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NMR Spectra of Some Nitro-substituted N-Alkylanilines

III. The Conformation of N,3-Dimethyl-2,4,6-trinitroaniline

BO LAMM and KJELL NORDFÄLT

Department of Organic Chemistry, University of Göteborg, Gibraltargatan 5 A, Göteborg S, Sweden

In the title compound, the methylamino group can assume two different positions with respect to the rest of the molecule. In one of the conformations thus obtained, the N-methyl group is closest to the 2-nitro group and in the other, it is closest to the 6-nitro group. The study of the NMR spectra of this compound and a number of similar ones makes it possible to select the first of these conformations as the most probable one. This choice is further supported by infrared spectroscopy.

In Parts I and II of this series,[1,2] the NMR spectra of a number of nitro-substituted N-alkylanilines have been studied. The difference in chemical shift between the methylene protons of an N-ethylaniline and the methyl protons of the analogously substituted N-methylaniline has been found to have an abnormally low value when two *ortho* nitro groups are present. A similar effect has been observed on comparison of N-neopentyl- and N-methylanilines. The phenomenon has been interpreted as being caused by the magnetic anisotropy of the nitro group.

It was now thought to be interest to extend the study to compounds with two nitro groups *ortho* to the alkylamino group, one or both of the nitro groups being buttressed with methyl groups in the adjacent positions.

Magnetic shielding effects from functional groups are known to have a strong directional dependence.[3] It is also known that aromatic nitro groups are twisted out of the plane of the benzene ring by many *ortho* substituents. In N-alkyl-3-methyl-2,4,6-trinitroanilines, the 2-nitro group should be more twisted than the 6-nitro group. It should therefore be possible to decide if the N-alkyl group is closest to the 2-nitro or to the 6-nitro group in the preferred conformation by determining the above-mentioned chemical shift difference between corresponding protons in N-ethyl- and N-methyl-3-methyl-2,4,6-trinitroaniline and comparing the value thus obtained with similar differences in the systems 2,4,6-trinitro and 3,5-dimethyl-2,4,6-trinitro. In

the last two cases, both *ortho* nitro groups are equivalent and similar to the 6-nitro and the 2-nitro group, respectively, of the monomethyl series.

A nitro group coplanar with the benzene ring ought to be more electron-rich and therefore a better hydrogen bond acceptor than a nitro group twisted out of the benzene ring plane (because of better conjugation). It is known [4] that the infrared NH stretching frequency generally decreases with increasing degree of hydrogen bonding. Therefore, by studying the infrared spectra of N-methyl-2,4,6-trinitroaniline and the two homologues with one or two aromatic methyl groups, it should be possible to assign the preferred conformation of the monomethyl compound in a similar fashion; if the preferred conformation is the one with the N-methyl group close to the 2-nitro group, the 6-nitro group will be the acceptor for the hydrogen bond from the amine proton, and the NH stretching frequency should be close to that in N-methyl-2,4,6-trinitroaniline. In the other conformation, the NH stretching frequency should approach that in N,3,5-trimethyl-2,4,6-trinitroaniline.

It should also be possible to evaluate the degree of hydrogen bonding from the NMR spectra of the three N-methyl compounds, since it was shown in Part II [2] that the position of the amine proton peak, determined by spin decoupling, is quite sensitive to changes in hydrogen bonding.

RESULTS

The information obtained from the 60 MHz NMR spectra is summarized in Table 1. The infrared measurements of the NH stretching frequencies are presented in Table 2. Both types of spectra were recorded in nitrobenzene solution.

Table 1. NMR chemical shifts and coupling constants.

Substituents	N-Methyl				N-Ethyl					Difference
	δ_{CH_3}[a]	δ_{ArCH_3}[a]	δ_{NH}[b]	J_{NHCH_3}[c]	δ_{CH_2}[a]	δ_{ArCH_3}[a]	δ_{CH_3}[a]	J_{NHCH_2}[c]	$J_{CH_2CH_3}$[c]	$\delta_{CH_2,ethyl} - \delta_{CH_3,methyl}$[d]
2,4,6-Trinitro	3.04	9.2		5.6	3.18	1.39		7.0	5.0	0.14
3-Methyl-2,4,6 trinitro	3.04	8.9	2.42	5.7	3.24	1.33	2.41	7.1	4.9	0.20
3,5-Dimethyl-2,4,6-trinitro	2.87	5.9	2.10	5.3	3.08	1.20	2.11	7.0	5.2	0.21

[a] In ppm downfield from TMS. Values good to ±0.02 ppm.
[b] In ppm downfield from TMS as determined by spin decoupling. Values good to ±0.2 ppm.
[c] In Hz. Values good to ±0.2 Hz.
[d] In ppm. Values good to ±0.04 ppm.

Table 2. IR frequency of the NH stretching band in N-methylanilines, solvent nitrobenzene.

Substituents	Wave number cm^{-1}
2,4,6-Trinitro	3332 ± 2
3-Methyl-2,4,6-trinitro	3329 ± 2
3,5-Dimethyl-2,4,6-trinitro	3398 ± 2

DISCUSSION

Two *a priori* possible conformations of N,3-dimethyl-2,4,6-trinitroaniline, I and II, are illustrated in Fig. 1. If I and II are to be distinguishable, it is required that the dihedral angle between the methylamino group and the benzene ring is less than 90°, which is most probably the case (*cf.* Ref. 2).

