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AROMATIC SOLVENT-INDUCED SHIFTS WITH BENZENE AND HEXAFLUOROBENZENE IN ^{1}H NMR SPECTRA OF PARA-BIS-SUBSTITUTED BENZENES

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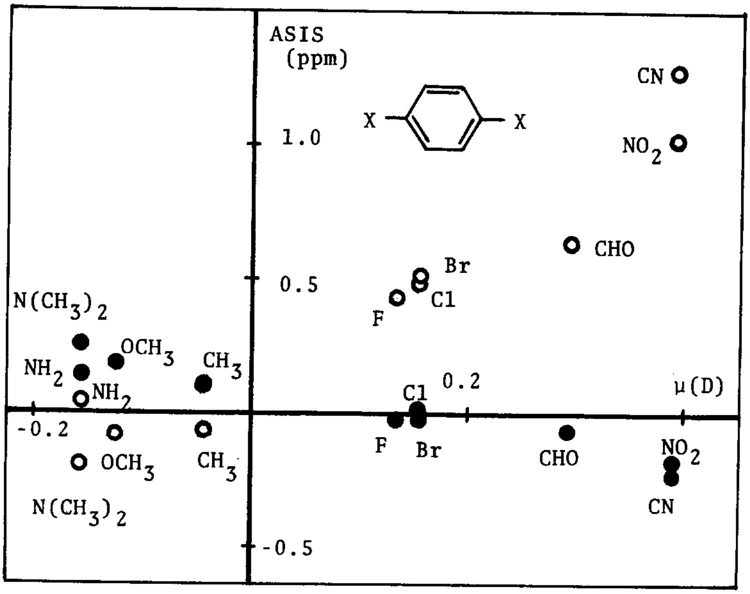
Aromatic solvent-induced shift (ASIS) with benzene in ^{1}H NMR spectroscopy has been a simple powerful tool for solving various problems in organic chemistry.[1] For a long time, however, the ASIS with benzene has been controversial in interpreting the nature of interaction.[1,2] Furthermore, the ASIS with hexafluorobenzene which gives a shift of an opposite direction to that with benzene has also been discussed.[3,4] In previous papers, we thus proposed a new concept for interpreting the nature of ASIS with C_6H_6[5] and C_6F_6[6] on the basis of an electrostatic dipole (solute)-quadrupole (solvent) interaction. This paper reports a good correlation between ASIS and solute dipole-moment, which provides a further experimental support for our theory.

Solvent shifts of ring-proton signals of para-bis-substituted benzenes which have polar substituents but no molecular dipole-moments, were observed with C_6D_6 and C_6F_6.[7] These shifts were found to be related to dipole moments of the corresponding mono-substituted benzenes,[8] as shown in the FIGURE. The relationships between dipole-moment versus ASIS have opposite signs for C_6D_6 and C_6F_6 to each other, as expected.

An electric field around a solute molecule (p-bis-substituted benzene) can be regarded as an electric quadrupole field; this field interacts with another quadrupole moment such as C_6H_6 or C_6F_6. In this system, C_6D_6 and C_6F_6 should have a different orientation around a solute because the sign of principal values of their quadrupole moments at the six-fold axis are opposite to each other as $Q_{zz}(C_6H_6) = -5.6 \times 10^{-26}$e.s.u. and $Q_{zz}(C_6F_6) = +17.2 \times 10^{-26}$e.s.u.[9] The solvent shifts are caused by the magnetic anisotropy of the solvent



molecules. Thus, the magnitude of the ASIS observed for p-bis-substituted benzenes should be dependent on the quadrupole moment of solvent.

FIGURE. ASIS of the ring-proton signal of p-bis-substituted benzenes with C_6D_6 (o) and C_6F_6 (•) vs. dipole moments of the coresponding mono-substituted benzenes.

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