Effect of 1,3 Carbon/Carbon Interactions on Spin Density in Organic Radicals

James Cessac and Nathan L. Bauld*

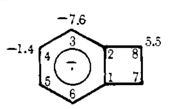
Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712. *Received August 25, 1975*

Abstract: The unexpectedly large ESR β hyperfine splittings (benzylic protons) of the benzocyclobutene and similar cyclobutenoid anion radicals are interpreted in terms of synergistically reinforcing 1,2 (hyperconjugative) and 1,3 (homohyperconjugative) carbon/carbon interactions, the latter across the relatively short diagonal of the cyclobutene ring. The observed effects are quite large and are foreseen by INDO/MO calculations. By zeroing the appropriate resonance integrals the proposed interactions are unambiguously identified as the cause of the enhanced splittings. Orbital symmetry is observed to control the relative phase of the two interactions, reinforcement occurring where the HOMO is S (as in the benzocyclobutene anion radical), interference where it is A. The cyclobutene anion (HOMO = A) and cation (HOMO = S) radicals are analyzed via INDO and found to sustain prodigious 1,3 interference and reinforcements, respectively. Analogous effects in the *trans*-2-butene anion and cation radicals are smaller, but still quite substantial, pointing to the universal role of 1,3 carbon/carbon interactions in relation to spin densities. The popular conception that cation > anion radical hyperconjugation in transmission of spin to β hydrogens is refuted, and it is posited that 1,3 interactions are the primary cause for the widely differing β hfs of anion and cation radicals, such as those of the *trans*-2-butene and cyclobutene systems, related to each other by the pairing theorem.

The neglect of nonneighbor (i.e., long range) interactions is endemic in the working structural theory of organic chemistry. Although this premise has been useful in constructing a powerfully simple structural theory, it is not wholly consistent with quantum theory. In particular, 1,3 interactions normally do not look trivial in quantum calculations. The present paper explores the inadequacies of the simple theory in an area, spin densities, where they are rather egregious. It is hoped, thereby, to contribute to our more certain understanding of the factors that affect spin densities and also to encourage closer scrutiny of the role of 1,3 effects in other areas of chemistry. Initially, the apparently dramatic effects of 1,3 carbon-carbon interactions on the spin densities of ion radicals of cyclobutenoid structure are discussed from the standpoint of both experimental (ESR hfs) and theoretical (INDO) criteria. The 1,3 effects discovered in these propitious systems are then explored theoretically in simple systems with normal valence angles.

Results and Discussion

Recent experimental studies[1,2] have been interpreted as reflecting dramatic effects of 1,3 carbon-carbon interactions on spin densities, as measured by ESR hyperfine splittings (hfs's), in primarily cyclobutenoid, but also a few other, anion radicals. The benzocyclobutene anion radical (**1**) is an outstanding illustration.



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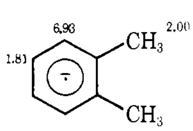

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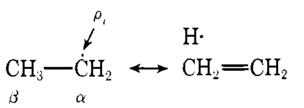
As MO theory predicts, the ring proton (i.e., α) hfs's of **1** are quite close to those of the *o*-xylene anion radical (**2**).[3] Despite this indication of similar spin density distributions in the benzenoid π systems of **1** and **2**, the benzylic proton (β) hfs of **1** (5.5 G) is grossly larger than that for **2** (2.0 G). The classical approximation is embodied in the McConnell equation[4] (eq 1).

$$a_\beta = [B_0 + B_2 \langle\cos^2\theta\rangle_{\rm av}]\rho_i \qquad (1)$$



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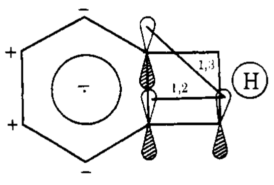

