A charge transfer complex exists between cyclopropane and iodine[20] and the occurrence of addition rather than substitution reactions[21] with halogens and halogen acids is also reminiscent of olefins.

These points led Walsh to suggest[16] that there are in cyclopropane weakly bound electrons which resemble the π electrons of an olefin. Coulson and Moffitt's results support this idea in a general way and the present results provide further confirmation since the localized MOs of the CC bonds* are formed from HAOs which are very close to pure 2p AOs. To discuss ionization potentials, UV spectra and conjugation effects, it is necessary in principle to transform the localized MOs into delocalized MOs of the correct symmetry (a'_1 and e' of D_{3h}).[1,22] Then these observables are, in a first approximation, properties of the e' MOs only. When this transformation is carried out, it is found that the HAOs of the delocalized MOs also contain very little of the 2s AO and, in particular, most of the available 2s character goes into the a_1 MO, leaving the e' MOs built from almost pure 2p AOs of carbon. This is probably the reason behind the failure[23] of Hall's ionization potential theory.[24] This theory deals correctly with the resonance terms in different hydrocarbons, but it assumes

---

* Like the earlier work,[1,16] the present results suggest that the CH bonds of cyclopropane are not involved in the unusual properties of the molecule in any direct way.

[15] C. A. Coulson, *Valence* p. 200. Clarendon Press, Oxford (1952).

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

[17] W. C. Price, R. Bralsford, P. V. Harris and R. G. Ridley, *Spect. Acta* **14**, 45 (1959); F. H. Field and E. A. Hinkle, *J. Chem. Phys.* **18**, 1122 (1950).

[18] P. Wagner and A. B. F. Duncan, *J. Chem. Phys.* **21**, 516 (1953).

[19] W. W. Robertson, J. F. Music and F. A. Matsen, *J. Amer. Chem. Soc.* **72**, 5260 (1950); E. M. Kosower, *Ibid.* **80**, 3266 (1958).

[20] S. Freed and K. M. Sancier, *J. Amer. Chem. Soc.* **74**, 1273 (1952).

[21] R. A. Raphael in *Chemistry of Carbon Compounds*, (Edited by E. H. Rodd) Vol. II. Elsevier, (1953).

[22] G. G. Hall and J. Lennard-Jones, *Proc. Roy. Soc.* **205A**, 371 (1951).

[23] J. L. Franklin, *J. Chem. Phys.* **22**, 1304 (1954).

[24] G. G. Hall, *Proc. Roy. Soc.* **205A**, 541 (1951); *Trans. Faraday Soc.* **49**, 113 (1953); G. G. Hall and J. Lennard-Jones, *Disc. Faraday Soc.* **10**, 18 (1951).

that the coulomb terms are constant in them. In cyclopropane, however, the coulomb term is abnormally small, because the ionization potential of a 2p electron is much smaller than that of a 2s electron,[25] so the theory gives too high a value (11·76 eV) for the ionization potential (10·1 eV) of the molecule.

The existence of low lying excited state in cyclopropane can also be understood in a general way as being due to the weakly bound CC electrons and the ability of the cyclopropyl group to conjugate more effectively than an alkyl group arises in the same way. Some detailed quantitative computations on this situation will be reported elsewhere.

Cyclopropene

There are too many unknown hybridization parameters in this molecule for a general treatment, but some comments are possible. The C=C distance (1·30 Å)[26] is shorter than that in ethylene (1·34 Å)[10] and this is no doubt due to the bending and shortening of the σ bond of the double bond in the same way that the CC bond of cyclopropane is shortened and bent. This allows the π electrons of the double bond to form a shorter and stronger bond and, as a result, the first ionization potential of cyclopropene (9·95 eV),[27] which is due to the π electrons, is high for an olefin of this general type (cyclopentene, 9·3 eV; MeCH=CHMe, 9·3 eV; MeCH=CH_2, 9·73 eV). This is an example of a resonance effect (increase in the MO parameter β) on an ionization potential.

Cyclobutane

The CC bond length in cyclobutane (1·548 Å) is slightly greater than that of a normal CC bond (1·53–1·54 Å) in an unstrained hydrocarbon.[28] Fig. 4 is then applicable. The amount of bond bending is not less than 4° ($\alpha = +4°$) and will presumably not be greater than 10° since this produces the tetrahedral angle of the HAOs at the carbon atom. The corresponding hybridization range is 0 to 8% of 2s character (h^2) in the HAOs of carbon. Coulson and Moffitt[1] found 9° for the bond bending in cyclopropane and 25% for the value of $\bar{h}^2$ which is the VB value for the tetrahedral angle of the HAOs. If we choose the upper end of the 0 to 8% range for α, the HAO will then contain rather less of the 2s AO than does that of the ethane CC bond 13%)[2] or the CC bond of an unstrained paraffin (16% from Fig. 4). Moreover, the non-orthogonality integral between two HAOs at one carbon atom then has a value of −0·22 in agreement with the magic number found elsewhere. As is hardly surprising, then, cyclobutane is much closer to an unstrained paraffin than is cyclopropane, both in the amount of bond bending and in the nature of the HAOs which it uses to form its CC bonds. The CH bonds of cyclobutane do not seem to be different from those of a normal paraffin.

---

[25] J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.* **84**, 540 (1962) and refs. therein.

[26] P. H. Kasai, R. J. Myers, D. F. Eggers, jr., and K. B. Wiberg, *J. Chem. Phys.* **30**, 512 (1959); J. D. Dunitz, H. G. Feldman and V. Schonmaker, *Ibid.* **20**, 1708 (1952).

[27] J. Collin and F. R. Lossing, *J. Amer. Chem. Soc.* **81**, 2064 (1959).

[28] A. Alemningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* **15**, 711 (1961); W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.* **36**, 2931, (1962).