

NMR Spectra of Some Nitro-substituted *N*-AlkylanilinesIV. *N*-Isopropylanilines

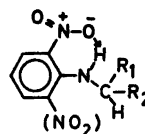
BO LAMM and KJELL NORDFÄLT

*Department of Organic Chemistry, University of Göteborg and  
Chalmers Institute of Technology, Fack, S-402 20 Göteborg 5, Sweden*

The influence of two *ortho* nitro substituents on the chemical shift of the protons on the carbon atom adjacent to the amine nitrogen atom in *N*-alkylanilines has been studied in the *N*-isopropyl series. The "anisotropy upshift" in *N*-ethyl and *N*-neopentyl compounds reported in earlier papers in this series has been demonstrated to have the same value in the *N*-isopropyl compounds.

In Parts I, II, and III of this series,<sup>1-3</sup> the NMR spectra of a number of nitrosubstituted *N*-alkylanilines have been studied in nitrobenzene solution. An unusually small difference in the chemical shift between the methylene protons of an *N*-ethylaniline and the methyl protons of the analogously substituted *N*-methylaniline has been found when two *ortho* nitro groups are present. A similar effect has been observed on comparison of *N*-neopentyl- and *N*-methylanilines. The magnetic anisotropy of the nitro group is considered to give rise to this phenomenon. Evidence of an intramolecular hydrogen bond between the amino group and an *ortho* nitro group when the latter is present has been presented in Part II<sup>2</sup> of this series.

Fig. 1. Conformation allowing intramolecular hydrogen bonding in nitro-substituted *N*-alkylanilines.



If the steric crowding is not too extensive, the alkylamino group will be coplanar with the benzene ring, allowing for optimum resonance stabilization.

In compounds with a second *ortho* nitro group (shown in parentheses in Fig. 1), an upfield shift on the protons of the alkyl carbon atom closest to the amine nitrogen atom is observed. This is very likely a result of magnetic anisotropy. In the compounds studied (*N*-methyl-, *N*-ethyl-, and *N*-

neopentylanilines),  $R_1$  in Fig. 1 has been equal to H, whereas  $R_2$  has been H,  $\text{CH}_3$ , and  $\text{C}(\text{CH}_3)_3$ , respectively. Since the chemical shift differences referred to above are necessarily *time-average* values of all possible conformations, an investigation was carried out to determine whether a still more marked effect of two *ortho* nitro groups of the chemical shift difference would be observed if both  $R_1$  and  $R_2$  in Fig. 1 were bulky groups. The remaining methine proton would then be still closer to one of the *ortho* nitro groups.

Since it was considered desirable to obtain as simple an NMR signal as possible for the one methine proton in question, spin coupling with protons in  $R_1$  and  $R_2$  should be avoided. If  $R_1$  and  $R_2$  were tertiary butyl groups for example, this condition would most probably have been fulfilled. The syntheses of the above mentioned compounds with  $R_1$  and  $R_2 = t$ -butyl, and also of some related ones in which  $R_1$  and  $R_2$  are joined to form cyclic structures, proved to be very difficult, however. These plans were therefore abandoned in favour of the compounds in which  $R_1 = R_2 = \text{methyl}$ , in other words, the *N*-isopropylanilines. These compounds were easily prepared, and their NMR spectra have been recorded in nitrobenzene solution.

## EXPERIMENTAL

*General remarks.* Melting points have been recorded on a Kofler micro hot stage. Since the syntheses of the compounds are straightforward, and all of the compounds, possibly with the exception of *N*-isopropyl-2,6-dinitroaniline, are reported in the literature, their identity was fully warranted by the NMR spectra and melting points.

*N*-Isopropylaniline. This compound was prepared by reductive alkylation of 12.3 g (0.1 mole) of nitrobenzene according to Emerson and Uraneck.<sup>4</sup> Yield 6.6 g (49 %). B.p. found 90–90.5° C/15 mm, lit.<sup>4</sup> 198–207°C at atm. pressure.

*N*-Isopropyl-2-nitroaniline was prepared from 5 g (0.035 mole) of 2-nitrofluorobenzene and 4.1 g (0.070 mole) of isopropylamine by refluxing for 5 h in 50 ml of ethanol. The solvent was then removed *in vacuo* and the remainder dissolved in ether. The ether solution was washed twice with 5 % hydrochloric acid and twice with saturated sodium chloride solution. After drying over Drierite, the ether was removed *in vacuo*. The product is a red oil, as indicated in the literature.<sup>5,6</sup> Yield 4.8 g (75 %).

*N*-Isopropyl-4-nitroaniline was prepared exactly as described above for the 2-nitro compound, using 4-nitrofluorobenzene as starting material. Yield after recrystallization from ethanol 5.1 g (80 %), yellow needles, m.p. 83–84°C, lit.<sup>7</sup> 81–82°C.

*N*-Isopropyl-2,4-dinitroaniline was prepared from 5 g (0.025 mole) of 2,4-dinitrochlorobenzene and 3 g (0.050 mole) of isopropylamine by refluxing for 30 min in 50 ml of ethanol. Yield after recrystallization from ethanol 5.3 g (95 %), yellow needles, m.p. 95–96°C, lit.<sup>8</sup> 94–95°C.

*N*-Isopropyl-2,6-dinitroaniline was prepared from 5 g (0.025 mole) of 2,6-dinitrochlorobenzene and 3 g (0.05 mole) of isopropylamine by refluxing for 30 min in 50 ml of ethanol. Yield after recrystallization from ethanol 4.3 g (77 %), m.p. 54–55°C. This compound has not been found in the literature.

