Heteronuclear Magnetic Double Resonance Measurement of Carbon-13 Chemical Shifts in *NN*-Dimethylformamide and Related Compounds

By W. McFarlane

(*Chemistry Department, Sir John Cass College, Jewry Street, London, E.C.3*)

Summary A ^{13}C chemical shift difference of 5 p.p.m. between the methyl groups of *NN*-dimethylformamide has its origin in the electric field of the carbonyl group; this effect may be as important as magnetic anisotropy in determining ^{1}H chemical shifts.

IMPORTANT contributions to intramolecular chemical shifts can arise from the magnetic and electric fields of groups or bonds which have significant anisotropy.[1] The first effect is well known but is often difficult to distinguish from the second, because for ^{1}H chemical shifts the two effects are of comparable magnitude. Thus for *NN*-dimethylformamide, where partial double-bond character restricts rotation about the C–N bond, a recent calculation[2] gives *ca.* 0·09 p.p.m. for the magnetic anisotropy contribution to the ^{1}H chemical shift difference between the two methyl groups, and *ca.* 0·07 p.p.m. for the electric field effect. However, for ^{13}C (and other heavy nuclei) chemical shifts the effects of magnetic anisotropy should be similar to those found with ^{1}H, while electric fields may produce changes an order of magnitude larger. Thus a comparison of ^{1}H and ^{13}C chemical shift differences can form the basis of a method for distinguishing the two effects.

I report measurements by heteronuclear magnetic double resonance of the methyl group ^{13}C chemical shifts of the *NN*-dimethyl-substituted amides listed in the Table. The compounds, which contained ^{13}C in natural abundance, were examined as *ca.* 20% solutions at 23° using a JEOL C-60-H spectrometer and Schlumberger FS-30 frequency synthesizer whose frequencies were controlled by a single quartz oscillator. In all cases the ^{13}C resonance of the methyl group *cis* to the carbonyl group is to high-field of that which is *trans*, as is also found for the ^{1}H resonance except when aromatic solvents are used.[3,4] In benzene, for example, there is association between the amide and solvent in such a way that the diamagnetic anisotropy of the benzene gives a downfield shift of the *cis* resonance relative to the *trans* of *ca.* 0·2 p.p.m. for both ^{1}H and ^{13}C. This is sufficient to invert the positions of the two lines in the ^{1}H spectrum but not in the ^{13}C, and emphasizes that local magnetic fields have effects of comparable magnitude on both ^{1}H and ^{13}C chemical shifts.

^{13}C *Chemical shift differences* ($\delta_{cis} - \delta_{trans}$) *in p.p.m. in* NN-*dimethylamides*

Solvent[a]	Neat	CCl_4	C_6H_6	MeOH	$(CD_3)_2SO$	D_2O
Amide	(37·6)[b]	(2·2)	(2·3)	(32·6)	(46)	(78)
$Me_2N{\cdot}CHO$	5·1	5·1	4·9	5·2	5·0	5·4
$Me_2N{\cdot}CMeO$	3·1	2·9	2·9	3·1	2·8	2·9
$Me_2N{\cdot}COCl$	1·8	2·0	1·5	—	1·9	—

[a] Dielectric constants in parentheses.
[b] For $Me_2N{\cdot}CHO$.

It is known[5] that reaction field effects can lead to ^{13}C chemical shift differences of up to 7 p.p.m. for polar molecules, and some such differential behaviour might occur here if the solvent cavity containing the amide molecule were sufficiently unsymmetrical. However, the magnitude of these effects should increase rapidly with increasing dielectric constant of the medium,[6] and as this is not found it appears that the observed differences arise from intramolecular causes. The ^{13}C chemical shifts might also be affected by differences in electron density on the carbon atoms, but studies[7] of methyl carboxylates suggest that a difference of 5 p.p.m. due to this would be accompanied by a difference of *ca.* 2·5 Hz in the corresponding ^{13}C–H coupling constant. In fact, the observed differences in $^1J(^{13}$C–H) are much less than this, are in the wrong direction, are strongly solvent dependent, and have been shown[2] to arise from local electric fields.

It thus appears that the principal contribution to the ^{13}C chemical shift difference between the *N*-methyl groups in these amides arises from an intramolecular electric field. This field will also affect the ^{1}H chemical shifts, although to a smaller extent since it is the paramagnetic contribution to the shielding which is involved. These conclusions are supported by a direct calculation[2] of the effect of the electric field due to the carbonyl group upon the ^{1}H chemical shifts in *NN*-dimethylformamide, and it is clear that calculations of magnetic anisotropy from nuclear shieldings which ignore electric fields must be suspect.

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[1] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.
[2] W. T. Raynes and T. A. Sutherley, *Mol. Phys.*, 1970, **18**, 129.
[3] J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1960, **4**, 253.
[4] F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, **87**, 5250.
[5] J. K. Becconsall and P. Hampson, *Mol. Phys.*, 1965, **10**, 21.
[6] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.
[7] W. McFarlane, *J. Chem. Soc.* (*B*), 1969, 28.