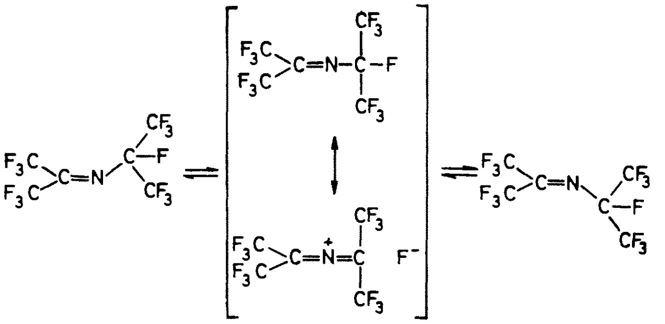
"*syn–anti*- Isomerization" of the *N*-Heptafluoroisopropylimine of Hexafluoroacetone; Steric Effects or Negative Hyperconjugation?

By WILLIAM H DAWSON, DUNCAN H HUNTER,* and CHRISTOPHER J WILLIS
(*Department of Chemistry, University of Western Ontario, London, Canada* N6A 5B7)

Summary The activation parameters for the *syn–anti*-isomerization of several *N*-alkyl and *N*-fluoroalkyl-imines of hexafluoroacetone have been obtained by dynamic ^{19}F n m r spectroscopy and have been interpreted in terms of steric effects, rather than negative hyperconjugation

IN studies of *syn–anti*-isomerization, the heptafluoroisopropylimine of hexafluoroacetone (**1**) has been of particular interest because of the low barrier to inversion (54 ± 12 kJ mol^{-1}) [1] It has been suggested that steric effects alone cannot account for this, and a linear transition state stabilized by negative hyperconjugation has been proposed (Scheme) [2] However, this hypothesis has not been tested on analogous systems, since no other reports of studies on *N*-alkylimines of hexafluoroacetone have appeared

In view of the controversial position of the concept of negative fluorine hyperconjugation, which has been both supported[3] and criticized,[4] we have synthesized and studied additional *N*-fluoroalkyl- and *N*-alkyl-imines of structure $(CF_3)_2C{=}NR$ in order to extend the basis of experimental evidence †



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† Satisfactory n m r and i r spectra and elemental analyses were obtained for all new compounds

TABLE. Activation parameters[a] for the isomerization of hexafluoroacetone *N*-alkyl and *N*-fluoroalkyl imines $(CF_3)_2C{=}NR$.

Compd.	R	$\Delta G^{\ddagger}_{298}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
(**1**)	$CF(CF_3)_2$[b]	57·6 ± 0·4	60·2 ± 1·7	6 ± 6
(**2**)	$CH(CF_3)_2$[c]	73·1 ± 0·8	74·4 ± 4	3 ± 12
(**3**)	$CCl(CF_3)_2$[c]	50·6 ± 0·2	56·4 ± 0·4	19 ± 2
(**4**)	CH_3[d]	86·1 ± 6	84·4 ± 7	−8 ± 20
(**5**)	$CH(CH_3)_2$[d]	77·7 ± 0·8	80·6 ± 3	8 ± 8
(**6**)	$C(CH_3)_3$[d]	54·7 ± 0·2	56·0 ± 1	3 ± 3

[a] kJ mol^{-1}; errors quoted are the 95% confidence limits. [b] In $CHCl_3$ solution. [c] In $CFCl_3$ solution. [d] In 1,2-dimethoxyethane solution.

First-order rate constants for the isomerization process were obtained by matching calculated[5] and observed ^{19}F n.m.r. spectra at temperatures below the coalescence point. By taking advantage of the two-site and single-site spectra corresponding to the two trifluoromethyl groups, activation parameters (Table) were obtained over a range of 25—60°.

The data in the Table show low activation energy barriers in all the imines. Where $R = CX(CF_3)_2$, the energies are sensitive to the nature of X, but they decrease in the order $H > F > Cl$. This order is not consistent with negative hyperconjugation only since, on the basis of electronegativities and orbital size, a fluorine atom should be more suitable to stabilize a transition state by negative hyperconjugation than a chlorine atom. Similarly, one would expect the order for assistance of isomerization by inductive withdrawal by the fluoroalkyl group to be $H < Cl < F$, contrary to that observed.

A consistent explanation for the order of dependence of the barrier height upon the nature of the alkyl group appears to be steric, the smallest barrier being found with the largest substituent ($X = Cl$). The figures for the unfluorinated *N*-alkyl substituents also support this, with the barrier decreasing as size increases in the order of energy $CH_3 > CH(CH_3)_2 > C(CH_3)_3$.[6]

Interestingly, the barriers for $R = CH(CH_3)_2$ and $CH(CF_3)_2$ are comparable, while that for the t-butyl falls between that for $CF(CF_3)_2$ and $CCl(CF_3)_2$. The Taft E_S parameters[7] attest to the large bulk of a CF_3 group, placing it on a level with the isopropyl group, and support the suggestion that the groups $CCl(CF_3)_2$ and $CF(CF_3)_2$ may approximate to the size of a t-butyl group. The generally low barrier energies presumably reflect the considerable interaction between each R group and the bulky CF_3 group *cis* to it across the C=N bond.

We suggest, therefore, that the low energy barrier to *syn–anti*-isomerization in (**1**) and other compounds of this type is attributable largely to steric interactions, rather than 'special' effects such as negative hyperconjugation.

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[1] S. Andreades, *J. Org. Chem.*, 1962, **27**, 4163; D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, 1966, **88**, 2775.

[2] C. G. McCarty, in 'The Chemistry of the Carbon-nitrogen Double Bond,' ed. S. Patai, Wiley, New York, 1970, pp. 378 and 408.

[3] R. C. Bingham, *J. Am. Chem. Soc.*, 1975, **97**, 6743; D. J. DeFrees, J. E. Bartmess, J. K. Kim, R. T. McIver, Jr., and W. J. Hehre, *ibid.*, 1977, **99**, 6451.

[4] R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley, New York, 1973, p. 68; W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' Benjamin, New York, 1969, p. 20; D. Holtz, *Chem. Rev.*, 1971, **71**, 139.

[5] G. Binsch, *J. Am. Chem. Soc.*, 1969, **91**, 1304; D. A. Kleier and G. Binsch, *J. Magn. Reson.*, 1970, **3**, 146; G. Binsch and D. A. Kleier, Program No. 165, Quantum Chem. Prog. Exchange, Indiana Univ., Bloomington, Indiana.

[6] W. B. Jennings, S. Al-Showiman, D. R. Boyd, and R. M. Campbell, *J. Chem. Soc., Perkin Trans.* 2, 1976, 1501.

[7] R. W. Taft in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13; E. Della, *Tetrahedron Lett.*, 1966, 3347.