557. *Bent Bonds in Cycloalkanes.*

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The first three cycloalkanes have been studied by the method of maximum overlap, to find expressions for the orbitals employed in forming the C–C bonds and the angles between the axes of these orbitals and the lines of centres of the carbon atoms.

It is well known [1] that the angle θ_{ij} between two real orthogonal hybrid orbitals $\psi_i = s + \lambda_i p_i$ must be obtuse, but in cyclopropane (say) this requirement has to be reconciled with that imposed by the chemical symmetry that the C–C–C valency angle is 60° if bonds

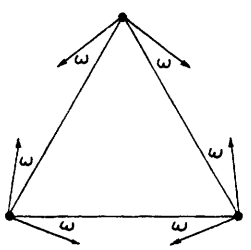

Fig. 1.

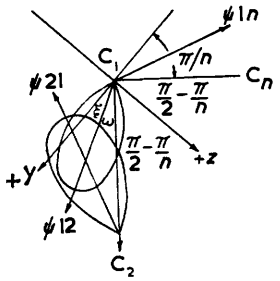

Fig. 2.

are formed along the lines of centres of the carbon atoms involved. By an elaborate valency-bond calculation Coulson and Moffitt [2] showed that the best compromise is reached (see Fig. 1) when the atomic orbitals forming the bond are directed, not at each other, but at angles $\omega = 22°$ outside the "equilateral angle." Thus the two hybrid orbitals ψ_{12} and ψ_{13} used in forming the bonds 1,2 and 1,3 diverge, not at 60°, but at $60 + 2\omega = 104°$; the bonds are therefore not rectilinear but "bent."

We here use a suggestion by Craig [3] that this result could have been obtained more simply, though rather less accurately, by using the principle of maximum overlap [4,5] and

[1] See, *e.g.*, Coulson, "Valence," 2nd edn., Oxford Univ. Press, 1961, p. 204.
[2] Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1.
[3] D. P. Craig, personal communication.
[4] Pauling, "The Nature of the Chemical Bond," 3rd edn., Cornell Univ. Press, Ithaca, 1960, p. 108.
[5] Maccoll, *Trans. Faraday Soc.*, 1950, **46**, 369.

the concept of a localised bond as represented by the overlap of two orbitals from the atoms of the bond. These orbitals will normally be hybrids, and we calculate their overlap integral. We next sum these overlap integrals for the bonds of the molecule, and assert that the best approximation of this form to the true wave function will be such that it corresponds to the greatest sum for these integrals, the justification for this assertion being that bond energies are closely parallel to overlap integrals. In this situation of maximum overlap, then, we wish to find (i) the form of the participant atomic orbitals and (ii) the angles between the axes of these orbitals.

Although it seems probable [6] that both cyclobutane and cyclopentane have non-planar rings, like the higher members of the series, we consider here planar cycloalkanes C_nH_{2n}, Fig. 2 being drawn for cyclobutane but inscribed for the general case.

If local cartesian co-ordinates are taken with origin at C_1, the hydrogen atoms in the xz-plane, and the carbon atoms in the yz-plane, the normalised atomic-orbital wave functions are:

$$\psi_{12} = as + \tfrac{1}{2}\sqrt{2}y + bz,$$
$$\psi_{1n} = as - \tfrac{1}{2}\sqrt{2}y + bz,$$
$$\psi_{1H_1} = bs + \tfrac{1}{2}\sqrt{2}x - az,$$
$$\psi_{1H_2} = bs - \tfrac{1}{2}\sqrt{2}x - az,$$

where, as throughout this paper, s,x,y,z, symbolise the $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals of carbon, and $a^2 + b^2 = \frac{1}{2}$. Pure tetrahedral hybrids would be associated with $a = b = \frac{1}{2}$. Resolving the p-parts of ψ_{12} along and perpendicular to the 1,2-bond we have:

