deformation, $q_e = 0.438$ Å, is calculated from the observed mean value, $\langle q \rangle = 0.427$ Å, taking the temperature to be that of the diffraction nozzle, 298°K. In comparsions with puckering values calculated from model force fields ("molecular mechanics"), the quantity q_e corresponding to minimum potential energy is the appropriate parameter to consider.

The earlier thermodynamic, model force field, and spectroscopic puckering displacements of 0.48 Å were in remarkable accord with each other and seemed to settle the matter. It now appears, however, that the physically significant mean and equilibrium displacements, $\langle q \rangle$ and q_e, are appreciably smaller than the effective displacements determined previously. The revised puckering is also somewhat less than that found in the D ring of steroids thus far investigated by X-ray diffraction,[48] the five-membered ring in this case being *trans*-fused to the chair form of a six-membered ring. Supporting the revised values are new infrared measurements by Hirakawa[49] and electron diffraction studies by Kuchitsu.[50] In the infrared work, a systematic, anharmonic trend was noted which led to the extrapolated value of $q_e = 0.45$ Å, in satisfactory agreement with both electron diffraction values and with the newer model force field calculations of Lifson and Warshel. The improved experimental values and physical interpretation should be helpful in establishing better model force fields for conformational calculations.

Acknowledgment. We are indebted to the Michigan Computing Center for a generous allowance of computing time, and to Professor Kuchitsu for making available his infrared and diffraction results prior to publication.

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Application of Simple Theoretical Methods to the Solution of Chemical Problems. III. Hyperconjugation *vs.* 1-3 Conjugation as the Mechanism for Electron Spin Delocalization to β Fluorines[1]

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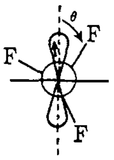
Contribution from the Department of Chemistry, New York University, University Heights, Bronx, New York 10453. Received October 28, 1969

Abstract: The dependence of the β-fluorine hyperfine splitting constant (hfsc) on the dihedral angle, θ, is studied. The experimental nitrogen and fluorine hfsc's for a series of *t*-butylperfluoroalkyl nitroxides were determined, and it was found that the fluorine hfsc decreases as θ increases. INDO calculations on CF_3-NO-CF_3 showed a maximum fluorine hfsc at θ = 0°. It is concluded that 1-3 conjugation between the p_z orbital on nitrogen and the p orbital of fluorine which is perpendicular to the plane formed by N, C, and F is not a significant mechanism of spin delocalization, but that the results are interpretable in terms of hyperconjugation.

The effect of geometry on the magnitude of epr hyperfine splitting constants (hfsc's) must be considered in evaluating the relative importance of the various possible spin delocalization mechanisms. For α and β hydrogens these mechanisms have been quite well established[2,3] and for more distant hydrogens certain empirical rules have been developed.[4]

In this paper we direct our attention to fluorine hfsc's with particular emphasis on the dependence of the β-fluorine hfsc upon the dihedral angle, θ, between the C-F bond and the π system containing the unpaired electron. This subject is of importance because there are two major mechanisms which have been proposed to account for the interaction between the β fluorines and an unpaired electron. The first is hyperconjugation, by which we mean the interaction of the electron on atom 1 with the electrons in the C_2-F σ bond so as to produce an excess of α spin at the fluorine nucleus. This mechanism, which is analogous to that proposed for β-hydrogen hyperfine interactions, would result in a maximum coupling constant at θ = 0°. These β-hydro-



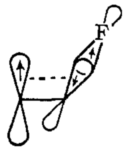


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Table I. Nitrogen and Fluorine hfsc's (G) for *t*-Butyl Nitroxides

Radical	a^N	$a_\beta{}^F$	$a_\gamma{}^F$
$C_4H_9NOCF(CF_3)_2$	12.08 ± 0.1	2.16 ± 0.03	2.16 ± 0.03
$C_4H_9NOCF_3$	11.8 ± 0.3	11.8 ± 0.3	
$C_4H_9NOCF_2CF_2CF_3$	10.94 ± 0.1	18.58 ± 0.2	
$C_4H_9NOCF_2(CF_2)_5CF_3$	11.10 ± 0.1	17.95 ± 0.2	

gen hfsc's are related to θ by the Heller–McConnell relationship,[3] $a_\beta{}^H = B\rho \cos^2 \theta$. On the other hand, support has been given to a mechanism of 1–3 conjugation[5] between the p_z orbital on atom 1 and that lone pair in the p orbital of fluorine which is perpendicular to the plane formed by atom 1, C_2, and the fluorine. Maximum interaction for this mechanism would be expected for $\theta = 90°$.

