Table II. Comparison between ^{13}C and ^{1}H Contact Shifts for Ni(AA)$_2$ Complexes and Corresponding Hyperfine Coupling Constants for Radicals with Isoelectronic Structure

Ligand	Position	Obsd[a] contact shift ^{13}C	Obsd[a] contact shift ^{1}H	Radical	Calcd[a,b] $a_{^{13}C}$	Calcd[a,b] $a_{^{1}H}$
Pyridine[c]	α (2)	10.0	−10.0[d]	Phenyl	−10.0	10.0
	β (3)	−16.7	−2.9[d]		22.3	3.3
	γ (4)	4.5	−0.8[d]		−5.4	2.1
Aniline[e]	1	10.0		Benzyl	−10.0	
	2	−8.9	10.0[f]		9.5	−10.0
	3	3.4	−4.2[f]		−6.9	5.6
	4	−5.6	10.0[f]		8.3	−8.7

[a] Values are relative to position 1 or 2. A positive hyperfine coupling contant corresponds to a negative contact shift (see ref 1). [b] Taken from ref 9. [c] Numbering as in **1**. [d] Taken from ref 7. [e] Numbering as in **2**. [f] Taken from ref 1d.

tion that metal–ligand binding is essentially σ in character and that the Fermi contact shift provides a dominant contribution to the isotropic ^{13}C paramagnetic shifts in the Ni(AA)$_2$–pyridine complex.

The ^{13}C contact shifts for aniline follow the pattern (alternating signs and magnitudes) expected for a π mechanism in which the electron spin on the pπ orbital induces spin density on the carbon s orbital, the orbital responsible for the ^{13}C contact shift. The proton contact shift is related to the π spin density on the carbon to which the proton is attached.[10] The linear relation between relative ^{13}C contact shifts and relative proton contact shifts[1d] for aniline (positive ^{13}C shifts correspond to negative proton shifts) provides further evidence for a π-delocalization mechanism (see Table II). The agreement between relative ^{13}C contact shifts in the aniline–Ni(AA$_2$) complex and relative $a_{^{13}C}$ values obtained theoretically for the corresponding radical, the benzyl radical, is also close as was the case for pyridine.

When triphenylphosphine, an aniline-type base,[2] was used as the ligand, unexpected downfield ^{13}C contact shifts of all the ligand carbons were observed (Table I). The study of proton contact shifts has shown that the odd electron distributes itself on the phenyl ring *via* π orbitals as in the case of aniline. Therefore with triphenylphosphine, ^{13}C contact shifts alternating in sign and magnitude might be expected. All the downfield ^{13}C contact shifts observed show the predominance of spin delocalization through the σ bond, as occurs with σ delocalization on the proton in pyridine. The structure most likely to account for σ spin delocalization in triphenylphosphine appears to be a skew conformation[11] of the phenyl ring in which the lone-pair orbital on the P atom is nearly parallel to the plane of the phenyl ring. It then follows that alternating proton contact shifts[2] reflect the small amount of the π spin density on the carbon p orbital, which conjugates slightly with the lone-pair orbital on the P atom, while the ^{13}C resonance is insensitive to this low π spin density and reflects the positive spin density delocalized on the carbon 2s atomic orbital.

We believe that ^{13}C contact-shift studies can provide an additional tool for the elucidation of the electron spin distribution on the ligand molecule and of the geometric structure of the paramagnetic metal complexes.

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(10) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956); H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(11) For the skew conformation of triphenylphosphine, see G. R. Miller, A. W. Yankowsky, and S. O. Grim, *ibid.*, **51**, 3185 (1969).

