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NMR Spectra of Some Nitro-substituted N-Alkylanilines II

BO LAMM and KJELL NORDFÄLT

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

In the systematic study of the NMR spectra of a number of nitro-substituted N-methyl-, N-ethyl-, and N-neopentylanilines, abnormal values of the differences in chemical shifts between corresponding N-alkyl protons have been observed for some ring substituent patterns, *viz.*, two *ortho* nitro groups or one *ortho* nitro group and one *ortho* *t*-butyl group. In the preferred conformation of the molecules having these *ortho* substituent arrangements, the distance between the N-alkyl group and one *ortho* nitro group is much shorter than in compounds with other substituent arrangements. The abnormal differences are considered to be caused by the anisotropy of the nitro group rather than its bulkiness.

The assignments of the preferred conformations are based on the NMR chemical shifts of the amine protons, determined with spin decoupling, and, in some cases, on the IR stretching frequencies of the NH bonds. Furthermore, UV spectroscopy has been used in estimating the extent of conjugation in some of the compounds.

In Part I of this series,[1] the NMR spectra of some nitro-substituted N-methyl- and N-ethylanilines were discussed. It had been observed that the difference in chemical shift between the N-methyl protons in one compound and the methylene protons in the corresponding N-ethyl compound amounts to 0.28—0.35 ppm in all compounds except those with two nitro groups *ortho* to the N-alkylamino group, the difference then being only 0.14 ppm. It was suggested that in the latter case, the normal difference is partially compensated by an effect in the opposite direction, *i.e.*, an upfield shift. The cause of this effect has now been further studied. In Part I,[1] it was left open whether the magnetic anisotropy of the nitro group closest to the alkyl group is responsible for the shift, or if it is caused by the mere bulkiness of the *ortho* substituents.

If N-alkylanilines with *ortho* groups other than nitro were studied, it should be possible to decide if the anisotropy of the nitro group is indeed responsible for the effect. Therefore, the N-alkyl-2-methyl-4,6-dinitroanilines and N-alkyl-2-*t*-butyl-4,6-dinitroanilines in which the N-alkyl is methyl, ethyl, or neopentyl were synthesized. The reason for including the N-neopentyl compounds will be apparent below.

Another aspect of the NMR spectra that was not discussed in detail in Part I [1] is the chemical shifts of the amine protons. Spin decoupling had been demonstrated to be useful in finding the chemical shifts of these protons, since they are coupled with the protons on the closest carbon atom in the N-alkyl group, but with the field-sweep method used on the available instrument, the Varian A-60 spectrometer with Model V-6058 spin decoupler, only the N-methyl compounds could be studied. The signals from the methylene protons of the N-ethyl compounds are split by coupling both with the amine and methyl protons, and the resulting patterns are too complex to be successfully dealt with by the instrument.

A series of compounds that gives NMR spectra of equal simplicity as the N-methylanilines is offered by the N-neopentylanilines. In the group $(CH_3)_3CCH_2NH-$, no coupling between the *t*-butyl and the methylene protons is observed, and the methylene group therefore only shows up as a doublet because of coupling to the amine proton. Spin decoupling experiments in order to locate the positions of the amine protons in the NMR spectra could therefore be performed in this series in the same way as with the N-methyl compounds. Incidentally, N-benzyl compounds would have shown the same behaviour, but the presence of another benzene ring might give rise to various complications, and benzyl was therefore avoided.

The syntheses of most of the N-neopentylanilines were straightforward. The unsubstituted compound was prepared by lithium aluminium hydride reduction of pivalanilide. The various nitro-substituted compounds were prepared by nucleophilic substitution of suitable aromatic compounds with neopentylamine.

Difficulty was initially experienced in the syntheses of N-ethyl- and N-neopentyl-2-*t*-butyl-4,6-dinitroanilines when 2-*t*-butyl-4,6-dinitroanisole was tried as starting material. Treatment of this methoxy compound with ethylamine or neopentylamine resulted in the formation of 2-*t*-butyl-4,6-dinitrophenolate ion through cleavage of the methyl-oxygen bond. Steric hindrance in the substrate apparently decreases the rate of nucleophilic aromatic substitution of the methoxy group by the amine to such an extent that the S_N2 attack on the methyl group by the amine becomes the predominant reaction. Only with ammonia and methylamine is nucleophilic aromatic substitution the main reaction. The desired substances could, however, be prepared from 2-*t*-butyl-4,6-dinitrochlorobenzene.