$$\tau_{12\sigma} = as + \left(\tfrac{1}{2}\sqrt{2}\cos\frac{\pi}{n} + b\sin\frac{\pi}{n}\right)p_Z$$
$$\tau_{12\pi} = \left(\tfrac{1}{2}\sqrt{2}\sin\frac{\pi}{n} - b\cos\frac{\pi}{n}\right)p_Y$$

which are equivalent to taking new axes Z_{12}, Y_{12} along and perpendicular to the 1,2-bond. Corresponding expressions for $\tau_{21\sigma}$, $\tau_{21\pi}$ are written with Z_{21} positive towards C_1 and Y_{21} parallel to Y_{12} to ensure that the overlap integrals S will be positive.

Then

$$S_{12} = S_{12\sigma} + S_{12\pi} = \int \tau_{12\sigma}.\tau_{21\sigma}\mathrm{d}v + \int \tau_{12\pi}.\tau_{21\pi}\mathrm{d}v,$$

S_{12} being the total overlap of ψ_{12} and ψ_{21}.

$S_{12\sigma}$ is composed of terms in the three σ-overlap integrals which can be formed between s- and $p\sigma$-orbitals, but $S_{12\pi}$ only involves the π-overlap of p-orbitals. If the C–C bond is taken to be 1·53 Å long in all the cycloalkanes these integrals are,[7] with an obvious symbolism,

$$I_1 = S(s_1,s_2) = 0{\cdot}3447; \qquad I_2 = S(s_1,p\sigma_2) = 0{\cdot}3684;$$
$$I_3 = S(p\sigma_1,p\sigma_2) = 0{\cdot}3298; \qquad I_4 = S(p\pi_1,p\pi_2) = 0{\cdot}1952.$$

Since the orbital ψ_{1H_1} involved in the bond C_1–H_1 depends on the parameter a, the contribution of the C–H bonds to the total overlap in the molecule must be included. There is no reason why these bonds should be supposed bent, and the overlap integral in each is therefore:

$$T_{1H} = \int \psi_{1H}\, h\mathrm{d}v = \int \{bs + (\tfrac{1}{2} + a^2)^{\frac{1}{2}}p\}\, h\mathrm{d}v$$

[6] Almenningen, Bastiansen, and Skancke, *Acta Chem. Scand.*, 1958, **12**, 1215; Bastiansen and Shancke, *Adv. Chem. Phys.*, 1960, **3**, 323.

[7] Sahni and Cooley, "Derivation and Tabulation of Molecular Integrals," New York Univ. and National Aeronautics and Space Administration, Washington. Technical Note D–146–I.

p now symbolising a $2p$-orbital of carbon directed towards the H atom, and h a $1s$ orbital of hydrogen. If the C–H bonds are 1·07 Å long, T involves the integrals:

$$I_5 = S(s,h) = 0{\cdot}4414; \qquad I_6 = S(p\sigma,h) = 0{\cdot}5380.$$

By symmetry the total overlap in the molecule is:

$$\begin{aligned} S &= nS_{12} + 2nT_{1H} \\ &= n\left\{a^2I_1 + a\left(2b\sin\frac{\pi}{n} + \sqrt{2}\cos\frac{\pi}{n}\right)I_2 + \left(b^2\sin^2\frac{\pi}{n} + \tfrac{1}{2}\sqrt{2}\sin\frac{2\pi}{n} + \tfrac{1}{2}\cos^2\frac{\pi}{n}\right)I_3\right. \\ &\qquad \left. + \left(b^2\cos^2\frac{\pi}{n} - \tfrac{1}{2}\sqrt{2}\sin\frac{2\pi}{n} + \tfrac{1}{2}\sin^2\frac{\pi}{n}\right)I_4 + 2[bI_5 + (a^2 + \tfrac{1}{2})^{\frac{1}{2}}I_6]\right\} \end{aligned}$$