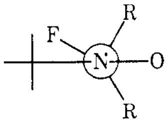
Strom and Bluhm[7] have discussed 1–3 conjugation with reference to the epr spectra of bis(trifluoromethyl) nitroxide (I) and compound II. They found that the β-fluorine hfsc for I was considerably smaller than that observed for II (8.26 *vs.* 13.79 G) and pointed out that

$$\underset{\text{I}}{CF_3NOCF_3} \qquad \underset{\text{II}}{CH_3O_2CCF_2CF_2NOCF_2CF_2CO_2CH_3}$$

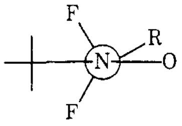
on substitution in the acyclic semidiones the reverse effect is observed.[8] By assuming similar conformational preferences in these two systems they concluded that the angular dependence of the β-fluorine hfsc was the reverse of that for β hydrogens and therefore proposed that the 1–3 conjugation mechanism was predominant. Scheidler and Bolton have used the temperature dependence of the epr spectrum of I[9] as further support for this mechanism[10] and Danner and Maki[12] have shown that the temperature dependence of the hexakis(trifluoromethyl)benzene anion could also be consistent with 1–3 conjugation.

Gerlock and Janzen,[13] on comparing the β-fluorine hfsc's for some cyclic and acylic perfluoroketyls, concluded that the hfsc increased as θ decreased below 45° and suggested as a compromise that the coexistence of two mechanisms may yield a minimum interaction at some angle between 0 and 90°.

We now present evidence which indicates that the maximum interaction between the unpaired electron and a β fluorine occurs near $\theta = 0°$ in the fluoroalkyl nitroxides. We have studied a variety of *t*-butylperfluoroalkyl nitroxides in which it was expected that the *t*-butyl group would force the radical to assume predominantly the conformations III and IV. Table I shows the experimental fluorine and nitrogen hfsc's for these radicals. The results listed in this table show that the fluorine hfsc decreases as the expected θ increases. We were thus led to reexamine the assumption concerning the preferred conformations of the perfluoroalkyl nitroxides. It appears to us that the conformational analogy between the neutral nitroxides and the negatively charged semidiones[7] may have been an unfortunate one. We suggest that acyclic aldehydes and ketones would be more appropriate models for the nitroxides as they possess one trigonal atom and have no overall charge. Electron diffraction[14,15] and microwave[16] studies in the gas phase as well as nmr studies in solution[17,18] of acyclic aldehydes and ketones are all in agreement that the preferred conformation of an ethyl group is one in which θ is less than 45° as in structure V.



III



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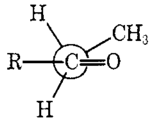

V

In the light of these results we question the importance of the 1–3 conjugation mechanism for spin delocalization to β fluorines. To examine this problem further we have performed extensive calculations on CF_3NOCF_3 to determine the most stable geometry and to establish the variation of the fluorine 2s orbital spin density (and therefore the hfsc) with dihedral angle.[11] We adopted an SCF prodecure for our calculations by making the INDO approximation.[19] The geometry of lowest energy was found to correspond to bond lengths O–N = 1.26, N–C = 1.41, and C–F = 1.34 Å, and bond angles N–C–F = 111 and C–N–C = 126°, with the O–N bond making an angle of *ca.* 10° to the C–N–C plane.[1] However, for greater generality, and since our calculations show a very small barrier to inversion at nitrogen, we have used a planar configuration to determine the fluorine 2s orbital spin density as a function of the angle θ. These results are plotted in Figure 1. The shape of the curve in this figure is not greatly affected by deviations of the radical from planarity. It will be noted that a negative spin density is calculated at the fluorine nucleus for $\theta = 90°$. Furthermore, the p_z orbital on fluorine is found to have a spin density of 0.0000. This result is therefore totally opposed to any interpretation in terms of 1–3 conjugation as a mechanism of spin delocalization.

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(5) This mechanism has been discussed by Sheppard[6] in relation to the acidities of substituted benzoic acids.

(6) W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).

(7) E. T. Strom and A. Bluhm, *Chem. Commun.*, 115 (1966).

(8) E. T. Strom, G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, **69**, 2131 (1965).

(9) P. J. Scheidler and J. R. Bolton, *J. Amer. Chem. Soc.*, **88**, 371 (1966).

(10) However, this has more recently been questioned.[1,11]

(11) K. Morokuma, *J. Amer. Chem. Soc.*, **91**, 5412 (1969).

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(15) L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Lett.*, 705 (1964).

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(17) (a) G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965); (b) R. J. Abraham and J. A. Pople, *Mol. Phys.*, **3**, 609 (1960).