An important point that was not discussed in Part I [1] is the actual conformations of the various N-alkylanilines studied. In that paper, it is tacitly assumed that the molecules are sufficiently planar for the sentence "...N-alkyl group in a relatively unhindered position on the remote side of the *ortho* nitro group" to be meaningful. Support for this view is provided by the work of Musso,[2] who has studied the infrared spectra of a number of substituted N-methylanilines. Among these, N,3,6-trimethyl-2-nitroaniline represents an interesting case. Two NH bands are observed in carbon tetrachloride solution, with wave numbers 3392 and 3463 cm^{-1}, which are explained by assuming two different conformations of the molecule of comparable energy. In one of these, hydrogen bonding can take place between the amine proton and the nitro group. The lower frequency band is ascribed to this conformation. The

Table 1. NMR data for N-alkylanilines.

Substituents	N-Methyl			N-Ethyl				N-Neopentyl			
	δ_{CH_3}[a]	δ_{NH}[b]	J_{NHCH_3}[c]	δ_{CH_2}[a]	δ_{CH_3}[a]	$J_{CH_2CH_3}$[c]	J_{NHCH_2}[c]	δ_{CH_3}[a]	$\delta_{C(CH_3)_3}$[a]	δ_{NH}[b]	J_{NHCH_2}[c]
Unsubstituted	2.80	4.2[d]	—[e]	3.08	1.20	7.1	—[e]	2.91	1.00	4.0[d]	—[e]
2-Nitro	2.93	7.9	5.1	3.25	1.28	7.3	5.1	3.04	1.03	8.2	5.2
4-Nitro	2.90	5.4	5.1	3.20	1.28	7.3	5.4	3.05	1.03	5.3	6.2
2,4-Dinitro	3.10	8.5	5.2	3.45	1.38	7.3	5.5	3.24	1.10	8.8	5.5
2.6-Dinitro	2.87	8.4	5.5	3.01	1.28	7.0	4.9	2.82	0.95	8.5	5.0
2,4,6-Trinitro	3.04	9.2	5.6	3.18	1.39	7.0	5.0	2.98	1.04	9.2	5.0
2-Methyl-4,6-dinitro[f]	3.18	7.7	5.6	3.52	1.31	7.2	5.4	3.38	1.03	7.3	5.2
2-*t*-Butyl-4,6-dinitro[g]	2.96	5.7	5.6	3.06	1.34	7.1	5.0	2.86	1.02	5.4	5.3

[a] In ppm downfield from TMS. Values good to ± 0.02 ppm.
[b] In ppm downfield from TMS. Values determined by spin decoupling, good to ±0.2 ppm. Bandwidth about 0.3 ppm.
[c] In Hz. Values good to ± 0.2 Hz.
[d] Directly observed.
[e] No coupling observed.
[f] Chemical shift of aromatic methyl protons 2.46, 2.44, and 2.48 ppm downfield from TMS for the N-methyl, N-ethyl, and N-neopentyl compound, respectively. Values good to ± 0.02 ppm.
[g] Chemical shift of aromatic t-butyl protons 1.50, 1.50, and 1.52 ppm downfield from TMS for the N-methyl, N-ethyl, and N-neopentyl compound, respectively. Values good to ± 0.02 ppm.

two conformations are illustrated in Musso's paper [2] with Stuart models from which it can be judged that the deviations from coplanarity, expressed in terms of the dihedral angles between the benzene ring and the nitro group and the methylamino group, respectively, are no larger than 45°. If only the latter one of these angles is less than 90°, the discussion in Part I [1] of this series retains its validity.

Although our main hypothesis is that the anisotropy of the nitro group is responsible for the chemical shift behaviour mentioned above, an alternative explanation might be the following one. The increased bulk of the N-ethyl group compared to the N-methyl group might cause an increased deviation from coplanarity of the various substituents with the benzene ring, thus decreasing the conjugation. As a result of this, the amine nitrogen should become more electron rich with increasing overall bulk, causing an increased magnetic shielding of the adjacent N-alkyl protons. This effect should of course be more important with two *ortho* nitro groups than with only one or none at all. In order to disprove this alternative explanation, two sets of experiments were designed. *First,* if significant conjugational changes occur when the bulk of the N-alkyl group is increased, the electronic spectra should be influenced.[3] Therefore, the spectra of the 2,4-dinitro and the 2,6-dinitro derivatives of N-methyl-, N-ethyl-, and N-neopentylaniline were recorded. For comparison, N,2-dimethyl-4,6-dinitroaniline and N-methyl-2-*t*-butyl-4,6-dinitroaniline were also included. *Second,* if two *ortho* nitro groups cause an abnormal chemical shift difference only because of their bulkiness, similar behaviour should be shown if one of the *ortho* nitro groups is replaced by an *ortho* alkyl group. As the *ortho* alkyl group, methyl and *t*-butyl were chosen.