The difference in chemical shift between corresponding N-alkyl protons in the N-ethyl- and N-methylanilines is listed in Table 1. The similarity of the values in the last two rows indicates that the N-alkyl group in these cases is positioned close to a buttressed nitro group. This favours formula I for N,3-dimethyl-2,4,6-trinitroaniline.

The chemical shift of the amine proton (Table 1) is another indication in favour of formula I. The value for the N,3-dimethyl compound resembles that of the N-methyl compound lacking methyl substituents on the aromatic ring, and it is reasonable to assume a similar degree of hydrogen bonding. Since a nitro group coplanar with a benzene ring can be expected to be a better hydrogen bond acceptor than a twisted one, again formula I is the best proposal for the N,3-dimethyl compound.

Finally, the infrared data (Table 2) support this assignment, since the wave number of the NH band is the same in two of the three N-methyl compounds. A similar degree of hydrogen bonding is therefore indicated by this method as well, leading to the same choice as above, *i.e.*, I. Since the NMR spectra were recorded in nitrobenzene, it was considered to be advisable to use the same solvent in the infrared measurements. Also, the solubility of the compounds in carbon tetrachloride is very low.

Fig. 1 gives the impression that conformation II is the preferred one, since in this form, steric crowding between the 3-methyl, the 2-nitro and the N-methyl groups seems to be smaller than in I. However, hydrogen bonding to the buttressed 2-nitro group from the amine proton is energetically less favourable than to the 6-nitro group, which speaks against formula II. Also, when it is realized that the 2-nitro group is already twisted out of the plane of the benzene ring because of the 3-methyl group, it becomes clear that the

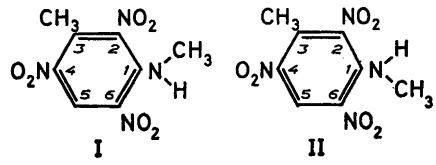

Fig. 1. Conformations of N,3-dimethyl-2,4,6-trinitroaniline.

N-methyl group can be accommodated as depicted in formula I, close to the 2-nitro group, at less free energy expense than is the case in formula II. The stability of I *versus* II may thus be well understood.

EXPERIMENTAL

Melting points have been determined on a Kofler micro hot stage. NMR spectra were recorded in nitrobenzene solution as described in Part I.[1] IR spectra were likewise recorded in nitrobenzene solution as described in Part II.[2]

N-Methyl- and N-ethyl-2,4,6-trinitroaniline were available from previous work.[1]

3-Methylanisole was prepared from *m*-cresol and dimethyl sulphate,[5] yield 87 %, b.p. 65°/14 mm.

3-Methyl-2,4,6-trinitroanisole was prepared from the preceding compound by nitration.[6] Yield after recryst. from methanol 78 %, m.p. 94°, lit.[6] 92°.

N,3-Dimethyl-2,4,6-trinitroaniline was prepared from the preceding compound in ethanol solution and a slight excess of methylamine (33 % solution in water) in an instantaneous reaction. Yield after recryst. from ethanol 87 %, m.p. 137—138°, lit.[6] 138°.

N-Ethyl-3-methyl-2,4,6-trinitroaniline was prepared from 3-methyl-2,4,6-trinitroanisole in ethanol solution and a slight excess of ethylamine in an instantaneous reaction. Yield after recryst. from ethanol 70 %, m.p. 97°, lit.[6] 98°.

5-Bromo-1,3-dimethylbenzene was prepared from 2,4-dimethylaniline [7,8] in 18 % overall yield, b.p. 81—83°/11 mm.

5-Bromo-1,3-dimethyl-2,4,6-trinitrobenzene was prepared from the preceding compound by nitration,[9] yield after recryst. from benzene 81 %, m.p. 224°, lit.[9] 224°.

N,3,5-Trimethyl-2,4,6-trinitroaniline was prepared from the preceding compound and a tenfold excess of methylamine (33 % solution in water) by refluxing for 24 h in methanol solution. Yield after recryst. from methanol 52 %, m.p. 166—167°, lit.[9] 165°.

N-Ethyl-3,5-dimethyl-2,4,6-trinitroaniline was prepared from 5-bromo-1,3-dimethyl-2,4,6-trinitrobenzene and a fourfold excess of ethylamine by refluxing for 3 h in benzene-ethanol solution 2:1. Yield after recryst. from ethanol 77 %, m.p. 121—123°, lit.[6] 122°.

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REFERENCES

1. Lamm, B. *Acta Chem. Scand.* **19** (1965) 2316.
2. Lamm, B. and Nordfält, K. *Acta Chem. Scand.* **20** (1966) 1208.
3. Jackman, L. M. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, Oxford 1959, chapter 7.
4. Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond*, Freeman and Co., San Francisco and London 1960, p. 70.
5. Vogel, A. I. *Practical Organic Chemistry*, 2nd Ed., Longmans, Green and Co., London 1951, p. 640.
6. Blanksma, J. J. *Rec. Trav. Chim.* **21** (1902) 331.
7. Fischer, E. and Windaus, A. *Ber.* **33** (1900) 1971.
8. Fieser, L. F. and Heymann, H. *J. Am. Chem. Soc.* **64** (1942) 376.
9. Blanksma, J. J. *Rec. Trav. Chim.* **25** (1906) 374.

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