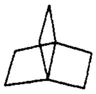
A New Model for the Bonding in Bicyclobutanes

Sir:

Bicyclobutane (I) is a most unusual molecule.[1] The dipole moment (0.675 ± 0.01 D),[2] bridgehead ^{13}C–H coupling constant (205 Hz),[3] and strain energy (64 kcal/mol) are especially large. The 1,3-diphenyl derivative has a uv spectrum suggesting conjugated phenyls, and 3-methylbicyclobutane-1-carboxylate has an uv extinction coefficient (λ_{max} 210, ϵ 6800) more akin to an α,β-unsaturated ester than to methylcyclopropanecarboxylate.[1] Bicyclobutanes are readily attacked by acids, bases,[4] halogens, carbenes, and radicals, many of these leading to addition across the central bond.[1] They do *not*, however, undergo facile Diels–Alder reaction.[4]

Excluding the latter instance, it is tempting to regard the bicyclobutane central bond as ethylenic or even acetylenic;[5] the latter accounts for the highly acidic bridgehead hydrogen.[1] However, a more appropriate model becomes apparent from *ab-initio* SCF calculation,[6] interpreted by Mulliken population analysis.[7] The new bonding model which emerges is consonant both with physical properties and reactivity.


I


II

A minimum basis set of contracted Gaussian-type functions[8] was employed and the microwave-determined geometry assumed.[2b] The SCF wave function (obtained with all integrals computed, without approximation) furnished a dipole moment of 0.686 D (along the C_2 axis, with positive end pointing up through the bridgehead carbons, I), in excellent agreement with the microwave value (0.695).[2,9] This lends credence to the

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

(2) (a) M. D. Harmony and K. Cox, *J. Amer. Chem. Soc.*, **88**, 5049 (1966); (b) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, 50, 1976 (1969).

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

(4) E. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 487, 496 (1966).

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

(6) For maximum overlap and CNDO treatments see Z. Maksić, L. Klasinc, and M. Randić, *Theor. Chim. Acta*, **4**, 273 (1966), and K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968), respectively.

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

(8) J. M. Schulman, C. J. Hornback, and J. W. Moskowitz, manuscript in preparation.

(9) The phenomenal agreement with experiment is, to some extent, fortuitous, but suggests a well-balanced basis. These calculations are presently being performed at the double ζ level with localized orbitals.

Table I. Carbon–Carbon Mulliken Overlap Populations in Bicyclobutane[a]

	Orbital pair				
	$2s_{C_a}$–$2s_{C_b}$	$2s_{C_a}$–$2p_{C_b}$	$2s_{C_b}$–$2p_{C_a}$	$2p_{C_a}$–$2p_{C_b}$	Bond order
Central bond ($a = 1, b = 3$)	−0.0712	0.0166	0.0166	0.3844	0.3464
Side bond ($a = 1, b = 2$)	0.0254	0.1956	0.1134	0.3026	0.6330

[a] Cyclopropane values for the 2s–2s, 2s–2p, and 2p–2p overlaps are −0.0020, 0.1248, and 0.321, respectively.

subsequent arguments. As regards the orbital energies, bicyclobutane is predicted to (adiabatically) valence ionize[10] more easily than cyclopropane and ethylene, but to less readily core ionize, with little ESCA chemical shift between the bridge and bridgehead carbons.

The unusual bonding in bicyclobutane is first encountered in the overlap populations (Table I). Unlike most carbon–carbon bonds with overlap populations containing substantial contributions from 2s and adjacent 2p orbital overlaps (for example, 48% for the side bond of bicyclobutane, 44% for cyclopropane[11]), for the central bicyclobutane bond this contribution is not appreciable (<10%). Moreover, the contribution from adjacent 2s pairs is also small. The central bond is therefore nearly pure p in character, and since the p-σ and p-π contributions partition approximately in the ratio 5:1, the central bond is best described as arising from largely σ interaction of two unhybridized p orbitals.[12] Such bonding might be anticipated to occur in II (as yet unknown), which may be viewed as a substituted ethane formed from two methyl radicals unable to rehybridize.[13] That such bonding occurs in bicyclobutane with two "free" ligands is somewhat surprising.

Turning to the CH bonds, the method of Yonezawa, *et al.*,[14] indicates that the exo, endo, and bridgehead hydrogens are attached to $sp^{2.02}$, $sp^{2.08}$, and $sp^{1.55}$ hybrids, respectively (cyclopropane is $sp^{1.96}$). The bridgehead value, between that of ethylene and acetylene, is in accord both with the high bridgehead acidity and the large ^{13}C–H coupling constant[15] (but does not require the C–C bond to be olefinic).