Finally it was thought to be of interest to study the NH stretching frequency in the IR spectra of the compounds N-methyl-2,4-dinitroaniline, N,2-dimethyl-4,6-dinitroaniline and N-methyl-2-*t*-butyl-4,6-dinitroaniline. As supported by the work of Musso,[2] the NH stretching frequency will increase with decreased degree of hydrogen bonding. Obviously, increased steric crowding will eventually interfere with optimal hydrogen bonding in these molecules. This can be easily demonstrated with Stuart molecular models.

Table 2. Chemical shift differences in ppm between corresponding protons (printed in bold-face type) in N-alkyl groups. Max. error in all values ± 0.04 ppm.

Substituents	$\delta_{NHCH_2CH_3} - \delta_{NHCH_3}$	$\delta_{NHCH_2C(CH_3)_3} - \delta_{NHCH_3}$
Unsubstituted	0.28	0.11
2-Nitro	0.32	0.11
4-Nitro	0.30	0.15
2,4-Dinitro	0.35	0.14
2,6-Dinitro	0.14	−0.05
2,4,6-Trinitro	0.14	−0.06
2-Methyl-4,6-dinitro	0.34	0.20
2-*t*-Butyl-4,6-dinitro	0.10	−0.10

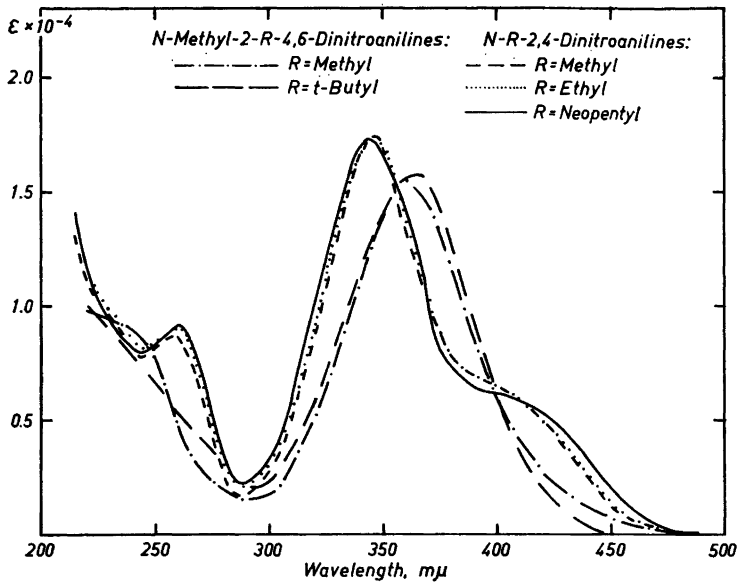

Fig. 1. Electronic spectra of N-alkyl-2,4-dinitroanilines, N,2-dimethyl-4,6-dinitroaniline and N-methyl-2-*t*-butyl-4,6-dinitroaniline.

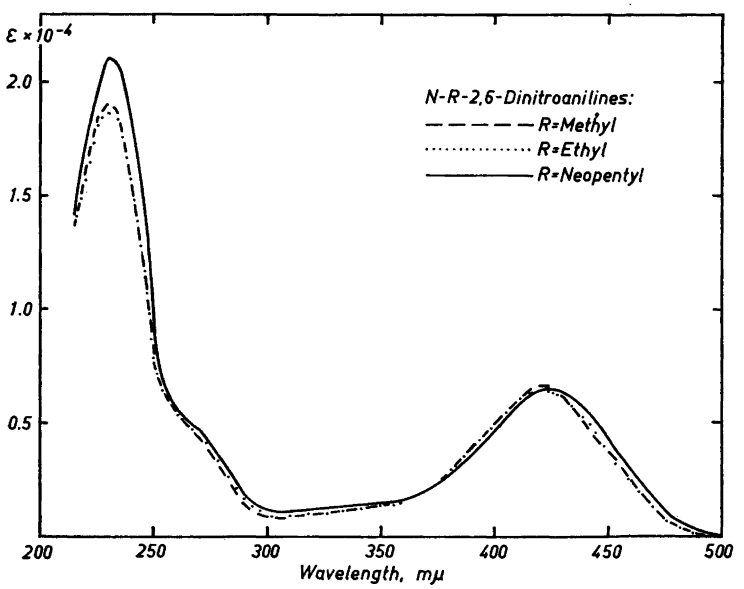

Fig. 2. Electronic spectra of N-alkyl-2,6-dinitroanilines.

