

If we assume that the protons have the values indicated in IIa, which are within the normal range expected for each type, then the isomerization IIa \rightleftharpoons IIb would give rise to a spectrum consisting of two areas of absorption at τ 4.1 and 5.5 in agreement with what is observed.

Such a process alone, of course, would not account for the single peak observed at room temperature, suggesting that at least one other process must also be occurring at the higher temperature. Several such processes can be considered: (a) a mechanism in which one double bond in I displaces another olefinic ligand, three such rapid reactions could then render all eight protons equivalent; (b) the $\text{Fe}(\text{CO})_3$ group moves from the center of one C-C bond to the next, in which case seven such reactions would render the protons equivalent; this mechanism would also require a double bond shift of the olefinic bonds; (c) the $\text{Fe}(\text{CO})_3$ group moves to the center of the ring to form a relatively unstable symmetrical complex and then returns to the diene formulation; depending on the nature of the ring in the symmetrical species this particular mechanism may or may not result in a shift of the double bonds.

The symmetry and multiplicity of the peaks observed in the spin-decoupling experiments with carbomethoxycyclooctatetraene-iron tricarbonyl at -55° indicate that the rearranging process is such that, on the average, the ligand possesses a plane of symmetry. Therefore, at least one mechanism involving a double bond shift (possibly b) must be operating at this temperature. With such a process, the chemical shifts employed in IIa would then lead to a single peak at τ 4.8, which again is what is observed.

We consider then that at least two types of degenerate valence tautomerism reactions are involved in the rearrangement of I at room temperature. The facility of the process is quite remarkable and is probably related to the size of the metal orbitals involved in the bonding; the orbitals being larger, the bond-making process can be much further advanced before the bond-breaking process begins to be felt in the metal reactions as compared to reactions involving purely carbon-carbon bonds. This would have the effect of lowering the activation energy for the rearrangement of the organometallic species.

(6) We thank the National Science Foundation and the U. S. Army Research Office (Durham) for financial assistance. We also thank Professor M. J. S. Dewar for helpful discussion.

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Fluoronitroaliphatics. I. The Effect of α Fluorine on the Acidities of Substituted Nitromethanes¹

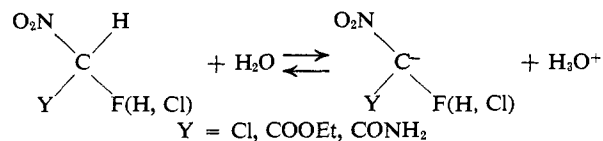
Sir:

Although a number of workers have concluded from deuterium exchange studies that the α -fluorine substituent increases the acidity of polyhaloaliphatic hydrocarbons, but to a lesser extent than α chlorine or α

(1) Presented in part at the Third International Symposium on Fluorine Chemistry, Munich, Sept 1965.

bromine,² direct measurements of C-H acidities in compounds of the type $\text{R}_1\text{R}_2\text{CFH}$ are confined to a single recent communication on fluorodinitromethane.³

We wish now to report ionization constant measurements for a series of substituted fluoronitromethanes as well as their hydrogen and chlorine analogs.



These systems differ from the polyhaloaliphatic hydrocarbons in two important regards: (a) the presence of a nitro group permits ready determination of the ionization constants by spectrophotometric means; (b) the central carbon in the nitrocarbanion is sp^2 hybridized with the negative charge delocalized over the π system formed by the central carbon, the nitro group, and the negative substituent Y.

Listed in Table I are the apparent $\text{p}K$ values for the three series of mononitromethanes,⁴ determined spectrophotometrically in aqueous solutions of ionic strength 0.06, as well as ionization enthalpies and entropies for two of the series as obtained from $\text{p}K$ measurements at 25 and 40° . Also included are literature data for dinitromethane and the halodinitromethanes.⁵

Table I. Apparent Ionization Constants of Substituted Nitromethanes

$\begin{array}{c} \text{O}_2\text{N} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Y} \end{array} \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array}$	$\text{p}K_a$ in water, $\mu = 0.06 \pm 0.01$		ΔH , kcal/mole	ΔS , eu
	$25 \pm 0.1^\circ$	$40 \pm 0.1^\circ$		
Y = COOEt				
X = Cl	4.16			
H	5.75			
F	6.28			
Y = CONH ₂				
X = Cl	3.50	3.56	-1.7	-22
H	5.18	5.15	0.9	-21
F	5.89	5.82	1.9	-20
Y = Cl				
X = Cl	5.99	5.98	0.3	-26
H	7.20	7.16	1.1	-29
F	10.14	9.92	6.3	-25
Y = NO ₂				
X = Cl	3.80			
H	3.57			
F	7.70 (20°) ³			
	7.70 (25°) ⁵			

It may be seen that, while α chlorine in most cases leads to the expected increase in C-H acidity relative to X = H, the effect of α fluorine is in the opposite direction,

(2) J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957); J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956); S. Andreades, *ibid.*, **86**, 2003 (1964).

