**Figure 1.** Indan anion radical (K⁺, DMF, −60°). Half spectrum shown. The starred absorption envelopes represent the γ hfs lines.

is the usual dihedral angle.[1] The $\cos^2 \theta$ law thus predicts $a^\beta_{ax}/a^\beta_{eq} = 3.72$. For $2\cdot^-$ the INDO calculated ratio is 4.34. The $1\cdot^-$ calculation, using benzene parameters for the aromatic moiety, gives 3.91. This anion radical, which we will call a-$1\cdot^-$, is not the experimental species, however; the odd electron in it occupies an antisymmetric benzene-like ABMO, that in the observed species occupies a symmetrical ABMO. To simulate s-$1\cdot^-$, the bridge and 2,3 C–C bonds were shortened (1.340 Å), as they should actually be in this species. The calculated hfs now agree well with experiment ($a_{4,7} = -8.78$, $a_{5,6} = -1.16$, $\bar{a}_\beta = 4.16$, $\bar{a}_\lambda = 0.47$). The $a^\beta_{ax}/a^\beta_{eq}$ ratio is now 1.66, far lower than predicted by $\cos^2 \theta$ and than calculated for the two antisymmetric species (a-$1\cdot^-$ and $2\cdot^-$). The latter, in contradistinction, have ratios greater than the $\cos^2 \theta$ prediction. Further, the λ hfs also exhibit the required dependence on symmetry: for s-$1\cdot^-$, $\Delta a = 1.22$; for a-$1\cdot^-$, $\Delta a = 0.44$; for $2\cdot^-$, $\Delta a = 0.50$. Finally, $\bar{a}$ (both calculated and observed) is abnormally large for s-$1\cdot^-$ in comparison to the acyclic, o-xylene case. The β (i.e., methyl) hfs in $3\cdot^-$ is only 2.0 G; adjusting for the different

1   2   3
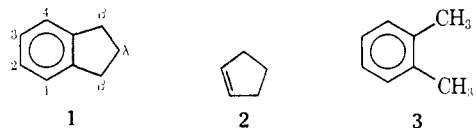
$\langle \cos^2 \theta \rangle$ in $3\cdot^-$ and s-$1\cdot^-$ raises this to 2.53 G. Consideration of spin density differences merely heightens the constrast. Therefore in the s species, specifically, $a^{\beta,\lambda}_{eq}$ are being selectively and greatly enlarged and, conversely, are attenuated in the two a species.

Homohyperconjugation explains these observations fully, fluently, and uniquely. Structures **4** and **5** illustrate the overlap in s-$1\cdot^-$ and a-$1\cdot^-$, respectively. One notes simply that hyperconjugative (1,2) and homohyperconjugative (1,3) overlap reinforce in **4** and interfere in **5**. The same applies for the γ-protons. That the effect is greater with an equatorial than an axial bond reflects more efficient σ–π overlap with the back lobe of an equatorial sp³ orbital than overlap with an axial orbital. Semidione, **6**, is an important

4   5   6
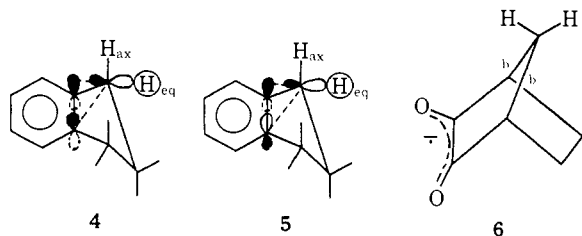
(1) Bond lengths and angles were adopted from M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, **74**, 1104 (1970).

precedent for stereospecificity in long range interactions.[2] The effect has also previously been seen in nonrigid systems and equatorial selectivity demonstrated.[3,4] However, s-$1\cdot^-$ constitutes a more unambiguous example of direct (through space) 1,3 overlap. In previous examples, such as $6\cdot^-$, bonds b are nonorthogonal to the π system and potentially provide an *indirect* (through bond) route to long range coupling.

An estimate of the magnitude of the energy perturbation in s-$1\cdot^-$ is not available, but whatever its magnitude, it is clear that at least three relatively strong 1,3 overlaps are present in the molecule and exert amazingly large effects on its spin and charge density distributions. Finally, the important effect of these findings upon esr based conformational analysis should not be overlooked.

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(4) G. A. Russell and A. Mackor, *J. Amer. Chem. Soc.*, **96**, 145 (1974).

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Quantitative Aspects of 1,3 p–σ Overlap across a Cyclobutane Ring in Anion Radicals

Sir:

1,3-Interactions in the indane anion radical engender quite dramatic effects on its spin and charge density distributions.[1] Cyclobutane rings, having shorter 1,3 C–C distances, should sustain 1,3-interactions of even greater magnitude. Esr data on the series of cyclobutenoid radicals **1–5**$\cdot^-$ confirm this expectation and permit the first quantitative experimental evaluation of the efficiency of 1,3 p–σ overlap relative to 1,2 overlap.