RESULTS

In Table 1, all chemical shifts and coupling constants obtained from the NMR spectra are given. The differences between the chemical shifts of the methylene protons in the N-ethyl compounds and the corresponding protons in the N-methyl compounds, and also the corresponding differences between the N-neopentyl and the N-methyl compounds are presented in Table 2.

The electronic spectra of the N-alkyl-2,4-dinitroanilines in ethanol solution are shown in Fig. 1 together with those of N,2-dimethyl-4,6-dinitroaniline and N-methyl-2-*t*-butyl-4,6-dinitroaniline. The spectra of the N-alkyl-2,6-dinitroanilines are given in Fig. 2.

The IR spectra of some of the compounds were recorded in the range 4000—2000 cm^{-1} in nitrobenzene solution and in the range 4000—2400 cm^{-1} in carbon tetrachloride solution. The NH bands were easily recognized, since no other absorption bands interfere in the region of interest, 3500—3300 cm^{-1}. The compounds studied are listed in Table 3, where the frequencies of the NH bands are given in cm^{-1}.

Table 3. IR frequency of the NH stretching band in some substituted N-methylanilines.

Substituents	Wave number (cm^{-1})[a]	
	$C_6H_5NO_2$ solution	CCl_4 solution
2,4-Dinitro	3382	3382
2-Methyl-4,6-dinitro	3340[b], 3416	3354[c], 3461
2-*t*-Butyl-4,6-dinitro	3475	3502

[a] Values good to ±2 units.
[b] Equally intense.
[c] Intensity ratio appr. 10:1.

DISCUSSION

NMR and electronic spectra. It has been demonstrated in Part I [1] of this series that the presence of two *ortho* nitro groups gives rise to an unusually small difference in chemical shift between the N-ethyl methylene protons and the N-methyl protons of correspondingly substituted compounds. Inspection of Table 2 shows that exactly the same phenomenon is observed when N-neopentyl and N-methyl compounds are compared, the difference even changing sign in the latter case. The discussion in Part I [1] can be equally well applied to the neopentyl series of compounds. It was, however, left open whether the effect is caused by the anisotropy of the nitro group or by its pure bulkiness.

Table 2 shows that the N-alkyl-2-methyl-4,6-dinitroanilines belong to the larger class of compounds displaying normal chemical shift differences. The compounds in this class have at most one *ortho* nitro group. Stuart models can be used to demonstrate that the preferred conformation of the 2-methyl-

4,6-dinitro compounds should be similar to that of the N-alkyl-2,4-dinitroanilines, the N-alkyl group being on the remote side of the *ortho* nitro group if the molecules are depicted as projected on the plane of the benzene ring. Admittedly, the introduction of an *ortho* methyl group makes the molecules less planar than before. This is borne out by the electronic spectra (Fig. 1). It is difficult to estimate quantitatively from the electronic spectra how large the deviations are, since it is known from other studies [3,4] that they can be considerable before any drastic changes occur in the spectra. Even the spectrum of N-methyl-2-*t*-butyl-4,6-dinitroaniline (Fig. 1) is not very different from the others, though the deformations from planarity must be still larger in this case, as is borne out by the study of Stuart models.

The positions of the amine protons in the NMR spectra (Table 1) are quite instructive. It is well-known [5a] that hydrogen bonding causes the resonance positions of the protons involved to move downfield. For the N-methyl compounds, the difference between the amine proton positions of 2,4-dinitro and 2-methyl-4,6-dinitro compounds is only 0.8 ppm. In the N-neopentyl series, the difference is 1.5 ppm, which is expected because of the increased bulk of the N-alkyl group. When the whole material is considered, the differences are not large, and it seems very probable that the preferred conformations of these systems are similar. This implies that the distance between the *ortho* methyl group and the N-alkyl group is short in the 2-methyl-4,6-dinitro system. Since no unusual behaviour of the chemical shift differences in the N-alkyl groups is observed, one is lead to the conclusion that the "abnormal" cases emerge from the anisotropy of the nitro group.

