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SOME DRAMATIC CONSEQUENCES OF 1,3 CARBON-CARBON INTERACTIONS IN ION RADICALS

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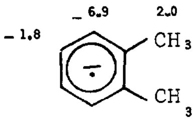
Recent experimental work on anion radicals has revealed several instances in which 1,3 carbon-carbon interactions perturb spin densities powerfully and energies significantly.[1-4] Strong theoretical support can now be added to the experimental evidence. This support, based on INDO MO calculations, not only verifies the extraordinary magnitude of the 1,3 effect in cyclobutenoid systems, but substantiates it as a significant factor even in systems with normal valence angles.

The experimental esr hfs (hyperfine splittings) of the o-xylene (1) and benzocyclobutene (2) anion radicals are displayed below. Despite the similarity of the ring (alpha) hfs in the two cases, the beta hfs is grossly larger in the latter (5.5G) than in the former (2.0).



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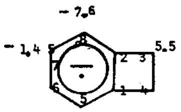

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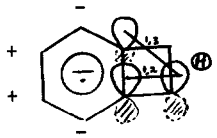

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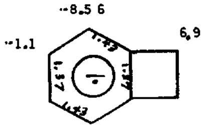

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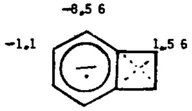

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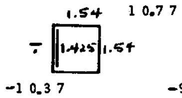

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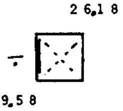

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A $\cos^2\theta$ dihedral angle dependence can be used to adjust the hfs of 1 to a basis conformationally comparable to 2. This gives the 'classically' expected value for 2 (3.0G).The proposal has been made and strongly supported by experimental evidence that 1,3 interactions (C_1-$C_3$and C_2-C_4) in 2 synergistically reinforce the normal hyperconjugative (1,2 overlap) mechanism in transmitting spin to the beta hydrogens (3). The symmetric HOMO of the system is appropriate, in orbital symmetry terms, to such reinforcement. An INDO calculation on 2 at geometry 4[5] gives the hfs listed in 4, in relatively good agreement with experiment. The postulate of 1,3 interactions can now be quantitatively tested by nullifying all resonance integrals corresponding to those interactions.[6] The beta hfs is seen to be drastically reduced (1.5661), while the ring hfs (5) remain relatively unaffected. The 1,3 interactions are thus associated with Δa=+5.3348G (they increase the hfs). With these interactions removed, the hfs is now too small.

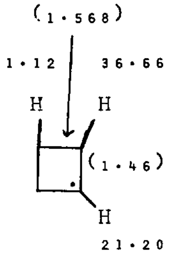
However, one further notes that C_5 and C_8 have even more spin (ca. 4x) than C_1,C_2 . Hence, even though the interaction distance is much larger, the C_3-C_8 and C_4-C_5 1,3 interactions are appreciable, and they oppose (interfere with) the 1,2 effect (Δa=-2.2464). When the system is simultaneously "de-perturbed" of all these 1,3 interactions, a=3.2676, in good agreement with 'classical' expectation.

The "de-perturbation" approach has been applied exhaustively to a simpler system, cyclobutene, for both anion and cation radicals. Only the salient results will be outlined here. In the anion, the HOMO is anti-symmetric. A normal INDO at geometry 6 (energy minimized C_1-C_2 length) gives a=10.7703.[7] 1,3 "de-perturbation" unmasks powerful 1,3 interference (7); a=25.5163. Of the remaining perturbations in the system, only one further effect merits attention. A "cyclic" effect is revealed by nullifying the p_{z_3},p_{z_4} interaction (Δa=7.2018). This is partly counteracted by concomitant interactions involving C_3 (C_4) and the hydrogens on C_4 (C_3). The net cyclic effect is Δa=-3.0183. "De-perturbation" with respect to both 1,3 and cyclic effects gives the classically expected value a=28.7663. Expunging, instead, the 1,2 and cyclic effects gives the isolated 1,3 effect (a=3.6141). The important inference here is that the solo 1,3 effect is still substantial (cf. the normal a=10.7703); however, operating in concert with the 1,2 effect it is utterly dramatic. When all of these spin carrying effects are nullified, a=-0.3464.

In the cation radical, the HOMO is symmetric. The normal INDO a=24.7401 and the 1,3 "de-perturbed" a=12.7799. The solo 1,3 effect yields a=3.5411 and the solo 1,2 (the classical value) a=26.9001.[8] Comparison of these latter two values with those for the anion yields another valuable insight: <u>The 1,3 and 1,2 effects are both about equally effective in anion as cation</u>, with regard to spin transmission. The slight edge goes to the anion in both cases. The calculated normal hfs for these species (10.7 and 24.7, respectively) indicate how the erroneous notion that 'cation radical is much more effective than anion radical hyperconjugation' might have arisen. The foregoing discussion demonstrates that 1,3 effects are largely responsible for the larger cation splittings.