(3) V. I. Slovetskii, L. V. Okhobystina, A. A. Feinzi'l'berg, A. I. Ivanov, L. J. Biryukova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2063 (1965); The $\text{p}K_a$ reported by these workers in water at 20° corresponds exactly with that observed by Dr. T. N. Hall of these laboratories at 25° .

(4) The synthesis of the fluoronitromethanes will be described elsewhere.

(5) Dinitromethane: R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953); redetermined by Slovetskii *et al.*;³ chlorodinitromethane: T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964); fluorodinitromethane: T. N. Hall, these laboratories, private communication; Slovetskii, *et al.*³

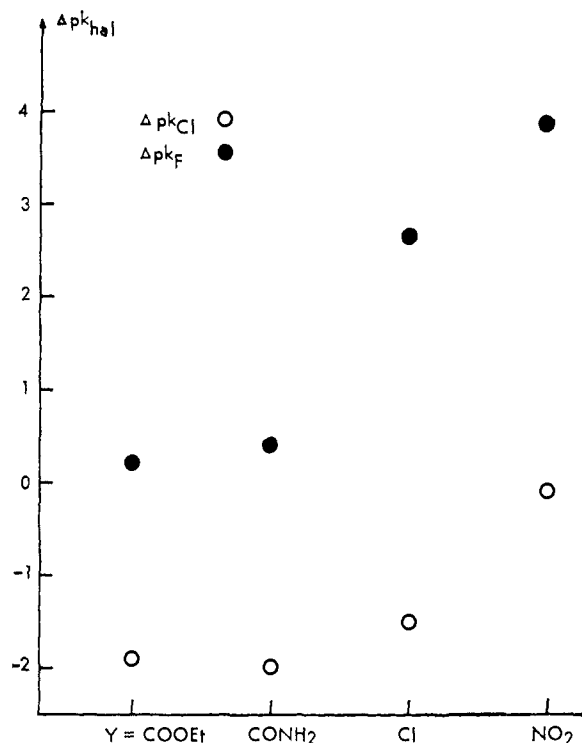


Figure 1. Variation of ΔpK_{hal} with Y.

such substitution causing a decrease in acidity in all four series. Entropy and enthalpy data for the nitroacetamides and chloronitromethanes (similar entropies of ionization within each series) suggest that these pK differences within any one series derive mainly from differing enthalpies of ionization.

It is also evident from the data in Table I that the magnitudes of α -chlorine and α -fluorine influences on pK depend strongly on the nature of the third substituent, Y. Acid weakening by α fluorine increases in the order, Y = COOEt, CONH₂, Cl, NO₂, while acid strengthening by α chlorine decreases in almost the same order. Moreover, in the nitroacetates and nitroacetamides, where fluorine's effects are small, chlorine's effects are large; in the chloronitromethanes the chlorine effect decreases while the fluorine effect becomes larger, and this trend continues in the dinitromethanes where fluorine substitution increases the pK by 4 units while the chlorine effect has become very small.⁶

The latter observations are shown more clearly in Figure 1 where pK differences between the α fluorine and hydrogen compounds, ΔpK_F , and the α chlorine and hydrogen compounds, ΔpK_{Cl} , are plotted for the four series. For the purpose of this comparison, log 2 was added to the pK values of the parent compounds to correct for the presence of two identical hydrogen atoms: $\Delta pK_{hal} = pK_{X=hal} - (pK_{X=H} + 0.3)$.

We assume that the observed acidity differences, ΔpK_F and ΔpK_{Cl} , result in each case from a summation of acid-strengthening and acid-weakening influences exerted by the halogen. Since the acid-strengthening factors, composed mainly of inductive effects, increased anion size with greater dispersal of the negative charge,

(6) It might be argued that the bulky chlorine hinders coplanarity of the nitro groups in the chlorodinitrocarbanion, which might account for the relatively low acidity of ClC(NO₂)₂H. This steric explanation is unlikely, however, as no decrease in acidity is noted with bromodinitromethane.