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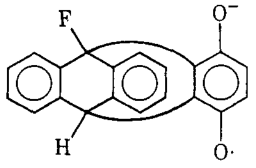
The results of Figure 1 imply that for fluorine there may exist a relation of the form

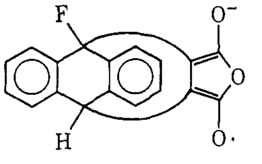
$$a_\beta^{F} = \rho_\pi(B_0 + B_1 \cos^2 \theta) \qquad (1)$$

as is also the case for β-hydrogen hfsc's. If this is so, then by using the observed experimental average value of $a^F = 8.76$ G for I and by assuming that a^F is directly proportional to the calculated 2s orbital spin density we obtain

$$B_0 = -6.2 \text{ G} \qquad B_1 = 114.9 \text{ G}$$

Recently Kosman and Stock[20] have reported the epr spectra of VI and VII in which were observed considerable hyperfine splitting from fluorine atoms lying in the nodal plane of the π orbital containing an unpaired electron ($\theta = 90°$). It would be of interest to know the sign of these hfsc's as analogy with our calculations predicts a negative value.


VI


VII

In order to estimate the spin density in the π system of VI we made use of the methyl proton hfsc obtained for 2,3-dimethylsemiquinone,[21] $a_{\mathrm{CH_3}}^{\mathrm{H}} = 1.714$ G, and a reasonable value of $Q_{\mathrm{CCH_3}}^{\mathrm{H}} = 23$ G.[22] These values result in $\rho_\pi = 0.075$. Substitution of this value into eq 1 results in a calculated value of $a^F = -0.47$ G for VI (*cf.* ±0.85 G, experimental). Similarly, if ρ_π is assumed to be 0.19[23] in VII then a^F is predicted to be -1.18 G (*cf.* ±1.26 G, experimental). This excellent agreement may be somewhat fortuitous, however, owing to the close proximity of oxygen and fluorine in VI and VII and to the lack of more appropriate models.

From the evidence cited above, we conclude that the predominant mechanism of spin delocalization to β-fluorine atoms in the fluoroalkyl nitroxides is hyperconjugation and not 1-3 conjugation as defined. There also appears to be no reason why this conclusion cannot be applied to systems other than nitroxides.[24]

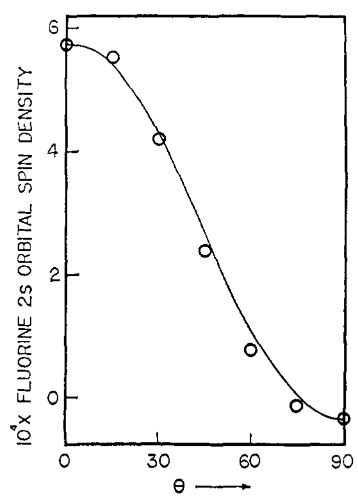


Figure 1. The variation of the β-fluorine 2s orbital spin density as a function of the dihedral angle θ between the C–F bond and the p_z orbital on nitrogen.

Acknowledgment. We wish to thank Professor Stock for allowing us to examine his manuscript prior to publication and Professors Jackman and Janzen for most valuable discussions. All calculations were performed in the Courant Institute of Mathematical Sciences at New York University on a CDC 6600 computer, and this work was supported by Grant No. PRF 1190-G1 from the Petroleum Research Fund administered by the American Chemical Society. V. L. V. wishes to acknowledge support from an NDEA Title IV fellowship.

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(24) Note Added in Proof. Several pertinent results have appeared in the literature since this paper was submitted for publication. K. J. Klabunde, *ibid.*, **92**, 2427 (1970); E. G. Janzen, B. R. Knauer, J. L. Gerlock, and K. J. Klabunde, *J. Phys. Chem.*, **74**, 2037 (1970); and J. L. Gerlock, E. G. Janzen, and J. K. Ruff, *J. Amer. Chem. Soc.*, **92**, 2558 (1970), have reached conclusions similar to those given in this paper. On the other hand, it is interesting to note that D. Holz, A. Streitwieser, and R. G. Jesaitis, *Tetrahedron Lett.*, 4529 (1969), have concluded that anionic hyperconjugation is a minor factor in the stabilization of perfluoroalkyl anions. There is, of course, no necessity that hyperconjugation should contribute equally to the two phenomena, however.

Electron Transfer and Agglomeration in the Systems Phenanthrenequinone, Acenaphthenequinone, Their Dianions, Radical Ions, and Dimers

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State University College of Forestry at Syracuse University,
Syracuse, New York 13210. *Received January 10, 1970*

