^{1}H Nuclear Magnetic Resonance Evidence for *cis–trans*-Isomerism in the $C_6H_3(NO_2)_3\cdot(SO_3^{2-})_2$ Adduct

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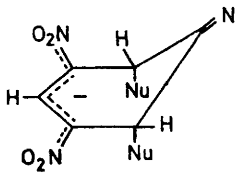
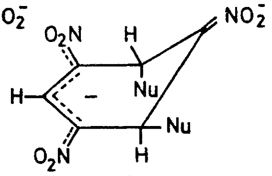
Summary By use of ^{1}H n.m.r. spectroscopy *cis–trans*-isomerism is demonstrated in the di-adduct formed from 1,3,5-trinitrobenzene with sodium sulphite.

There is considerable current interest in the structures and stabilities of the σ-complexes formed by the reversible addition of nucleophiles (Nu) to activated aromatic compounds such as 1,3,5-trinitrobenzene (TNB).[1–4] In the case of adducts with stoicheiometry 1 TNB : 2 Nu the possibility of formation of *cis*- (**1a**) and *trans*- (**1b**) isomers has been considered.[1,2] Until now there has been no spectroscopic evidence for such isomerism. However, in a recent kinetic study of the interactions of 1,3,5-trinitrobenzene with aqueous sodium sulphite, Bernasconi and Bergstrom[5] found evidence for the formation of two distinct species of similar stability each having a stoicheiometry of 1 TNB : 2 SO_3^{2-} and suggested that these might be the isomeric adducts.



(**1a**)



(**1b**)

We now report direct structural evidence by ^{1}H n.m.r. spectroscopy for the formation of such isomers. The spectra of a solution of 1,3,5-trinitrobenzene in 1·0M-aqueous sodium sulphite recorded at 60 MHz (Figure) show bands due to the two isomers. Thus, the solution cooled to 5° shows two sharp bands at δ 8·6 and 8·5 attributed to the hydrogens at the sp^2 hybridised carbon atoms in the di-adducts and two sharp bands at δ 6·05 and 5·9 attributed to the hydrogens at the sp^3 hybridised carbon atoms. As required for complexes of 1 : 2 stoicheiometry the bands at 8·6 and 6·05 have relative intensities of 1 : 2 as do the bands at 8·5 and 5·90. At this temperature the isomers are present in the ratio 6 : 4. On warming the sample to 30° the bands at 8·6 and 6·05 remain sharp while the bands from the other isomer broaden considerably. The broadness of these latter bands at probe temperature explains the failure to observe them in previous measurements.[6] This broadening, which is reversed on re-cooling, might be explained by an increase in rate, for one isomer, of sulphite exchange either between ring positions or with the solution. Alternatively, an explanation for this effect might be found in terms of the non-planarity of the 1 : 2 complexes.

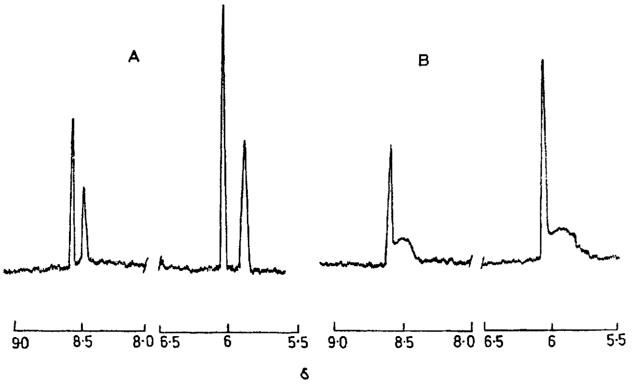


Figure. ^{1}H *N.m.r. spectra of* 1,3,5-*nitrobenzene*: A, 5 °C; B, 30 °C.

Thus, in structures (**1a**) and (**1b**) it is possible that the substituents, H and SO_3^-, at the sp^3 hybridised carbon atoms may take up pseudo-axial or -equatorial positions. Nevertheless, in the *trans*-complex repulsion between NO_2^- and SO_3^- groups will probably result in a near planar molecule rendering the two hydrogens equivalent. However in the *cis*-form one of the two possible conformations may be much preferred. It is possible to envisage a situation where change in rate of 'flipping' of the molecule with temperature could result in the observed broadening.

In the light of these results it seems possible that the energies of *cis*- and *trans*-isomers of other di-adducts, for example those from 1-X-2,4,6-trinitrobenzenes,[6] may be similar.

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