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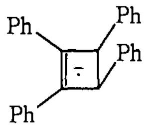
The β proton hfs constant, a_β, is seen to be proportional to the spin density, ρ_i, whence a hyperconjugative interaction with the β C-H bond may be viewed as transmitting spin to the β protons [e.g., as in the ethyl radical (**3**)]. In **1** the pertinent spin density for the protons at C_7 is ρ_1; for those at C_8 it is ρ_2. The $\langle\cos^2\theta\rangle_{\rm av}$ factor, where θ is the appropriate dihedral angle, represents the conformational dependence of the hyperconjugative interaction. Since B_0 is an order of magnitude smaller than $B_2\langle\cos^2\theta\rangle_{\rm av}$, the simpler equation $a_\beta = B_2\rho_i\langle\cos^2\theta\rangle_{\rm av}$ usually suffices. The $\langle\cos^2\theta\rangle_{\rm av}$ factor for the rapidly rotating methyl groups of **2** is, of course, 0.500. For the β hydrogens of **1**, $\langle\cos^2\theta\rangle \simeq 0.79$. The β hfs of **2** can then be adjusted to a basis conformationally comparable to **1** (3.0 G). The disparity is still large, and the only remaining variable in the usual theory (ρ_i) appears to differ little between **1** and **2**, as noted earlier. The classically expected value of a_β for **1** may therefore be said to be 3.0 G. The problem, simply stated, is to account for a virtual doubling of the expected a_β in **1** (from 3.0 to 5.5 G) without invoking major π spin density shifts in **1** relative to **2**. The proposal has been made and supported by additional experimental evidence that 1,3 interactions (C_1/C_8 and C_2/C_7) in **1** *synergistically reinforce* the normal hyperconjugative (C_1/C_7 and C_2/C_8) mechanism in transmitting spin to the β hydrogens (**4**).[1,3] The justification for this proposal follows. The 1,3 carbon-carbon distance in cyclobutane and its isoannular congeners is the shortest of any cyclic system (the 1,3 distance is undefined in cyclopropanes). Interactions involving C_1-C_3 overlap should thus be maximal in cyclo-C_4 systems. Important roles for these interactions have been posited by a number of investigators. Dunitz and Shomaker[6] have interpreted cyclobutane's long C-C bond and the major part of its ring strain in terms of 1,3 interactions. Katz and Gold[7] interpreted the uv spectra of cyclobutenylium ions in terms of 1,3 π overlap intermediate in extent to the allyl and cyclopropenylium cations. Engler, Andose, and Schleyer have commented, apropos of their molecular mechanics calculations, "Explicit inclusion of a 1,3 non-bonded interaction term seems to be required in order to more accurately reproduce the bond lengths in four-membered rings and small polycyclic molecules."[8] Secondly, the symmetry of the HOMO in **1** (viz., S) is appropriate for homohyperconjugative-hyperconjugative reinforcement (**4**), as opposed to interference. Incidentally, interference (abnormally low β hfs) has been observed in an instance (**5**) in which the HOMO is antisymmetric.[1] In another instance (**6**) in which virtually degenerate (rapidly equilibrating) A and S states are to be expected, normal β hfs's were found.[1] The 1,3 carbon-carbon interaction is therefore at least qualitatively capable of explaining all of the apparent "anomalies". INDO molecular orbital calculations were carried out in order to assess more quantitatively the validity of the proposed explanation. This type of calculation has acquitted itself extraordinarily well in numerous applications involving calculations of ESR hfs's, including long range hfs's. The benzocyclobutene anion radical, anomalous in the classical approximation, is no exception. An INDO calculation on **1** at geometry **7** gives the hfs's listed in **8**, in relatively good agreement with experiment (see **1**). The postulate of a_β enhancement, without substantial benzenoid π electron shift, by synergistic 1,3/1,2 reinforcement is thus subject to speedy and decisive test. Program CN/INDO was modified so as to permit any appropriate one-electron resonance integrals (β) to be zeroed. This merely entailed zeroing the overlap integral (S), to which β is taken proportionate. A new calculation was then performed in which all β's involving C_1-C_8 and C_2-C_7 interactions, and only these, were zeroed. Note that this includes both π and σ 1,3 interactions. The resulting hfs's are displayed in **9**, where it can be seen that the ring (α) hfs are indeed virtually unchanged, but the β hfs is drastically reduced (to 1.5661). The 1,3 interactions are thus associated with $\Delta a_\beta = +5.3348$ G (they increase a_β). With these interactions removed, the β hfs is actually a bit too small (recall the 3.0 G classical prediction), a point to which we shall return momentarily. To further trace the origin of the a_β enhancement one can zero the π and σ 1,3 interactions separately. As befits a π radical, the π 1,3 effect is overwhelmingly dominant, as shown by the results of a calculation (**10**) in which only the $p_z(C_1)/p_z(C_8)$ and $p_z(C_2)/p_z(C_7)$ interactions were zeroed. The a_β (1.4603 G) is virtually the same as when both π and σ 1,3 interactions were zeroed. The now somewhat low a_β aroused our curiosity and prompted a check of all other long range C/C interactions in the system. Only one other set, viz., C_3/C_8 and C_6/C_7, revealed an appreciable interaction. Zeroing these yielded $a_\beta = 9.1473$ ($\Delta a = -2.2464$). The π effect alone corresponded to $\Delta a = -2.3288$, and again is the preponderant contributor. The effect (−2.2) is smaller than the previously discussed transcyclobutene 1,3 effect (+5.3), as would be expected on the basis of the relative 1,3 C-C distances. For perspective it should be recalled that the spin density at C_3 and C_6 is approximately four times that at C_1 and C_2. Were it not for this fact the relatively long C_3-C_8 and C_6-C_7 distance would no doubt have precluded a substantial interaction relative to the trans cyclobutane one. The magnitude of the effect does, however, alert one to the possibility, realized as we shall see later, that the short C_1-C_3 distances of a cyclo-C_4 system are not essential to the realization of appreciable 1,3 effects. The fact that Δa is negative for this interaction (interference) is easily predictable from **1** (the HOMO coefficients at C_3 and C_8 are opposite whereas those at C_2 and C_8 are the same). Upon zeroing *both* types of 1,3 effect the INDO result is $a_\beta = 3.2676$ ($\Delta a = +3.6333$). A comparison of this with the "classical" prediction ($a_\beta = 3.0$) is now satisfying.