At this point, a comment should be made on the fact (Table 1) that the N-methyl protons in N,2-dimethyl-4,6-dinitroaniline are deshielded compared to those in N-methyl-2,4-dinitroaniline, and that the same holds for the larger N-alkyl groups. Both the inductive effect and the twisting of the alkylamino group further out of the ring plane would be expected to produce increased magnetic shielding. Other deshielding effects apparently dominate in the present case. The effects are too complex to treat quantitatively, however. [5b,6a]

The study of the N-alkyl-2-*t*-butyl-4,6-dinitroanilines was undertaken with the hope that in this very hindered system, the alkylamino group would be turned around, so that the N-alkyl group is close to the *ortho* nitro group (at the expense of a hydrogen bond to the amine proton). It is impossible to construct a Stuart model having a conformation with such a hydrogen bond. Inspection of the data in Table 2 shows that indeed, the chemical shift differences are of the same kind as observed with two *ortho* nitro groups. This shows that the guess was correct; the N-alkyl group must be close to the *ortho* nitro group in the preferred conformation of the molecules.

The proposed conformation of the N-alkyl-2-*t*-butyl-4,6-dinitroanilines is further supported by the positions of the amine proton resonance peaks. Table 1 shows that these fall at significantly higher fields than in the systems with less bulky 2-substituents, *i.e.*, the amine protons are more shielded. This is most readily explained by the absence of hydrogen bonding of these protons. It is interesting to note that the chemical shifts of the amine protons are very close to those of the corresponding protons in the 4-nitro compounds (Table 1), where intramolecular hydrogen bonding naturally must be absent.

The electronic spectra of the three N-alkyl-2,6-dinitroanilines (Fig. 2) are very similar. Therefore, in so far as these spectra provide good criteria of the planarity of the molecules, increased bulkiness of the N-alkyl group does not produce any change in geometry. This is an argument against the alternative suggestion made above that the chemical shift differences are due to decreased conjugation in the most hindered compounds.

An inspection of the chemical shift values (Table 1) of the terminal parts of the N-ethyl and N-neopentyl groups reveals that in both series of compounds, fairly constant values are observed. The differences are too small to warrant any attempts at explanation.

The chemical shifts of the amine protons in the NMR spectra are in most cases impossible to determine directly, either because of the broadness of the peaks and/or because they fall under the solvent peak. They have been determined for substituted N-methyl- and N-neopentylanilines using spin decoupling. This technique was discussed in detail in Part I [1] of this series. As was pointed out above, hydrogen bonding to an *ortho* nitro group is held responsible for the low-field positions usually found for these protons. It could, of course, be argued that purely inductive and conjugative effects from the nitro groups play a more important role, but inspection of the values (Table 1) makes this less likely. In particular, a comparison of the values obtained for N,2-dimethyl-4,6-dinitroaniline and N-methyl-2-*t*-butyl-4,6-dinitroaniline is instructive. The electronic spectra (Fig. 1) show that these molecules have approximately the same extent of conjugation. The inductive effects of the methyl and the *t*-butyl groups are probably very similar in the present case. Yet, the difference in chemical shift of the amine protons amounts to 2.0 ppm. We consider this to be a strong argument in favour of hydrogen bonding as the cause of the downfield shift of the protons.

The coupling constants within the ethyl groups all fall in the range 7.0—7.3 Hz. Likewise, the coupling constants between the amine protons and the protons on the adjacent carbon atoms all fall in the range 4.9—6.2 Hz. Also here, the variations seem to small to warrant discussion, in particular since no definite trends can be observed. In the unsubstituted compounds, no coupling with the amine protons is observed. Rapid intermolecular hydrogen exchange is the most probable explanation.[6b] This exchange ought to be absent in those compounds which have their basicity decreased by one or more nitro groups conjugated with the alkylamino group.

IR data. The wave numbers of the NH stretching vibration (Table 3) will now be discussed. It is interesting to compare the results obtained in carbon tetrachloride and in nitrobenzene solution with respect to hydrogen bonding. Fundamentally, IR studies of hydrogen bonding should be carried out in solvents of the former type, in which solvent-solute interactions are minimized.[7] Nitrobenzene was also used here since the same solvent had been used in the NMR work (for solubility reasons). Nitrobenzene has acceptor properties and might therefore form hydrogen bonds with solutes that can act as proton donors. For two of the compounds in Table 3, such behaviour is probably observed, since lower values are obtained for the NH bands in nitrobenzene than in carbon tetrachloride. Hydrogen bonding is known to decrease the NH stretching vibration frequency.[7]

In the first compound, N-methyl-2,4-dinitroaniline, no frequency difference is observed when the solvent is changed. The explanation for this might be that this compound is free to assume a planar conformation in which the intramolecular hydrogen bond is strong enough to cause no solvent influence.