Thus, by equating dS/da to zero, the value of a can be found which makes S a maximum. Hence there can easily be obtained (i) ψ_{12}, (ii) the coefficient of mixing, $\lambda_{12} = \frac{1}{a}(b^2 + \frac{1}{2})^{\frac{1}{2}}$ in $\psi_{12} = a(s + \lambda_{12}p)$, (iii) ξ_{12} from $\lambda_{12} = \sqrt{(\sec 2\xi_{12})}$, (iv) $\omega_{12} = \frac{\pi}{n} - \xi_{12}$, (v) $\pi - 2\xi_{12} =$ angle between axes of ψ_{12} and ψ_{21}, (vi) ψ_{1H} and the corresponding λ_{1H}, ξ_{1H}, $\pi - 2\xi_{1H}$. These are listed for cyclopropane ($n = 3$), cyclobutane ($n = 4$), and cyclopentane ($n = 5$) in the Table. This also includes the calculated values of $S_{max.}$ and $S_{tet.}$ for the whole molecule of each compound, $S_{tet.}$ being the magnitude of the total overlap obtained with perfect tetrahedral hybridisation, *e.g.*, $\psi_{12} = \frac{1}{2}(s + \sqrt{2}y + z)$. As for recent experimental measurements only values of the H–C–H angle are significant in connection with our calculations. For this Almenningen, Bastiansen, and Skancke [6] give 113·6° ± 2° for cyclopropane and Dunitz and Schomaker [8] 114° ± 8° for cyclobutane, no value being recorded for cyclopentane. These angles may be compared with $\pi - 2\xi_{1H}$. The following results of a very recent micro-wave study [9] of the related 1,1-dichlorocyclopropane can be regarded as confirmation of the C–C and C–H bond lengths we have used. C_1–C_2 = 1·532, C_2–C_3 = 1·534, C–H = 1·085, C–Cl = 1·734 Å; H–C–H = 117° 35′, Cl–C–Cl = 114° 38′. The Cl–C–Cl angle is similar to our calculated H–C–H angle, though their value for the H–C–H angle is appreciably larger.

	$n = 3$	$n = 4$	$n = 5$
a	0·4935	0·5175	0·5328
b	0·5064	0·4818	0·4649
λ_{12}	1·7625	1·6533	1·5881
ξ_{12}	35° 36′	34° 16′	33° 19′
ω_{12}	24° 24′	10° 44′	2° 41′
$\pi - 2\xi_{12}$	108° 48′	111° 28′	113° 22′
λ_{1H}	1·7038	1·8186	1·9047
ξ_{1H}	34° 56′	36° 12′	37° 00′
$\pi - 2\xi_{1H}$	110° 08′	107° 36′	106° 00′
$S_{max.}$	5·9363	8·0760	10·1428
$S_{tet.}$	5·9361	8·0728	10·1280

For cyclopropane $\omega = 24\frac{1}{2}°$, to be compared with Coulson and Moffitt's value of 22°, a result which may encourage the use of this simple method of maximum overlap in similar cases. The angle between the orbital axes for cyclopropane is so near the tetrahedral angle that $S_{max.}$ and $S_{tet.}$ are almost identical and the method is therefore eminently suitable in this case. For planar cyclobutane and cyclopentane ω falls successively, as would be expected since the ring angles are so much closer to 109° 28′, especially in the second compound. However, the interorbital angles rise to $111\frac{1}{2}°$ and $113\frac{1}{2}°$, respectively.

[8] Dunitz and Schomaker, *J. Chem. Phys.*, 1952, **20**, 1705.
[9] Flygare, Narath, and Gwinn, *J. Chem. Phys.*, 1962, **36**, 200.

This is rather unexpected and may be due to using for all three compounds the C–C and C–H lengths somewhat arbitrarily suggested by Kirkpatrick and Spitzer.[10]

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[10] Kirkpatrick and Spitzer, *J. Chem. Phys.*, 1946, **14**, 463.