*N*-Isopropyl-2,4,6-trinitroaniline was prepared from 5 g (0.02 mole) of picryl chloride and 2.4 g (0.04 mole) of isopropylamine in 50 ml of ethanol in an instantaneous reaction. Yield after recrystallization from ethanol 4.9 g (91 %), yellow needles, m.p. 106–107°C, lit.<sup>9</sup> 106–107°C.

*NMR spectra.* Using exactly the same techniques as in Parts I, II, and III of this series,<sup>1–3</sup> 60 MHz NMR spectra were recorded on a Varian A60 instrument in nitrobenzene solution.

## RESULTS AND DISCUSSION

Because of spin coupling both within the isopropyl group and between the methine proton and the amine proton (except for unsubstituted *N*-isopropylaniline, in which the amine coupling is lacking because of hydrogen exchange), the methine protons appear as two overlapping septets. The chemical shifts were obtained from the positions of the center of the multiplets. All values thus obtained for the chemical shifts and coupling constants are presented in Table 1.

Table 1. Chemical shifts and coupling constants for *N*-isopropylanilines.

Substituents	$\delta$ -CH- <sup>a</sup>	$\delta$ -CH <sub>3</sub> <sup>a</sup>	$J$ -CHCH <sub>3</sub> <sup>b</sup>	$J$ -NHCH- <sup>b</sup>
Unsubstituted	3.55	1.15	6.2	—
2-Nitro	3.74	1.27	6.2	6.6
4-Nitro	3.68	1.27	6.3	7.4
2,4-Dinitro	3.96	1.42	6.4	6.7
2,6-Dinitro	3.51	1.19	6.2	8.2
2,4,6-Trinitro	3.68	1.33	6.2	8.2

<sup>a</sup> In ppm downfield from TMS. Values accurate to  $\pm 0.02$  ppm.

<sup>b</sup> In Hz. Values accurate to  $\pm 0.2$  Hz.

Spin decoupling experiments to determine the position of the amino protons were unsuccessful, mainly because of instrumental limitations.

The data in Table 1 and the data for the corresponding *N*-methylanilines obtained in earlier work<sup>2</sup> can be used to calculate the "anisotropy upshift" in compounds with two *ortho* nitro groups. This value,  $0.16 \pm 0.06$  ppm, is obtained in the following manner.

The difference between the chemical shifts of the methine proton of the *N*-isopropyl group and the chemical shift of the *N*-methyl protons is calculated for the unsubstituted, the 2-nitro, the 4-nitro, and the 2,4-dinitro compounds, respectively and the average value is calculated. The same procedure is

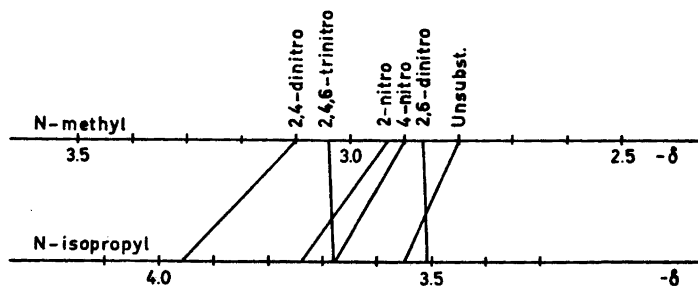


Fig. 2. Chemical shifts (ppm downfield from TMS) of methyl protons in *N*-methylanilines and methine protons in *N*-isopropylanilines. Note that the  $\delta$  values are offset by 0.65 ppm.

carried out with the compounds having two *ortho* nitro groups *i.e.* the 2,6-dinitro and the 2,4,6-trinitro substituted ones. The difference between these two average values represents the "anisotropy upshift". Fig. 2 illustrates the chemical shift differences between the corresponding protons in the *N*-isopropyl and *N*-methyl compounds. Based on data from Part II of this series<sup>2</sup> a comparison of the *N*-ethyl and *N*-methyl compounds with the same substituents as the *N*-isopropyl anilines (*i.e.* unsubstituted, 2-nitro, 4-nitro, 2,4-dinitro, 2,6-dinitro, and 2,4,6-trinitro) gives the value of  $0.17 \pm 0.04$  ppm for the "anisotropy upshift". The same comparison of *N*-neopentyl and *N*-methyl compounds gives the value  $0.18 \pm 0.03$  ppm (values from Part II<sup>2</sup>).

In view of what was said above, it is somewhat surprising that the comparison of the *N*-isopropyl and *N*-methyl compounds does not give a larger value than those of *N*-ethyl/*N*-methyl and *N*-neopentyl/*N*-methyl. Apparently, the conformational restrictions in the *N*-ethyl and *N*-neopentyl compounds are severe enough for the maximum anisotropy effect of an *ortho* nitro group to be operating. Inspection of Stuart models does not contradict this result.

*Acknowledgement.* Our thanks are directed to Professor Lars Melander and Docent Robert E. Carter for their constructive criticism.

#### REFERENCES

1. Lamm, B. *Acta Chem. Scand.* **19** (1965) 2316.
2. Lamm, B. and Nordfält, K. *Acta Chem. Scand.* **20** (1966) 1208.
3. Lamm, B. and Nordfält, K. *Acta Chem. Scand.* **20** (1966) 1221.
4. Emerson, W. and Uraneck, C. A. *J. Am. Chem. Soc.* **63** (1941) 749.
5. Davoll, J. *J. Chem. Soc.* **1960** 308.
6. Rossi, A. *et al. Helv. Chim. Acta* **43** (1960) 1298.
7. Behr, L. *et al. J. Am. Chem. Soc.* **68** (1946) 1296.
8. *Beilsteins Handbuch der Organischen Chemie*, 4th Ed., Vol. XII, p. 750.
9. *Beilsteins Handbuch der Organischen Chemie*, 4th Ed., Vol. XII, p. 764.

Received November 6, 1969.