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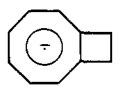

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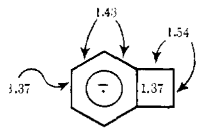

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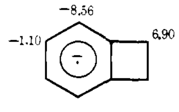

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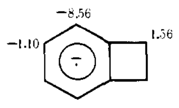

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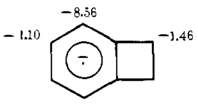

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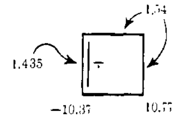
The use of the experimental a_β for **2** as a "classical" value warrants some comment since, undoubtedly, the 1,3 effects discussed for **1** are operative in some measure for **2**. The INDO calculation of **2** gives an "axial" $a_\beta = 2.2178$, which would correspond to an experimental (free rotation) splitting of 1.1 G, considerably smaller than that measured. However, zeroing all of the important 1,3 π interactions (C_1/C_8, C_2/C_7, C_3/C_8, and C_2/C_7) gives $a_\beta = 3.8411$, corresponding to a predicted splitting of 1.9 G. This suggests that 1,3 effects are indeed small in **2**.

Zeroing just the C_1/C_8 and C_2/C_7 integrals gives $a_\beta = -0.1465$, while zeroing the C_3/C_8 and C_6/C_7 integrals affords $a_\beta = 6.6150$. The opposing 1,3 effects are evident but, at least at the assumed geometry, the interference effect is overestimated relative to the reinforcement effect. Naturally the blend of these two effects is critically dependent on the (experimentally unknown) value of the exocyclic C-C-C angle. The value assumed here (120°) may be unrealistic. The key point, however, is that the experimental value of a in **2** appears to reflect an insignificant contribution from 1,3 interactions. This, of course, is wholly untrue for **1**.

