Magnetic Non-equivalence of Methyl Groups attached to Hetero-atoms

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THE necessary stereochemical conditions which may lead to magnetic nonequivalence of methylene protons, or of the methyl groups of an isopropyl group are now established.[1] Normally there are contributions from *intrinsic asymmetry*,[2] and from unequal population of the different conformations that the molecule may adopt, but the factors which govern their relative magnitudes are not well understood. In order to extend the range of types of compound in which this phenomenon is observed we have examined the species $(Me_2ECHMePh)^+Br^-$ (E = PhN, PhP, S, Se), wherein the effects of varying the size of the atom bearing the non-equivalent groups can be studied. Previously the results of changing the groups about the centre of effective asymmetry, and of altering the distance of the nonequivalent groups from this centre, have been studied;[3] however, this is the first example of magnetic nonequivalence of groups that are not attached to a carbon atom.

The results (Table) display marked solvent dependence, and this implies an appreciable contribution arising from differences in conformational populations, since conformations with high dipole moments will predominate in polar solvents. The extent of the nonequivalence is temperature-dependent; this again indicates that the intrinsic asymmetry is not the sole source, but so far we have been unable to obtain spectra characteristic of individual conformations, although some broadening does occur at low temperatures. Decomposition of the salts begins at *ca.* 85°, but inversion at S and Se is still slow on an n.m.r. time-scale at this temperature. This is consistent with the successful resolution of sulphonium and selenonium compounds.[4] The small differences in the $^{31}P\cdots H$ coupling constants are of interest. Similar differences in ^{13}C–H coupling constants have been interpreted in terms of differences in electron densities in the C–H bonds of the non-equivalent groups. No such explanation need be invoked here, since the observed effect could arise from a small difference in the CH_3–P–C inter-bond angles.

Chemical shift difference (*p.p.m.*) *of methyl groups attached to* E *in dilute solutions of* $(Me_2ECHMePh)^+Br^-$

	Solvent[a]			
E	$CDCl_3$ (4·8)	CH_2Cl_2 (9·1)	CH_3OH (33)	D_2O (80)
PhN[b]	±0·20	±0·15	∓0·09	∓0·11
PhP[c,d]	0·24	0·22	0·015	<0·015
S:[c]	0·38	0·35	0·30	0·27
Se:[c]	0·19	0·18	0·22	0·20

[a] Dielectric constant in parentheses.

[b] Measurements in mixtures of solvents show that high- and low-field groups are interchanged, as indicated by the relative signs.

[c] No interchange of high- and low-field groups in different solvents.

[d] ^{31}P coupling to high-field protons 13·8 Hz.; to low-field protons, 14·1 Hz. The assignments were confirmed by $^1H-\{^{31}P\}$ double resonance.

The observed non-equivalences are strongly concentration-dependant; this is presumably a result of stereospecific ion-pair formation which may eventually lead to absolute assignment of the resonances of the two methyl groups.[5]

We thank the S.R.C. for funds for the JEOL spectrometer and the Governors of Sir John Cass College for a Research Assistantship (to J.A.N.).

(*Received, March* 11*th*, 1969; *Com.* 348.)

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