Recent results have revealed abnormally large esr hfs for **1–3**$\cdot^-$.[2] Although cyclobutene methylenes, on the basis of their dihedral angle, should have hfs *ca.* 60% greater than freely rotating (e.g., methyl) protons, the values of a_{CH_2} for **1**$\cdot^-$, **2**$\cdot^-$, and **3**$\cdot^-$ exceed a_{CH_3} of the o-xylene (**6**$\cdot^-$), 2,3-dimethylnaphthalene (**7**$\cdot^-$), and 2,3-dimethyl-1,3-butadiene (**8**$\cdot^-$) anion radicals by 165,

1   2   3   4

5   6   7   8
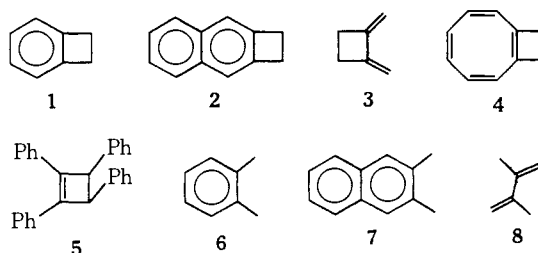
244, and **538**%, respectively. Since the spin densities at, e.g., positions 2–5 of **1**$\cdot^-$ are not decreased at all relative

(1) N. L. Bauld and F. R. Farr, *J. Amer. Chem. Soc.*, **96**, 5633 (1974).
(2) N. L. Bauld, F. R. Farr, and G. R. Stevenson, *Tetrahedron Lett.* 625 (1970).

to the comparable positions in $6 \cdot^{-}$ (cf. the α hfs), the effect could not even qualitatively be attributed to increased spin density at, e.g., positions 1 and 6 in $1 \cdot^{-}$, relative to those same positions in $6 \cdot^{-}$. Noting that the odd electron in each of $1-3 \cdot^{-}$ occupies a symmetrical orbital just as in the case of the indane radical the impressive enhancement of a_{β} in these three species must surely also be attributed to 1,3 p–σ interactions of very considerable potency.

Systems $1-3 \cdot^{-}$ are exceptionally well constituted for a quantitative treatment of the relative magnitudes of 1,3 vs. 1,2 p–σ overlap. Equation 1 is an elaborated version

$$a_{CH_2} = B_2(c_i \cos \theta_i + \lambda c_j \cos \theta_j)^2 \quad (1)$$

of Whiffen's equation[3] giving the hfs of a proton engendered by its interactions with spin from two sites (i and j) in terms of the MO coefficients c_i and c_j of the singly occupied MO, the dihedral angles θ_i and θ_j, and the relative overlap efficiency λ of the two interactions. In the present case the overlap with site i is 1,2 and that with site j is 1,3. Further, in the present instances $c_i = \pm c_j$, $\theta_i = 26.5°$, and $\theta_j = 0°$, thus leading to eq 2.

$$a_{CH_2} = B_2 c_i^2 (0.89 \pm \lambda)^2 = B_2 \rho_i (0.89 \pm \lambda)^2 \quad (2)$$

The values of a_{CH_2} are experimental; the values of $B_2 \rho_i$ were determined as follows. First, an approximate $B_2 \rho_i$ was obtained from the a_{CH_3} of the appropriate methyl analog $6-8 \cdot^{-}$ and the simple relation $a_{CH_3} = {}^1/_2 B_2 \rho_i$. Then differences in spin distribution between $1-3 \cdot^{-}$ and $6-8 \cdot^{-}$ were corrected for by subtracting the sum of the α hfs of the olefinic or aromatic protons at unsubstituted positions of $1-3 \cdot^{-}$ from the corresponding sum for $6-8 \cdot^{-}$ and adding this difference to the approximate $B_2 \rho_i$. Equation 2 can then be solved independently for λ for each of the three systems ($1-3 \cdot^{-}$). For $1 \cdot^{-}$, $a_{CH_2} = 5.30$ G, $B_2 \rho_i$ (approx) = 4.00 G, $B_2 \rho_i$ = 3.84 G, and $\lambda = 0.31$. For $2 \cdot^{-}$, $a_{CH_2} = 5.85$, $B_2 \rho_i$ (approx) = 3.50, $B_2 \rho_i$ = 4.04, and $\lambda = 0.31$. For $3 \cdot^{-}$ $a_{CH_2} = 7.65$, $B_2 \rho_i$ (approx) = 4.00, $B_2 \rho_i$ = 5.12, and $\lambda = 0.33$. These three values agree reassuringly well; the value $\lambda = 0.32$ has been adopted for further use. In conclusion, at the prevailing 1,3 C–C distances in cyclobutanes $1-3 \cdot^{-}$, optimal ($\theta_i = 0°$) 1,3 p–σ overlap is 0.32 as efficient as optimal ($\theta_i = 0°$) 1,2 p–σ overlap.