In N,2-dimethyl-4,6-dinitroaniline, two bands were obtained in both solvents. Partial replacement of the amine proton by deuterium was effected by dissolving the compound in a mixture of equal volumes of dry pyridine and heavy water and then evaporating to dryness *in vacuo*. This caused the intensity of both bands to decrease, and they were therefore both associated with the NH group. Possibly, comparable amounts of two conformers exist in equilibrium with life-times at room temperature long enough to give rise to two distinct lines. As has already been mentioned, Musso [2] has observed a similar phenomenon in N,3,6-trimethyl-2-nitroaniline. If the two conformers had been interconverting sufficiently slowly, band broadening effects in the NMR spectra would have been observed. The NMR spectra of N,2-dimethyl-4,6-dinitroaniline and N,3,6-trimethyl-2-nitroaniline were recorded at various temperatures from 38° to −50°, and even at the lowest temperature, no band broadening was detected. This brackets the interconversion rate between the limits given by the resolution times of the IR spectroscopic method and the NMR method. The ratio between these times can be estimated to 10^{-12}. The situation is therefore by no means unique.

It is interesting that, while in carbon tetrachloride the areas of the high-frequency and the low-frequency band (corresponding to the less and the more hydrogen-bonded conformation) are of the approximate ratio 1:10, in nitrobenzene the ratio is approximately 1:1. This leveling effect of nitrobenzene can be explained if one assumes that in carbon tetrachloride, the conformational equilibrium is mainly governed by intramolecular forces, while in nitrobenzene, solvent-solute interactions also have to be considered.

The two conformers of N,2-dimethyl-4,6-dinitroaniline are illustrated in Fig. 3.

It is remarkable that the wave number of the lower frequency band in N,2-dimethyl-4,6-dinitroaniline (3354 cm^{-1} in carbon tetrachloride) is still lower than that of N-methyl-2,4-dinitroaniline (3382 cm^{-1}). Musso [2] has observed exactly the same behaviour upon comparing N,2-dimethyl-6-nitroaniline and N-methyl-2-nitroaniline. His explanation, compression of the hydrogen bond caused by the buttressing effect of the *ortho* methyl group on the methylamino group, thus bringing it closer to the nitro group, might apply equally well in the present case. The reason why this tighter hydrogen bond is not reflected in the NMR chemical shift of the amine proton (Table 1)

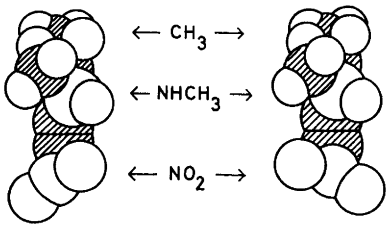

Fig. 3. Stuart models of the two conformations of N,2-dimethyl-4,6-dinitroaniline. Benzene rings viewed from the edge.

is that the latter value is the average for the two conformers. It would have been interesting if the two conformers could have been frozen to yield the two values from which the average is obtained, but, as mentioned above, this was not possible.

In the IR spectrum of N,2-dimethyl-6-nitroaniline, Musso [2] found only one NH stretching band at 3377 cm^{-1} in carbon tetrachloride solution. We find in the same solvent for N,2-dimethyl-4,6-dinitroaniline two bands at 3354 and 3461 cm^{-1}. Since these compounds only differ by a *para* substituent, it is surprising that Musso's compound does not give two bands also. No obvious explanation for this can be given.

The strong band at 3354 cm^{-1} of the N,2-dimethyl-4,6-dinitroaniline has a lower frequency than the corresponding band in N,2-dimethyl-6-nitroaniline at 3377 cm^{-1}. In these molecules, the *ortho* substituent pattern is similar. One would expect that the normal vibration modes that closely involve the NH band, *e.g.*, the NH stretching mode, would be invariant to substitution with a *para* nitro group. The wave numbers show, however, that the NH stretching vibration is sensitive to the *para* substituent. The difference can be readily explained if the hydrogen bond between the amine proton and the *ortho* nitro group is considered. The *para* nitro group inductively decreases the electron density of both the NH bond and the *ortho* nitro oxygen atoms by a small amount. Far more important, however, is the conjugative effect of the *para* nitro group, which acts only on the amino group, making the proton more acidic. The donor property of this proton is therefore increased more than the acceptor property of the *ortho* nitro group is decreased, resulting in a better hydrogen bond and therefore a decrease in frequency.[7]

On the other hand, the weak band at 3461 cm^{-1} of N,2-dimethyl-4,6-dinitroaniline is probably less influenced by removal of the *para* nitro group. Though no corresponding band was observed by Musso,[2] he found in N,3,6-trimethyl-2-nitroaniline two bands, the one at 3463 cm^{-1} ascribed to a non-hydrogen-bonded conformation. The similarity of these numbers is extremely satisfying, since they are both ascribed to non-hydrogen-bonded conformers of the two compounds, and in these conformers, inductive and conjugative substituent effects on the NH stretching mode should be absent.

