

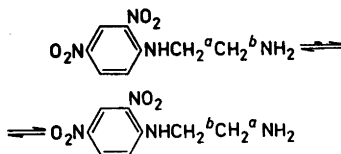
## Nucleophilic Aromatic Substitution with Ethylenediamine

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The recent report<sup>1</sup> of a spirocyclic Meisenheimer complex from ethylene glycol has prompted the publication of some observations that have been made in connection with work on intramolecular nucleophilic substitution reactions.

The idea of the present author was to determine whether under suitable conditions the following reaction takes place through a cyclic intermediate in which the methylene groups *a* and *b* in the formula below have become scrambled.



NMR spectroscopy was thought to be a suitable technique for following the rate of such a reaction, either by observing band broadening in the case of rapid interchange or by labelling one of the methylene groups with deuterium in the case of a slow reaction.

In actual fact, in the 60 MHz NMR spectrum of N-(2,4-dinitrophenyl)ethylenediamine in deuterated nitromethane as solvent, the methylene protons appeared as two triplets centered at  $\delta = 3.01$  and 3.51 ppm, respectively, downfield from tetramethylsilane. The separation between successive peaks in each triplet was 6 Hz. The shape of the spectrum was uninfluenced by heating the sample to 90°C.

In the same solvent, the corresponding 2,4,6-trinitro compound could not be studied because of its instability, but in methanol, the NMR spectrum showed only one line that could be ascribed to the methylene protons.

The compound N-(2,6-dinitro-4-methanesulphonylphenyl)ethylenediamine could be studied, however, in deuterated nitromethane, and the methylene protons appeared as a strongly coupled  $A_2B_2$  spectrum centered at  $\delta = 2.99$  with a width of about 7 Hz.

Finally, N-(2,6-dinitrophenyl)ethylenediamine was studied and only one sharp line was observed for the methylene protons,  $\delta = 2.92$ .

These results may be explained in terms of conformational changes, the "inner" methylene group being shifted 0.5 ppm upfield when flanked by two *ortho* nitro groups rather than one *ortho* and one *para* nitro group. Since the nature of the substituent in the *para* position seems to have little influence on the position of the NMR signals from both methylene groups, one may assume that if the NMR spectrum of the 2,4,6-trinitro compound could have been observed in nitromethane, only one line would have appeared, as was indeed the case in methanol.

It is important to note that in the cases where only one line occurs, no conclusions can be made about the rate of the postulated rearrangement. The possibility that some of these compounds have a structure analogous to the intermediate in nucleophilic aromatic substitution could be excluded from their electronic spectra, since these were quite similar to those of monoamine analogues and not at all characteristic of the quinonoid Meisenheimer complexes.

In view of the present investigation, it should be apparent that the NMR spectrum alone would have constituted a far weaker proof of the spirocyclic structure in the ethylene glycol case<sup>1</sup> than the NMR, electronic and IR spectra together.

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1. Foster, R., Fyfe, C. A. and Morris, J. W. *Rec. Trav. Chim.* **84** (1965) 516.

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