That 1,3 p–σ overlap is indeed the correct explanation for the observed enhancement in $1-3 \cdot^{-}$ is also vividly attested by results from the anion radical of bicyclo[6.2.0]deca-1,3,5,7-tetraene ($4 \cdot^{-}$). As with parent cyclooctanetetraene (COT), s-$4 \cdot^{-}$ and a-$4 \cdot^{-}$ are degenerate in the HMO approximation. From eq 2, their respective hfs should be 9.37 and 2.05 G. This greater than fourfold disparity is, incidentally, solely the result of 1,3 overlap. A rapidly equilibrating 50:50 mixture of s-$4 \cdot^{-} \rightleftarrows a$-$4 \cdot^{-}$ should have $a_{CH_2} = 5.71$ G. The result is, interestingly, that the 1,3 effect is exactly expunged, giving an ideal model for cyclobutyl behavior in the absence of the 1,3 effect. The experimental value of $a_{CH_2} = 5.40$ G (electrochemical, acetonitrile, n-Bu_4NClO_4, ambient) is in relatively good agreement. The enhancement of 68% compared to the free rotation value is virtually exactly that predicted for a purely conformational effect. The olefinic protons in $4 \cdot^{-}$ are characterized by $a_H = 3.25$ G (6 H). The similarity of this value

to that for COT (3.21 G) assures the absence of significant ring spin density differences between the two systems.

An antisymmetric anion radicals, that of cis-1,2,3,4-tetraphenylcyclobutene ($5 \cdot^{-}$), was also investigated. Here, interference between 1,3 and 1,2 overlap should and does engender an abnormally low hfs. The hfs of $5 \cdot^{-}$ (K^+, THF, $-60°$) are 4.25 (4 H, $2p$ + 2 saturated methines), 2.78 (2 H, ortho), 2.15 (2 H, ortho), 0.75 (2 H, meta), and 0.55 (2 H, meta). The dimethyl analog was not studied in this instance, but $B_2 \rho_i$ could still be obtained, as follows. The sum of all observed phenyl ring hfs in $5 \cdot^{-}$ (taking a_m as positive and $a_{o,p}$ as negative) was subtracted from an assumed total splitting of 27 G (tantamount to assuming $Q_\alpha = -27$). This difference was divided by two to obtain a_α resulting from spin density at each of the benzylic carbons in the stilbene-like π system. Assuming $Q_\beta = 27$, this is also the free rotation value of a_β in $5 \cdot^{-}$, and is thus equal to $^1/_2 B_2 \rho_i$. Substituting the value of $B_2 \rho_i$ thus derived (11.6) into eq 2 then generates the following interesting predictions. Hypothetical s-$5 \cdot^{-}$ should have $a = 16.8$ G; $a = 9.3$ should obtain for a purely conformational effect (negligible 1,3 interaction); a-$5 \cdot^{-}$, the experimental species, should have $a = 3.7$ G. The agreement (with 4.25 G) is only moderately good, but the qualitative effect of interference is clearly evident. It seems likely that the phenyl rings in $5 \cdot^{-}$ are actually not instantaneously equivalent, thus causing $|c_i| \neq |c_j|$ and slightly diminishing the effect of the 1,3-interaction.

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Photochemical and γ-Ray-Induced Reactions of Nucleic Acid Constituents. Suppression of the Reactivity of Pyrimidines in the Presence of Purines

Sir:

We have shown recently that some photochemical reactions of nucleic acid bases in partially aqueous solutions are selective for purines.[1] The selectivity has been examined in reactions of mixtures of the pyrimidines and purines or their nucleosides with 2-propanol, employing light of $\lambda > 290$ nm and di-*tert*-butyl peroxide [$(t\text{-}BuO)_2$] as a photoinitiator. In these reactions uracil and its derivatives yield 6-α-hydroxyalkyl-5,6-dihydrouracil (I), thymine undergoes substitution at the C-5 methyl group to yield II, while purines give the appropriate 8-α-hydroxyalkyl derivatives (III). Irradiation of mixtures of purines and pyrimidines led to the predominant formation of the purine photoproducts. We wish to report that this decrease in the reactivity of the pyrimidines is due to the presence of the purines and that such an effect is of a more general scope, as the presence of purines also affected the extent of the photodimerization of pyrimidine bases.

We found that the quantum yields for the formation of the pyrimidine–alcohol photoproducts were usually

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