For completeness, it should also be mentioned that in N-methyl-2,4-dinitroaniline, the NH stretching band is at 3382 cm^{-1}, and in N-methyl-2-nitroaniline, where the *para* nitro group is lacking, the corresponding band was found by Musso [2] to occur at 3392 cm^{-1}. Stronger hydrogen bonding in the dinitro compound probably causes the frequency decrease; the discussion above applies also to this case.

Finally, the NH stretching band in N-methyl-2-*t*-butyl-4,6-dinitroaniline will be discussed. In either solvent, the wave number is unusually high (Table 3). This is perfectly consistent with the assumption that no intramolecular hydrogen bond is present. A lower value is obtained in nitrobenzene than in carbon tetrachloride, which is ascribed to hydrogen bond formation with the former solvent. This contrasts with the behaviour of N-methyl-2,4-dinitroaniline, which has a strong intramolecular hydrogen bond and therefore displays the same wave number in either solvent.

A word of caution at this point might be in order: Even though the absence of hydrogen bonding is held responsible for the high frequency in the *t*-butyl compound, it should be kept in mind that, quite generally, steric compressions have the effect of increasing the frequency of the normal modes of vibration in a molecule through stronger interatomic repulsions.[8] In the present case, however, the observed solvent dependence clearly indicates that the arguments based on absence of hydrogen bonding must be valid.

We can thus conclude that the conformational assignments based on the IR data are in complete agreement with those founded on the NMR studies.

EXPERIMENTAL

General remarks. Melting points have been determined on a Kofler micro hot stage. In several cases, the yields in the final stage are probably essentially quantitative. The low values stated are due to purification losses, particularly since the compounds that are new (denoted by an asterisk) had to be recrystallized to constant melting point. For brevity, this is not repeatedly indicated in the text. No elementary analyses have been made, since the NMR spectra are completely conclusive. Compounds not described here were available from previous work.[1]

NMR spectra were recorded on a Varian A-60 instrument as before.[1]

Electronic spectra were recorded on a Perkin-Elmer Spectracord 4000 A instrument n spectro grade absolute ethanol solution, path length 1 cm.

IR spectra were recorded on a Beckman IR-9 instrument. The spectra in nitrobenzene were run using 10 % solutions in a 0.1 mm KBr cell in the wavelength range 2.5—5.0 μ. A variable-thickness cell containing pure solvent and adjusted for optimum compensation of the solvent absorption was used in the reference beam. The spectra in carbon tetrachloride solution were run with 10^{-3} M solutions. Fused silica cells, path length 4 cm, were used, which limited the wavelength range to 2.5—4.1 μ.

Pivaloyl chloride was prepared from pivalic acid and benzoyl chloride according to Brown.[9] Yield 90 %, b.p. 100°, lit.[9] 104°.

Pivalanilide was prepared from the preceding compound and excess aniline according to a standard procedure.[10] Yield after recryst. from benzene-petroleum ether (1:1 by vol.) 75 %, m.p. 133°, lit.[11] 132°.

N-Neopentylaniline. With the aid of a continuous extractor, 8.0 g (0.045 mole) pivalanilide was added to a refluxing solution of 4.0 g (0.105 mole) lithium aluminium hydride in 500 ml ether. The operation took 2 h, pivalanilide being sparely soluble in ether. Boiling was continued for another 2 h, and the mixture was left overnight. Water was then carefully added, followed by 10 % sodium hydroxide solution. The ether layer was decanted from the precipitated alumina, washed with water and dried over solid potassium hydroxide. The ether was stripped off on a steam bath and the remaining viscous oil distilled through a short Vigreux column to give 6.1 g (0.037 mole) N-neopentylaniline as a colourless oil, representing 82 % yield. The boiling point remained constant during the entire distillation, 122°/22 mm. The reported[12] boiling range is 109—111°/13 mm.

Neopentylamine was prepared from pivalonitrile and lithium aluminium hydride according to Curtin and Gerber.[13] Yield 52 %, b.p. 82°, lit.[13] 80°.

N-Neopentyl-2-nitroaniline * was prepared from equimolar amounts of 2-nitrofluorobenzene, neopentylamine and triethylamine, dissolved in the minimum amount of 95 % ethanol, by keeping this mixture for a week at room temp. 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* and the remainder recryst. from methanol. Yield 50 % of orange plates, m.p. 57—58°.

