Inorganica Chimica Acta, *83* (1984) L81–L82

Scale Factor between Fluorine-19 Spin Density and Hyperfine Coupling Constant Appropriate to the MNDO Parameterization

CHRISTOPHER GLIDEWELL

Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.

Received November 2, 1983

In connection with other work, we required an estimate of the relationship between the ^{19}F hyperfine coupling constant, as observed in the e.s.r. spectra of fluorine-containing radicals, and the F(2s) spin density calculated using the MNDO method [1]. Estimates have been made of the scale factors which linearly relate calculated ^{19}F spin density to observed hyperfine couplings using both the INDO [2] and MINDO/3 [3] methods: for the INDO parameterization, the scale factor is 4.48×10^4 G and for the MINDO/3 parameterization it is 4.82×10^4 G. In each of these studies [2, 3] the number of radical species was modest (nine and six, respectively), and in the MINDO/3 study in particular the correlation between the calculated spin densities and the observed A values was poor: it is perhaps surprising that no geometry optimisation was performed in this latter study [3], although the ^{19}F aspect was confined to tri- and tetra-atomic radicals.

Previous work [2, 3] on hydrogen-containing radicals has led to estimates of the appropriate scale factors relating ρ[H(1s)] and A(^{1}H) in both the INDO and MINDO/3 treatments: the values derived are quite close, 539.9 G for INDO and 516.4 G for MINDO/3. On the other hand, we have found in MNDO studies of a number of distinct classes of organic radicals, that not only is the ^{1}H scale factor appropriate to the MNDO parameterization significantly larger than for either INDO or MINDO/3, but that it appears, on the basis of results so far available, that radicals containing hetero-atoms of different electronegativities may require different scale factors [4–6]. Thus the value appropriate for hydrocarbon radicals is *ca.* 1100 G, for sulphur-containing radicals *ca.* 1000 G, and for oxygen-containing radicals *ca.* 850–900 G. On this basis it may be anticipated that the ^{19}F scale factor derived in the MNDO treatment may be quite different from those established using INDO or MINDO/3 methods.

In the present communication we report the results of a study involving a rather larger number of fluorine-containing radicals than either of the earlier investigations. Fluorine spin densities were calculated for completely optimised structures using the published MNDO parameterization [1, 7].

Table I records the calculated values of ρ[F(2s)] together with the observed values of A(^{19}F):

TABLE I. Calculated F(2s) Spin Densities, and Observed Calculated ^{19}F Hyperfine Couplings.

Radical	ρ[F(2s)] × 10^3	A(^{19}F)/G observed[a]	A(^{19}F)/G calculated[a]	Reference
BF_2	9.141	190.0	186.5	b
NF_2	3.054	60	62.3	c
FO_2	0.326	12.8	6.7	d
CF_3	4.387	142.4	89.5	e
CF_2H	3.576	84.2	73.0	e
CFH_2	3.693	64.3	75.3	e
CF_2Cl	3.504	110.0	71.5	f
$CFCl_2$	3.716	84.7	75.8	f
CF_2CF_3 (α)	4.009	87.6	81.8	g
CF_2CH_3	3.516	94.0	71.7	h
$CF(CF_3)_2$ (α)	4.815	70.3	98.2	g
$HOCF(CH_3)$	3.285	110.6	67.0	g
Et_3SiOCF_2	4.229	147.6	86.3	i
$Et_3SiOCF(CH_3)$	3.181	95.1	64.9	g
$Et_3SiOCF(CF_3)$ (α)	3.487	88.2	71.1	g
$CF_3OCF(CF_3)$ (α)	4.276	91.1	87.2	g

[a] G = 10^{-4} T. [b] Reference 9. [c] Reference 10. [d] F. J. Adrian, *J. Chem. Phys.*, *46*, 1543 (1967). [e] Reference 8. [f] A. Hasegawa, M. Shiotani and F. Williams, *Disc. Farad. Soc.*, *63*, 157 (1977). [g] P. J. Krusic and R. C. Bingham, *J. Am. Chem. Soc.*, *98*, 230 (1976). [h] K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, *96*, 794 (1978). [i] P. J. Krusic, K. S. Chen, P. Meakin and J. K. Kochi, *J. Phys. Chem.*, *78*, 2036 (1974).