Abstract: The kinetics of the electron transfer from phenanthrenequinone dianion (PQ^{2-},$2Na^+$) to the parent quinone (PQ) was investigated. The reaction produces a paramagnetic "red" species ($PQ\cdot^-$,Na^+) which dimerizes in a subsequent slower step into a diamagnetic "green" species (D^{2-},$2Na^+$). The results are described by the equations (PQ^{2-},$2Na^+$) + (PQ) $\rightleftharpoons$ 2($PQ\cdot^-$,Na^+) ("red"), $k = 2\text{–}3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$; and 2($PQ\cdot^-$,$Na^+$) ("red") $\rightleftharpoons$ (D^{2-},$2Na^+$) ("green"), $k \sim 10^4\ M^{-1}\ \text{sec}^{-1}$. However, the free $PQ\cdot^-$ ions do not dimerize. The spectra of all the pertinent species were examined and fully recorded. The green species further agglomerate forming $(D^{2-},2Na^+)_2$, etc., which are spectrally indistinguishable from (D^{2-},$2Na^+$). The thermodynamics of the reversible dimerization and tetramerization was studied quantitatively. The nature of the dimer was discussed and a tentative structure for it was proposed. The acenaphthenequinone system behaves similarly, its comprehensive study being prevented by technical reasons. The "blue" species, described recently by some investigators and believed to be the acenaphthenequinone dianion (ACQ^{2-}), probably is the diamagnetic dimer of $ACQ\cdot^-$,Na^+. The genuine spectrum of ACQ^{2-},$2Na^+$ was recorded and shown to be unmistakably different from that of the blue species.

Dimerization of ion pairs, or their association into still larger aggregates, is a well-known phenomenon caused by the Coulombic attractions.[1] Such forces, we believe, may facilitate the formation of π–π bonds between suitable partners and yield associates having properties fundamentally different from those of the electrostatically bonded dimers of ion pairs. The salts of radical ions derived from phenanthrenequinone (PQ) and acenaphthenequinone (ACQ) seem to form such π–π bonded dimers.

Experimental Section

9,10-Phenanthrenequinone and 9,10-acenaphthenequinone were acquired commercially and purified by crystallization and vacuum sublimation. The solutions of quinones were prepared on a high-vacuum line, and their concentrations were determined spectrophotometrically. Solutions of phenanthrenequinone were found to be light sensitive, their yellow color rapidly disappearing on exposure to daylight. Therefore, they had to be stored and handled in darkness.

Results

On contact with sodium mirror the quinones are reduced, the reaction being completed after a day or two. Titration with HCl of samples withdrawn after completion of the reduction demonstrated that 2 equiv of sodium reacted with each mole of quinone, *i.e.*, dianions of the quinones were produced. The reduction of phenanthrenequinone by magnesium mirror in THP led to a product possessing only 1 equiv of base/mol of quinone. Apparently, no dianion of quinone is formed with Mg. The dianions are diamagnetic, but paramagnetic species are formed on the addition of the respective quinones.

Reactions Involving Phenanthrenequinone (PQ). The optical spectra of PQ and of its dianion (PQ^{2-},$2Na^+$) are shown in Figure 1. Their shape is not affected either by dilution or by variation of temperature. Addition of a slight excess of PQ to PQ^{2-},$2Na^+$ drastically changes the spectrum; the characteristic 381-nm peak disappears. However, as was first shown by Maruyama,[2] the shape of the resulting spectrum depends on temperature and on the concentration of the product. These spectral variations were investigated by recording the absorption of the relevant solution, kept in an evacuated optical cell which was immersed in a dewar equipped with optical windows and maintained at the desired temperatures. The concentration was then varied by pouring a fraction of the investigated solution into a calibrated side arm attached to the main container and then back-distilling the solvent.

The spectrum indicated that only one species ("red") is present in $10^{-5}\ M$ solution at 25°, while in $10^{-3}\ M$ solution below −30° another species ("green") is the only component. Their spectra are displayed in Figure 2. $\lambda_{\max}$ of the red species is at 499 nm (ϵ 0.46×10^4), and this species does not absorb light of $\lambda > 600$ nm, while the green species exhibits $\lambda_{\max}$ at 670 (ϵ 0.49×10^4) and 440 nm (ϵ 0.46×10^4). Accordingly, the OD at 499 nm is a linear function of the OD at 670 nm and of the total concentration, C, of the investigated species; *i.e.*

$$\mathrm{OD}(499) = [(\epsilon_{499,\mathrm{G}} - \epsilon_{499,\mathrm{R}})/\epsilon_{670,\mathrm{G}}]\mathrm{OD}(670) + \epsilon_{499,\mathrm{R}}C$$

Such a linear relation is fulfilled in THP over the whole accessible range of concentrations and temperatures; however, in THF some curvature was noted at the lowest temperatures and for the highest concentrations. Examination of the spectra revealed that in THF, but not in THP, the absorption maximum of the green species shifts to 660 nm as the temperature is lowered to −80°. This may account for the observed deviations.

On dilution, the equilibrium is displaced toward the red (R) species, as illustrated in Table I. In THP the plots of log [G] (G = the green species) *vs.* log [R] are linear and mutually parallel at each temperature, their slopes being equal to 4 (see, *e.g.*, Figure 3). Ap-

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[1] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **55**, 2387 (1933).

[2] K. Maruyama, *Bull. Chem. Soc. Jap.*, **37**, 553 (1964).