N-Neopentyl-4-nitroaniline * was prepared from 4-nitrofluorobenzene and excess neopentylamine by refluxing for 3 h in ethanol solution. Yield after recryst. from ethanol 10 %, yellow needles, m.p. 76—77°.

* This compound is believed to be new.

N-Neopentyl-2,4-dinitroaniline * was prepared from 2,4-dinitroanisole and a slight excess of neopentylamine in ether solution in an instantaneous reaction. Yield after recryst. from ethanol 64 %, yellow needles, m.p. 107.5—108.5°.

N-Neopentyl-2,6-dinitroaniline * was prepared from 2,6-dinitroanisole and a slight excess of neopentylamine by refluxing for 10 min in ethanol solution. Yield after recryst. from ethanol 35 %, orange needles, m.p. 91°.

N-Neopentyl-2,4,6-trinitroaniline * was prepared from equimolar amounts of 2,4,6-trinitroanisole and neopentylamine in methanol solution in an instantaneous reaction. Yield after recryst. from ethanol 80 %, yellow needles, m.p. 107.5—108°.

2-Methyl-4,6-dinitroanisole was prepared through dinitration of 2-methylanisole according to Brady and Day.[14] Yield after recryst. from methanol 57 %, m.p. 68—69°, lit.[15] 72°.

N,2-Dimethyl-4,6-dinitroaniline was prepared from the preceding compound and a slight excess of methylamine in methanol solution by refluxing for 5 min. Yield after recryst. from ethanol 70 %, yellow needles, m.p. 127—127.5°, lit.[16] 126.5—127.5°.

N-Ethyl-2-methyl-4,6-dinitroaniline * was prepared from 2-methyl-4,6-dinitroanisole and a slight excess of ethylamine by refluxing for 10 min in ethanol solution. Yield after recryst. from ethanol 50 %, yellow needles, m.p. 80—80.5°.

N-Neopentyl-2-methyl-4,6-dinitroaniline * was prepared from 2-methyl-4,6-dinitroanisole and a slight excess of neopentylamine by refluxing for 10 min in ethanol solution. Yield after recryst. from ethanol 64 %, yellow needles, m.p. 81—81.5°.

2-t-Butyl-4,6-dinitroanisole was prepared from 2-*t*-butylphenol *via* dinitration and methylation according to Fierens *et al.*[17] Overall yield after recryst. from ethanol 30 %, m.p. 77—79°, lit.[17] 81°.

N-Methyl-2-t-butyl-4,6-dinitroaniline. * Of the preceding compound, 2.54 g (0.01 mole) were refluxed for 8 h with 10 ml 33 % methylamine in water and 50 ml ethanol. This roughly corresponds to a tenfold excess of methylamine. The mixture was then left aside at room temp. for two days. Yellow crystals had then formed and were filtered from the supernatant red liquid and recryst. from ethanol. Yield 0.95 g (0.0037 mole) or 37 %, yellow rods, m.p. 164—165°.

2-t-Butyl-4,6-dinitrochlorobenzene was prepared from 2-*t*-butyl-4,6-dinitroanisole *via* treatment with ammonia to give the aniline, diazotization and a Sandmeyer reaction, all according to Fierens *et al.*[17] and Cortier *et al.*[18] Overall yield after recryst. from methanol 21 %, m.p. 61—62°,[18] lit. 63°.

N-Ethyl-2-t-butyl-4,6-dinitroaniline * was prepared from the preceding compound and a tenfold excess of ethylamine by refluxing for 18 h in toluene solution. The solvent and excess ethylamine were removed *in vacuo* and the remaining solid recryst. from ethanol. Yield 63 %, yellow rods, m.p. 119.5—120.5°.

N-Neopentyl-2-t-butyl-4,6-dinitroaniline * was prepared from 2-*t*-butyl-4,6-dinitrochlorobenzene and a threefold excess of neopentylamine by refluxing for 18 h in toluene solution. After cooling, the solution was filtered from a colourless, crystalline precipitate of neopentylamine hydrochloride, the solvent and excess neopentylamine were removed *in vacuo* and the remaining solid recryst. from ethanol. Yield 50 %, yellow needles, m.p. 92.5—93°.

N,3,6-Trimethyl-2-nitroaniline was prepared from *p*-xylene *via* dinitration, separation of the isomers and reaction with methylamine according to Musso.[2] Overall yield 29 %, red oil, b.p. 116°/1 mm, lit.[2] 115°/2 mm. The chromatography step described by Musso can be omitted, since no impurities could be detected in the crude product, according to NMR.

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