0020-1693/84/$3.00

least-squares analysis of these data yields a scale factor, appropriate to the MNDO parameterization, of 2.04 × 10^4 G. Table I also records values of A calculated using this derived scale factor. The scale factor is based on data which include only the α-fluorines in fluorocarbon systems. The calculated spin densities for β-fluorines appear always to be grossly underestimated: least-squares analysis including β-fluorines yields a different form of relationship between $A(^{19}F)$ and spin density:

$$A(^{19}F)/G = 15.9 + 2.03 \times 10^4 \rho[F(2s)]$$

This relationship was rejected on the grounds of its physical implausibility, as it predicts a lower limiting value of A of 15.9 G, even for negligibly small spin densities.

There is one short series of radicals for which calculations have been made by all three methods; INDO, MINDO/3, and MNDO, namely CF_3, CF_2H, and CFH_2, for which the observed $A(^{19}F)$ values are 142.4, 84.2, and 64.3 G respectively [8]. The INDO calculated values are 159.5, 87.1, and 71.3 G [2]; the MINDO/3 values are 100.6, 129.1, and 123.4 G [3]; and the MNDO values are 89.5, 73.0 and 75.3 G. Of these series, the INDO results are clearly the best while the MNDO and MINDO/3 results are both poor: the r.m.s. deviations for the INDO, MINDO/3, and MNDO results are 10.8, 49.5, and 32.4 G, respectively.

For the radicals BF_2 and NF_2 however the MNDO results are clearly superior to those obtained using MINDO/3. The observed values of $A(^{19}F)$ are [9, 10] 190.0 G and 60 G respectively; the values calculated here by MNDO are in good agreement, 186.5 G and 62.3 G, whereas the values found [3] by the MINDO/3 method are much in error, 266.8 G and 18.1 G respectively. For σ radicals it appears that the MNDO method, while markedly superior to MINDO/3 in this respect, is still inferior to INDO for the calculation of ^{19}F spin densities.

One category of hydrocarbon radicals for which MNDO gives consistently poor results is planar π radicals: for this class of radicals, the INDO method generally performs reasonably well, as judged by both ^1H and ^{14}N results [2]. However both INDO and MNDO fail completely in the case of $C_6F_6^-$ and related radical-ions [11]. The anion has a spectrum characterised by coupling to six identical ^{19}F nuclei, with an A value of 137 G [11, 12]: it has been suggested that this coupling is far too large to accommodate a π^* radical and that instead either $C_6F_6^-$ exists as a planar σ^* radical, or it adopts a puckered structure with a chair conformation C_6 ring [12].

The MNDO method predicts that the LUMO of neutral C_6F_6 is of E_{2u} symmetry: consequently attachment of an electron yields a Jahn-Teller sensitive ion, predicted to change geometry along a vibrational coordinate of symmetry A_{2g} or E_{2g}. In full accord with this, the calculated structure of $C_6F_6^-$ has a ^2A_u state in D_{2h} symmetry, corresponding to distortion along one component of one of the E_{2g} vibrations, ν_{15} and ν_{18}. All of the out-of-plane vibrations which could lead to a non-planar C_6 skeleton are Jahn-Teller inactive: in particular the B_{2g} vibrations, ν_7 and ν_8, which can lead to boat-shaped rings are inactive.

References

1 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc., 99,* 4899 (1977).

2 J. A. Pople and D. L. Beveridge, 'Approximate molecular orbital theory', McGraw-Hill, New York (1970).

3 P. K. K. Pandey and P. Chandra, *Canad. J. Chem., 57,* 3126 (1979).

4 C. Glidewell, *J. Chem. Research,* (S) 22 (1983).

5 C. Glidewell, *J. Chem. Soc., Perkin Trans II,* 1285 (1983).

6 C. Glidewell, *J. Chem. Soc., Perkin Trans II,* in press.

7 M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc., 100,* 58 (1978).

8 R. W. Fessenden and R. H. Schuler, *J. Chem. Phys., 43,* 2704 (1965).

9 W. Nelson and W. Gordy, *J. Chem. Phys., 51,* 4710 (1969).

10 J. B. Farmer, M. C. L. Gerry and C. A. McDowell, *Mol. Phys., 8,* 253 (1964).

11 M. B. Yim and D. E. Wood, *J. Am. Chem. Soc., 98,* 2053 (1976).

12 M. C. R. Symons, R. C. Selby, I. G. Smith and S. W. Bratt, *Chem. Phys. Letters, 48,* 100 (1977).