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THE ELECTRONIC EFFECT OF THE TRICYANOMETHYL GROUP BY ^{19}F NUCLEAR MAGNETIC RESONANCE. A CONSEQUENCE OF ALTERNATING INDUCED CHARGE (AIC).

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Sheppard and co-workers[1] have employed Taft's methodology[2] in order to assess the electronic effect of the tricyanomethyl group. Besides demonstrating that this substituent is one of the strongest neutral inductive electron-withdrawing groups known ($\sigma_I = 0.98$), the analysis indicated quite unexpectedly that the substituent has a negligible resonance effect ($\sigma_R^o = \pm 0.02$). The major significance of this result is that it militates against the π-inductive effect being the electronic mechanism by which a trifluoromethyl group polarizes an adjacent aromatic system [1].

More recently[3], we disclosed that the fluorophenyl tag used in the Taft approach can be bedevilled by certain factors (substituent-induced structural effects, substituent-probe interactions, and σ- and π-electron effects), depending on the nature of the substituent under investigation, which are readily circumvented by employing 6- and 7-substituted β-fluoronaphthalenes (6β and 7β dispositions respectively) and their respective dual substituent parameter (DSP) correlative equations. In the light of this relevation, and since the electronic effect of the trifluoromethyl group is still a subject of much interest and continuing controversy,[4,5] we believed a re-examination of the tricyanomethyl group utilizing the fluoronaphthyl probe was warranted. Accordingly, we have synthesized and measured the ^{19}F nmr spectra[6] of 6- and 7-$C(CN)_3$-substituted β-fluoronaphthalenes as well as 1-fluoro-4-tricyanomethylnaphthalene (4α disposition). The results are shown in the table.

Table ^{19}F Substituent Chemical Shifts (SCS)[a,b,c] for $C(CN)_3$-Substituted Fluoronaphthalenes.

Disposition	Solvent	
	Benzene	DMF
6β	-5.22	-4.66
7β	-3.89	-3.55
4α	-8.74	-8.76

a. Defined as the difference between the chemical shift of the unsubstituted fluoroaromatic and the substituted fluoroaromatic compound. b. In ppm. c. A negative sign implies deshielding.

Substituent parameters disssected from this data by means of the 6β and 7β DSP correlative[3] equations are as follows: σ_I (benzene) = 0.91; σ_R^o (benzene) = -0.097; σ_I (DMF) = 0.81; σ_R^o (DMF) = -0.098. These parameters can then be employed to calculate SCS [-7.97(ppm;DMF); -8.01(ppm; Benzene)] for the sterically hindered 4α orientation by substitution in the appropriate DSP correlative equations for this disposition.[3]

Several important conclusions follow from these results. Firstly, it is obvious that the substituent parameters are significantly different from those previously determined. Moreover, the fact that the calculated ^{19}F SCS for the 4α orientation are in reasonable agreement with the observed values (Table), given that SCS in this disposition are influenced in a minor way by geometrical factors (approx., 1 ppm downfield)[3], attests to their validity.

Secondly, note that the sign of σ_R^o is *negative*! This suggests that the C(CN)$_3$ substituent has an apparent electron-donating mesomeric effect comparable in magnitude to that observed for CH$_3$(σ_R^o = -0.11)[7] in the neutral ground state. Since possible π-polarisation by the π-inductive effect in terms of induced charges either by the classical σ-inductive model or the alternating induced charge model (AIC)[8] can only be envisaged as an electron-withdrawing influence, the observed result must be ascribed to hyperconjugation. Hence, according to the specific requirements for σ-π conjugation[9], electron-donation by the C(CN)$_3$ group demands that the carbon atom directly attached to the aromatic ring must bear a *formal* negative charge. This induced charge is theoretically respectable only in terms of the AIC model since the classical σ-inductive model predicts the reverse polarity for the interacting σ-bonds which would favour electron-withdrawal involving the anti-bonding molecular orbitals[9] of the C(CN)$_3$ substituent i.e. σ_R^o would be *positive*.

We believe the *negative* σ_R^o value for C(CN)$_3$ is the most convincing experimental evidence to date in support of the AIC model for a saturated carbon chain[10].

Thirdly, an important corollary of the AIC model is that the positive σ_R^o value (0.08; electron-withdrawal)[7] for the trifluoromethyl substituent must have its origin in hyperconjugation and *not* the π-inductive effect. This conclusion obviously follows from a consideration of the induced charges by this model; whereas σ-π conjugation would be manifested by electron-withdrawal, the π-inductive effect would lead to apparent electron-donation. It is important to note that a recent ESCA study of trifluoromethylbenzenes has led to the same conclusion.[5] Thus our suggestion[3] in favour of the π-inductive effect for the CF$_3$ group requires reappraisal along the lines presented here.

References and Notes

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