# Solvent Effects on Hydrogen Bonding in *ortho*-Nitroanilines

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INTRAMOLECULAR hydrogen bonding in *o*-nitroanilines is now accepted[1–3] and Dyall and Kemp have recently sought to rationalize former doubts about the existence of such bonding. Most of the evidence against the suggested hydrogen bonding rested on solvent-shift studies of infrared spectra[3,4] but it is now clear that such shifts depend on the possibilities for relief of steric strain in the solvent-bonded amine molecule as well as on the intrinsic strength of the intra- and inter-molecular hydrogen bonds.

Direct support is now provided for the model suggested by Dyall and Kemp[3] in which an approaching solvent molecule (dimethyl sulphoxide in this case) competes with the nitro-group for the hydrogen-bonding site, resulting in rotation of both amino- and nitro-groups from the ring plane. The proton magnetic resonance spectra of *o*-nitroanilines reveal, by an upfield shift of the 3-proton, this rotation of the nitro-group[5] when the solvent is changed from deuterochloroform to dimethyl sulphoxide.

The upfield shifts (Table) are quoted relative to that of the 6-proton which is believed to suffer minimal environmental change in the solvation process. With the reduction in both the electronic and anisotropic[6] effects of the nitro-group the 3-proton moves upfield by 25—34 c./sec., while the 5-proton, affected by electronic changes only, suffers a consistently smaller shift. The *downfield* shift of the 4-proton in 2-nitroaniline appears to be general for the other amines studied, and probably arises from the reduction in mesomeric donation by the amino-group as it is rotated from the plane. That the aromatic proton *para* to the amino-group should be more affected than that *ortho* is concordant with other data from the literature[5,7] and also with the principle of least motion as recently restated by Hine.[8]

TABLE

*Relative upfield shift of aromatic protons: c./sec. for dimethyl sulphoxide against deuterochloroform solutions*

| Compound | Shift H-3 | H-4 | H-5 |
|---|---|---|---|
| 2-Nitroaniline | 30 | −15 | 19 |
| 2,4-Dinitroaniline | 34 | — | 19 |
| *N*-Methyl-2,4-dinitroaniline | 31 | — | 15 |
| *N*-Benzyl-2,4-dinitroaniline | 26 | — | 12 |
| 4-Methyl-2-nitroaniline | 25 | — | 10 |
| *p*-Toluidine | 3 | — | 3 |
| 2,5-Dichloroaniline | 4 | 11 | — |
| 2,5-Dimethoxyaniline | −1 | 7 | — |

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