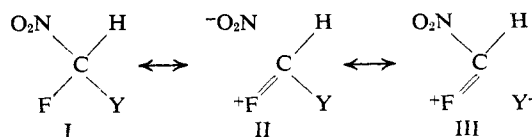
and d-orbital stabilization of the carbanion are not likely to be of sufficiently different magnitudes to effect such changes (inductive effect greater for fluorine; anion size and d-orbital stabilization greater for chlorine), we believe that the differences in sign of ΔpK_F and ΔpK_{Cl} must largely be due to appreciably more effective acid-weakening factors operative in the fluorine compounds.

From the ΔpK plots of Figure 1, changing Y causes parallel changes in the summations of these factors. Rationales for the anomalous acidities of the fluoronitromethanes are consistent with the assumption that the nature of Y has only a nominal influence on the acid-strengthening factors with the more profound influence being exerted on mechanisms whereby the halogen can weaken acidity.

Decreased acidity on replacement of α hydrogen by halogen may result from either stabilization of the unionized acid or destabilization of the carbanion conjugate base. Proximity of fluorine and to a lesser extent chlorine to a π system, such as is present in the nitrocarbanion, has been suggested to lead to repulsion of charge in the π system by the p electrons of the halogen (I- π repulsion⁷). Such would tend to destabilize the fluoronitrocarbanion relative to the chloro- and the chloro- relative to the parent nitrocarbanion. This effect should depend on the charge density on the central carbon which increases on going from the nitroacetates and nitroacetamides to the chloronitromethanes. While this is paralleled by an increase in ΔpK_F , the large effect in fluorodinitromethane is not accounted for.

Hine has suggested that the halogen bond to sp^2 carbon is weaker than to sp^3 carbon because the former is more electronegative, and that this effect, which depends on the square of the electronegativity difference between the atoms involved, is larger for fluorine than for chlorine.⁸ Since such a change to sp^2 hybridization occurs on ionization of the nitromethanes, this would again tend to destabilize the fluoro- relative to the chloro- or parent nitrocarbanion unless the increase in electronegativity of carbon is compensated by a decrease due to the partial negative charge on carbon. While it is not obvious how this effect should vary with Y, one might speculate that it should be largest for fluorodinitromethane where more of the negative charge in the anion is removed from the central carbon than in the mononitro compounds.

Among factors which influence the stability of the free acid, double bond-no bond resonance as formulated by Hine⁹ and, in alternative terms, by Williams¹⁰ should stabilize the fluoronitromethane relative to the chloro- or parent nitromethane because of fluorine's greater ability to share one of its lone pairs in halogen double bonding (canonical structures I-III).



(7) J. Burdon and W. B. Hollyhead, *J. Chem. Soc.*, 6327 (1965), and references cited therein; W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965).

(8) J. Hine and P. B. Langford, *ibid.*, **78**, 5003 (1956).

(9) J. Hine, *ibid.*, **85**, 3239 (1963).

(10) J. F. A. Williams, *Trans. Faraday Soc.*, **57**, 2089 (1961); *Tetrahedron*, **18**, 1477 (1962).

Much of this stabilization would be lost in the anion where the negative charge discourages electron donation by fluorine. Although the importance of such stabilization for ground states has been questioned,¹¹ it predicts correctly in a qualitative manner the variation in magnitude of ΔpK_{hal} with Y. The relative contribution of III to the resonance hybrid should increase with the ability of Y to form a stable anion; chlorine and nitro being much better leaving groups than carbethoxyl and carbamyl, stabilization of the un-ionized species should be greatest for Y = Cl and NO₂.

Slovetskii and co-workers³ attribute the lowered acidity of fluorodinitromethane to a positive mesomeric effect of fluorine and consider also the possibility of intramolecular hydrogen bonding to fluorine.

(11) S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964), footnote 23.