Several significant chemical consequences attend this bonding scheme. First, use of unhybridized p orbitals implies a high density of electrons behind the central bond and slightly below it.[16] The resulting external lobe may play an important role in bicyclobutane chemistry, for example, accounting for the ready decarboxylation of *endo*-1,3-diphenylbicyclobutane-2-carboxylic acid (85°) relative to the diexo isomer of 1,3-diphenyl-4-carbomethoxybicyclobutane-2-carboxylic acid (200°).[17] The endo acid proton can reach the external lobe to give a cyclic transition state, whereas the exo proton cannot.[5] Similarly, an incoming proton may first attack bicyclobutane from behind the central bond (fixing the stereochemistry at that center) rather than from above it. This former path is in accord with the observed stereochemistry[18] and it need not preclude the initial "p-σ complex" continuing on to, say, an edge-protonated cyclopropane. A somewhat analogous mode of attack has been suggested for the reaction of bicyclobutane with benzyne.[19]

The σ p–p-bond model also suggests why bicyclobutane is reluctant to undergo Diels–Alder reaction. Unlike the π bond of an olefin, with electrons oriented toward the incoming diene, the central bond of bicyclobutane is not disposed to overlap early in the reaction coordinate. The transition state is therefore of relatively high energy although the reaction would be very exothermic.

Finally, consider the uv band of 1,3-diphenylbicyclobutanes at *ca.* 270 mμ,[20] suggesting phenyls in conjugation. To interact through the p–p bond the benzene rings must align themselves face to face. Space-filling models suggest substantial steric hindrance to such orientation in the presence of a large exo substituent. It is, in fact, observed that the 270-mμ maximum is absent in esters of *exo*-1,3-diphenylbicyclobutanecarboxylic acids.[20]

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(10) T. Koopmans, *Physica*, **1**, 104 (1933).

(11) Unpublished results.

(12) It is about as bent as the cyclopropane bond which partitions 10:1.

(13) Similar calculations are currently being performed on II.

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

(15) J. N. Shoolery, *J. Chem. Phys.*, **30**, 1427 (1959).

(16) Or, what is operationally equivalent, a highly polarizable p–p bond.

(17) S. Masamune, *Tetrahedron Lett.*, **14**, 945 (1965).

(18) K. B. Wiberg and G. Szeimes, *J. Amer. Chem. Soc.*, **92**, 571 (1970). Our path conflicts with the CNDO results of this reference, however, and since the latter predicts the stereochemically incorrect top-side attack to be preferred, the question must be considered still open.

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(20) R. B. Woodward and D. L. Dalrymple, *ibid.*, **91**, 4612 (1969).

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Mechanism of the Wolff Rearrangement. III

Sir:

With regard to the intermediacy of the cyclic oxirene structure in the photochemical Wolff rearrangement of diazo ketones, recent investigations have led to conclusions which were in apparent conflict with those derived from earlier studies.

Nearly 30 years ago Huggett, *et al.*,[1] converted benzoic acid, ^{13}C labeled in the carboxyl group, into phenylacetic acid by the Arndt–Eistert method, $C_6H_5{}^*COOH \rightarrow C_6H_5{}^*COCl \rightarrow C_6H_5{}^*COCHN_2 \rightarrow C_6H_5CH{=}{}^*C{=}O \rightarrow C_6H_5CH_2{}^*COOH$ (oxidation) $\rightarrow {}^*CO_2$, and found that all the originally present heavy isotope, which amounted to only 2.5%, appeared after oxidation in the CO_2 product, indicating that no scrambling took place during rearrangement.

Later Franzen[2] applied the ^{14}C-labeling technique for the elucidation of the mechanism of the photolytic and thermal Wolff rearrangement of azibenzil. Experiments were carried out in dioxane–water–tri-

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(2) V. Franzen, *Justus Liebigs Ann. Chem.*, **614**, 31 (1958).