The Cyclobutene System

The simpler cyclobutene system was analyzed exhaustively in the foregoing manner, including all long range interactions (H/H, C/H, C/C). Both anion and cation radicals were considered. The HOMO symmetries (A, anion; S, cation) suggest interference for the anion, reinforcement for the cation. For the anion radical the INDO calculation (**11**) gives $a_\beta = 10.7703$ G. With 1,3 C/C interactions zeroed, the result is $a_\beta = 25.5163$ ($\Delta a = -14.7460$, **12**). Powerful interference is verified and, as with **1**, the effect is wholly π in nature. Only one additional set of long range interactions contributes significantly to the β hfs, viz., the set exemplified by $p_z(C_3)/H_4$. The latter notation refers to the interaction of the p_z orbital on C_3 with a hydrogen attached to C_4. This will be abbreviated to the "C_3/H_4" effect. There are four such 1,3 C/H interactions in cyclobutene. Zeroing these lowers a_β to 6.5865 G ($\Delta a = +4.1935$). No 1,4 or 1,5 interaction exerts an appreciable effect on a_β.



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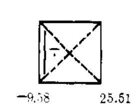

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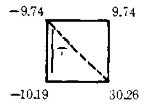

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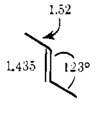
The approach applied above to long range interactions is basically a perturbation treatment and is, consequently, applicable to any interaction which represents a valid (i.e., not too large) perturbation. It can therefore be used on neighboring (i.e., 1,2) p_z/p_z (π) interactions in predominantly single bonds. Two sets of such interactions are found in cyclobutene. The interaction typified by $p_z(C_1)/p_z(C_4)$ is of the familiar hyperconjugative type which has been said to represent the principal mode (the only one in the classical model) for transmitting spin to the β protons. Effects engendered by these interactions will be referred to generically as 1,2 effects. The second hyperconjugative interaction type is the $p_z(C_3)/p_z(C_4)$ interaction, designated here the "C_3/C_4" effect. Zeroing this latter interaction gives a_β = 17.9721 (Δa = −7.2018). The C_3/H_4 and C_3/C_4 effects may be viewed as concomitants and combined, since they both depend on the attachment of C_3 and C_4. The net 3/4 effect (−3.0183) is small in comparison to the 1,3 effect (−14.7460) and of the same sign. The importance of the 1,3 effect is further underscored by the hfs's in **13**, in which the 1,3 but not the equivalent 2,4 interaction is zeroed. The β protons opposite the zeroed 1,3 interaction have a = 30.2621 G; those opposite the still operative 2,4 interaction have a = 8.3086. Several further exercises may be interesting and reassuring. Zeroing both the 1,3 and 3/4 sets of interactions should leave only the 1,2 interaction intact, and thus yield the classical value of a_β. The result is a_β = 28.7663. Nullifying the previous two sets plus the 1,2 set should leave no effective mode of spin transmission. Indeed, a_β = −0.3464 (σ transmission). Zeroing the 1,2 and 3,4 effects should isolate the 1,3 effect. This calculation gives a_β = 3.6141. The solo 1,3 effect is thus quite substantial in comparison with either the net hfs (10.7703) or the solo 1,2 effect (28.7663). It is, however, far more dramatic when operating in conjunction with the 1,2 effect.