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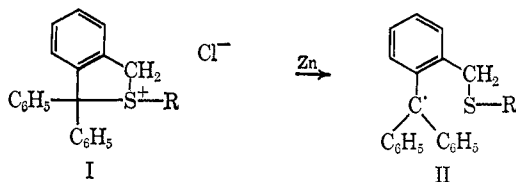
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Observation of Conformational Isomers by Electron Nuclear Double Resonance

Sir:

Conformational isomerism and rotation barriers have been extensively studied by nuclear magnetic resonance (nmr) methods,¹ and to a lesser extent by electron paramagnetic resonance (epr) techniques.² Epr can be used to investigate much faster processes than nmr, since line separations are typically 10⁴ larger, but the technique is somewhat limited by the complexity of epr spectra for large molecules of low symmetry.

Electron nuclear double resonance (ENDOR) of free radicals in solution^{3,4} permits the direct observation of hyperfine couplings of much more complicated molecules than can be analyzed by epr. We wish to report an example of the use of endor to detect rapid conformational equilibration in a derivative of the triphenylmethyl radical.



The radical IIa was prepared by treating a 10⁻³ M solution of Ia⁵ in ethylbenzene with zinc pellets, and the endor spectrum (Figure 1) was examined over the temperature interval -80 to -20°.

(1) Cf. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965, Chapter 9; C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965).

(2) Cf. T. M. McKinney and D. H. Geske, *J. Chem. Phys.*, **44**, 2277 (1966).

(3) J. S. Hyde and A. H. Maki, *ibid.*, **40**, 3117 (1964); J. S. Hyde, *ibid.*, **43**, 1806 (1965).

(4) J. S. Hyde, to be published.

(5) Unpublished work of R. Breslow, L. Kaplan, and D. LaFollette.

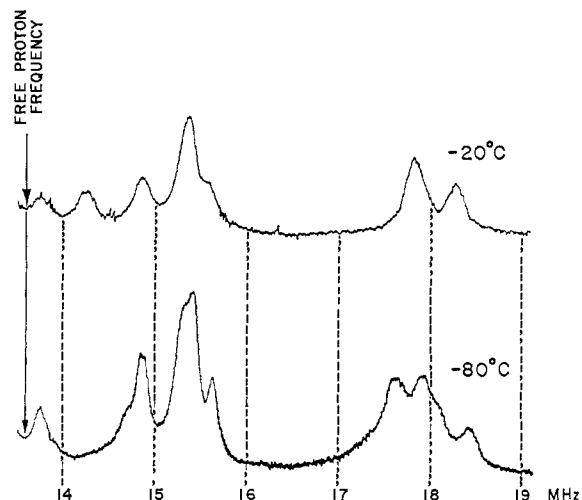


Figure 1. The proton endor spectrum of IIa at -80 and -20°.

For every class of equivalent protons two endor lines are found, one for the local field at the protons from the coupled electron parallel to the applied field and one with these fields antiparallel. Customarily, we begin the scan of the nuclear radio frequency at the free proton frequency and scan to higher frequencies, recording only one line for each class of equivalent protons. About 11 different couplings can be resolved at -80°. The portion of the spectrum between the free proton frequency and 14.7 MHz arises from the methylene and methyl protons of the pendant group. We have not made a detailed assignment of the other lines in the spectrum, but addition of the pendant group to one phenyl ring probably decreases the couplings to the protons on that ring and increases the couplings to the protons on the other two phenyl rings relative to the unsubstituted triphenylmethyl radical. The lines between 17.5 and 18.5 MHz are thus assigned tentatively to the *ortho* and *para* protons of the unsubstituted phenyls.

In the temperature interval between -80 and -20°, several pronounced changes in the character of the spectrum are observed. Lines at 17.9 and 17.7 MHz collapse to a single line at 17.8 MHz; lines at 18.4 and 18.2 MHz collapse to a line at 18.3 MHz; a line at 14.7 MHz evident as a shoulder has disappeared; and a new line is found at 14.25 MHz.

The endor spectrum of the deuterated compound IIb also was studied between -80 and -20°. The nuclear precession frequency of the deuteron differs so substantially from that of the proton that the deuterated sites are eliminated from the proton endor display. At -20° the endor spectrum of IIb is essentially identical with that of IIa except that the line below 14 MHz is missing. The methyl hyperfine coupling is thus 325 kHz.

The next weakest coupling is with the methylene group, producing the line at 14.25 MHz at -20°; at -80° this has split symmetrically into lines at 13.8 and 14.7 MHz. While in principle this simply shows that there are two equally populated methylene proton environments, there can be little doubt that what has been resolved here is the interconversion of left-hand and right-hand propeller conformations of the radical II. In any one of these the two protons of a methylene