In the <u>trans</u>-2-butene anion the maximum ("axial") hfs in the normal INDO calculation is 35.9845; in the cation radical it is 48.3614.[9] 1,3 "de-perturbation" gives 45.4873 and 41.5081, respectively. Again, 1,3 effects, reinforcing in the cation and interfering in the anion, engender a greater cation than anion hfs.

Though conspicuous in the cyclobutene and benzocyclobutene anion radicals, the effect of 1,3 interactions is curiously muted, ostensibly, in the cyclobutyl radical (experimental hfs's listed in 8; see particularly the modest γ hfs). INDO calculated hfs's are listed in 9 and 10 for the 30° puckered and planar forms, respectively, of the radical (radical site sp^2 hybridized in each case).



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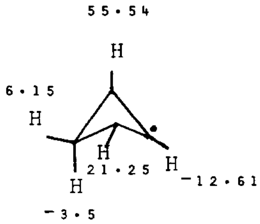

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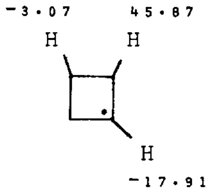

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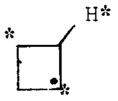
In the puckered form (9) the calculated γ hfs's are quite substantial but of opposite sign, so that conformational equilibration would result in a small average γ hfs ($\bar{a}_\gamma = (a_{ax}+a_{eq})/2 = 1.2853$). Confirmation of the strong involvements of 1,3 interactions comes from zeroing the 1,3 (and 2,4) resonance integrals, which shifts a_γ^{eq} to -3.6729(Δa=+9.8296) and a_γ^{ax} to +4.2715(Δa=-7.8576). That 1,3 interactions can either decrease or increase the γ hfs is interesting and may merit comment. The cyclobutyl HOMO can be represented crudely as in 11, where the asterisks indicate the positions of highest spin density. The delocalization of spin from C_1 to the beta hydrogens represents well known hyperconjugative effect. Delocalization to C_3 involves 'extended hyperconjugation'. The positive spin density at C_3 in the HOMO polarizes subjacent orbitals, accumulating negative spin on adjacent atoms (the γ hydrogens and C_2). Thus, extended hyperconjugation (it is cyclic in this case) gives rise to negative hyperfine increments at the γ hydrogens. The 1,3 interaction exerts a large perturbation on this effect by delocalizing more (positive) spin to C_3 (the coefficient of C_3 in the HOMO is increased). As a result, the (negative) contribution to the γ hfs is even larger because of the 1,3 interaction. This effect is felt most powerfully at the axial γ hydrogen (see the negative quasi axial hydrogen splitting in 9). The 1,3 interaction also has a more direct effect on a_γ since this interaction delocalizes spin in the HOMO from C_1 to the γ hydrogens (see 12 and regard C_1-C_3-H_γ as an allylic system with spin on the terminal positions in its HOMO). This effect is therefore positive and is more prominent with the equatorial γ hydrogen (and incidentally in the puckered form). Incidentally the 1,3 effect can be explored in another way, viz., by first shutting off all but sigma bond spin carrying mechanisms (this involves <u>all</u> long range interactions plus hyperconjugation) and then re-introducing the 1,3 effect. With only sigma spin trans-



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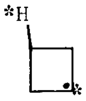

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mission $a_\gamma^{ax}=-0.2258$ and $a_\gamma^{eq}=-1.2963$. Restoration of the C_1/C_3 resonance integrals yields $a_\gamma^{ax}=5.2918$, $a_\gamma^{eq}=7.1048$. In the planar cyclobutyl radical the negative γ hfs reveals that the C_1/C_3 perturbed extended hyperconjugative effect dominates the direct 1,3-HOMO effect. Zeroing the C_1/C_3 interaction gives $a_\gamma=-1.1168(\Delta a=-1.9608)$. The sigma transmissions only value is $a_\gamma=-0.6765$; restoring C_1/C_3 gives $a_\gamma=3.6362(\Delta a=4.3127)$.

The "de-perturbation" approach permits quantitative study of 1,3 interactions and, indeed, virtually any perturbing interaction at a relatively sophisticated level (INDO). As will be shown in subsequent works, the consequence of 1,3 effects for energy are also significant and are not limited to radicals.

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5) When supplied with the normal benzene geometry for the ring moiety of benzocyclobutene, INDO responds with the antisymmetric anion radical, not the experimentally observed symmetric one, as previously noted in the case of the indane anion radical.[1] The small distortions represented in 4 preferentially stabilize the symmetric species. Cyclobutene parameters were used for the remainder of the molecule.

6) Program INDO was modified to permit any desired one electron resonance integral to be set equal to zero.

7) Cyclobutene coordinates were adopted initially, then energy minimized with respect to the C_1 C_2 length.

8) The energy minimized C_1 C_2 length is the same (1.435A) as in the anion radical.

9) *Trans*-2-butene geometry, with energy minimized C_2 C_3 length.