The β hfs calculated for the cyclobutene cation radical, 24.7402 G, is much larger than that of the anion. Experimentally, this phenomenon is familiar, and is usually attributed to larger McConnell B_2 values (more efficient hyperconjugation) for the cationic species.[9] Zeroing the 1,3 set yields a_β = 12.7799 (Δa = +11.9602), demonstrating strong reinforcement, as foreseen by orbital symmetry. The C_3/C_4 and C_3/H_4 effects are both opposed to the 1,3 effect (Δa's = −10.6988 and −3.3887, respectively). The overall 3,4 effect is thus even slightly larger than the 1,3 effect, leaving a small residual negative effect. Thus, when the 1,3 and 3,4 effects are simultaneously zeroed a_β has the value 26.9001 (Δa = −2.1600). In this latter calculation only the 1,2 effect carries spin to the β hydrogens, as mentioned in the anion radical discussion, and this value of a_β corresponds to our classical (1,2 only) case. Interestingly, the classical value for the cation (26.9001) is not, as current generalizations would suggest, larger than that for the anion (28.7663). In fact, there is very little difference between the two values, and the anionic one is slightly the larger. The same observation can be repeated for the solo 1,3 effect (3.6141 in the anion; 3.5411 in the cation). One is impelled to the conclusion that *cationic and anionic hyperconjugation (and homohyperconjugation) are essentially equally efficient at spin transmission*, with the anionic type having a very slight edge. Basically the same result has been predicted by valence bond calculations.[10,11] The experimental phenomenon of cation radical > anion radical hfs's, where observed, is decisively indicated to be the result of 1,3 interactions, which interfere in those particular anion radicals and reinforce in the cation radicals. Clearly such an experimental order is not inevitable, depending, as it does, on HOMO symmetry.

trans-2-Butene

The presence and potency of 1,3 interactions having been experimentally and theoretically inferred for cyclobutenoid systems, it is now important to ask whether these effects continue to assert themselves significantly in systems having normal valence angles. On the basis of experimental cation vs. anion radical hfs's, considered in the light of the foregoing discussion, an affirmative reply might well be expected. The *trans*-2-butene system was selected for the calculations. Unfortunately, the experimental ESR hfs's of the anion and cation radicals of the system (and of all other suitable simple systems) are unknown. The bond lengths and angles used are shown in **14**, the arbitrarily chosen conformations in **15**. In the latter, H_1 and H_4 are "axial". The calculated anion radical hfs's are



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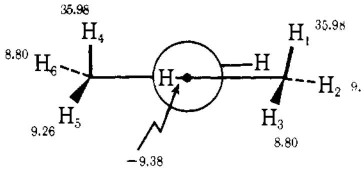

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a_β = 35.9845 (H_1,H_4), 9.2687 (H_2,H_5), and 8.8055 (H_3,H_6). Zeroing 1,3 interactions (C_1/C_3, C_2/C_4) converts the hfs's to 45.4873, 11.5592, and 11.1530. For the axial hydrogens Δa = −9.5028, revealing sizable interference. Once again, the effect is virtually pure π. In this acyclic system 1,3 C/H interactions have insignificant effects on spin density; zeroing the $C_2/H_{4,5,6}$ and $C_3/H_{1,2,3}$ interactions, to illustrate the point, leaves the axial hfs at 35.5668. The 1,3 C/C interaction is, in fact, the only important long range interaction in this system. Turning to the cation radical, the calculated axial hfs is 48.3614, again much larger than that calculated for the anion (35.9845). However, zeroing the 1,3 C/C interactions yields a_β 41.5081 (a reinforcement of 6.8533). Since the 1,3 C/C effect is the only secondary effect of importance in the system, the zeroing of this effect gives the "classical" (1,2 only) value (45.4873 for the anion; 41.5081 for the cation). As in earlier cases, the cation hfs is not larger than the anion one.

Conclusions

That long range interactions can have substantial effects on spin density distributions (ESR hfs's) has been known for quite some time, primarily from work on bicyclic systems.[12-14] The potential relevance of symmetry to such effects has also been considered.[15] The results reported here are believed to signal the importance of 1,3 carbon/carbon interactions, in particular, in virtually all relevant systems, not excluding the monocyclic and acyclic. More explicitly, they suggest that spin densities simply cannot be understood adequately without recognition of these interactions. This is true a fortiori for cyclo-C_4 systems. The inclusion of 1,3 carbon/carbon interactions, further, relieves the necessity for assuming the cation > anion radical spin transmission efficiency, which assumption is inconsistent with theory.

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