

Structure of *N*,4-dinitroaniline and its complex with sulfolane at 85 K; on the proton donor–acceptor affinity of the primary nitramine (HNNO₂) group

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The NNO₂ group of the title compound is significantly less twisted with respect to the aromatic ring in comparison to a typical secondary nitramine. The amide nitrogen is trigonally hybridized. The nitramino group is almost planar. The C–C–N–N torsion angles vary between *ca* 13 and 42°, whereas the twist along the N–N bond is much smaller and amounts to between *ca* 1 and 15°. Those twist angles are governed by a crystal packing and are much larger in the case of crystals of pure *N*,4-dinitroaniline in comparison to that of its complex with sulfolane. The deviations of the internal angles of the aromatic ring from 120° do not exceed 3°. The presence of the nitro group increases the C–C–C valence angle of *ca* 2.0–2.6°, whereas an analogous effect associated with the nitramino group is much smaller (*ca* 0.3–1.3°), pointing to its weak electron-withdrawing properties. The nitramino group displays no tendency to conjugate with an electron-demanding substituent across the ring. It participates in hydrogen bonding only as a hydrogen-bonding donor. It does not act as a proton acceptor, despite the fact that nitramine rearrangement is catalysed by acids.

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1. Introduction

The structure of the simplest aliphatic secondary nitramine, *viz.* *N,N*-dimethylnitramine, was studied in detail with the use of various methods. The molecule is planar, or nearly planar, indicating trigonal hybridization of the amide nitrogen. The estimated N–N bond length ranged from 1.323 (Filhol *et al.* 1980) to 1.342 Å (Krebs *et al.*, 1979) and was significantly larger than a typical distance between two double-bonded N atoms. Consequently, some electron pairs, within the nitramino group, must occupy π -orbitals of non-bonding character. In more complex, cyclic or open-chain secondary nitramines, serious deformations from planarity were observed. The torsion angle along the N–N bond may reach 19° and the dihedral angle between the NNO₂ group and the C₂N planes may increase up to 34° (Choi & Bulusu, 1974). The stronger the deviations from planarity, the longer the N–N bond, up to 1.400 Å. It seems that the nitramino group is rather sensitive to the sterical and electronic properties of the substituents to which it is bound, *i.e.* to the non-valence intramolecular interactions. The intermolecular interactions in a crystal network may also determine the geometry of a nitramine to some extent.

In secondary nitramines another problem appears; in the tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline) molecule, a large torsion angle, along the Ar–N bond (65°), may be the result of sterical interaction between the *N*-nitro group and the nitro

Table 1

Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	C ₁₆ H ₁₈ N ₆ O ₁₀ S	C ₆ H ₅ N ₃ O ₄
Chemical formula weight	486.42	183.13
Cell setting, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.043 (3), 17.131 (4), 12.299 (4)	6.947 (1), 7.773 (2), 13.836 (3)
α , β , γ (°)	90, 107.95 (3), 90	84.25 (3), 79.77 (3), 81.27 (3)
<i>V</i> (Å ³)	2013.1 (10)	724.7 (3)
<i>Z</i>	4	4
<i>D_x</i> (Mg m ⁻³)	1.605	1.679
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	24	28
θ range (°)	16–23	17–24
μ (mm ⁻¹)	0.232	0.144
Temperature (K)	85.0 (1)	85.0 (1)
Crystal form, colour	Plates, yellow	Plates, yellow
Crystal size (mm)	0.5 × 0.3 × 0.25	0.5 × 0.45 × 0.4
Data collection		
Diffractometer	Kuma KM4	Kuma KM4
Data collection method	ω scans	ω scans
No. of measured, independent and observed parameters	4440, 4200, 3360	3500, 3255, 2972
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.0611	0.0179
θ _{max} (°)	26.99	28.06
Range of <i>h</i> , <i>k</i> , <i>l</i>	–12 → <i>h</i> → 0 –21 → <i>k</i> → 0 –14 → <i>l</i> → 14	–9 → <i>h</i> → 0 –9 → <i>k</i> → 9 –18 → <i>l</i> → 18
No. and frequency of standard reflections	2 every 50 reflections	2 every 50 reflections
Intensity decay (%)	0.45	–0.51
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.053, 0.165, 1.187	0.0313, 0.0899, 1.052
No. of reflections and parameters used in refinement	4200, 298	3255, 265
H-atom treatment	Mixed	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 7.0136P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.3180P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.033	0.009
$\Delta\rho$ _{max} , $\Delta\rho$ _{min} (e Å ⁻³)	0.606, –0.414	0.33, –0.25

Computer programs used: *KM4b8* (Kuma Diffraction, 1997), *DATARED9* (Kuma Diffraction, 1997), *SHELXTL* (Sheldrick, 1990), *SHELXL97* (Sheldrick, 1997).

groups in the *ortho* positions (Cady, 1967). However, in *N*-(4-chlorophenyl)-*N*-methylnitramine and *N*-methyl-*N*,4-dinitroaniline, the nitramino group is also nearly perpendicular to the aromatic ring (Ejsmont *et al.*, 1998; Anulewicz *et al.*, 1993). Consequently, mesomeric interaction of the nitramino and the aromatic sextets is not possible. The same is true in the case of secondary nitramines of the pyridine series; the geometry of some derivatives on *N*-methyl-*N*-(4-pyridyl)nitramines with substituents on N1 is analogous (Zaleski *et al.*, 1999*a,b*). Despite the formal positive charge in the aromatic ring, there is no conjugation between the ring and the π -electrons of the substituent. The lone pair on the amide nitrogen is completely shifted towards the *N*-nitro group and does not interact with the aromatic sextet.

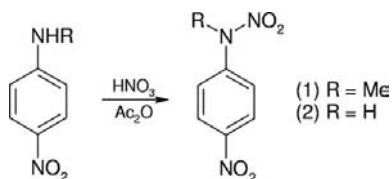
Primary phenylnitramines are not so readily accessible as their secondary analogues, hence there is no data on their structures. We use these compounds as model substrates in our investigations on the mechanism of nitramine rearrangement, hence we are interested in their molecular structures, and especially in similarities and differences between the analogous primary and secondary nitramines.

The acidities of primary nitramines are similar to those of carboxylic acids. Their dissociation constants are strongly temperature dependent. It has been interpreted as a result of the pseudo-acid equilibrium in solutions (Wright, 1969). A typical carboxylic acid exists as a hydrogen-bonded dimer, even in solutions in non-polar solvents and in a vapour state. Some acids exist, at least partially, in the hydrogen-bonded polymeric form (Colthup *et al.*, 1964). We expected either dimerization or multimerizations of the title nitramine molecules, involving N–H...O hydrogen bonds between H atoms of the primary nitramino group and either of the O atoms of the nitro groups. The position of the acidic proton should be directed to a basic center within the nitramino group. This is a very important problem, from the point of view of the mechanism of the nitramine rearrangement involving the migration of the *N*-nitro group to the *ortho* and *para* positions of the aromatic ring. In such a discussion, it is presumed without any proof that protonation on the amide nitrogen is a preliminary step

of the transformation (Williams, 1996). In the structure of *N,N'*-dinitroethylenediamine, the dipole–dipole interaction is the predominant crystal binding force. One short intermolecular distance (N–H...O 3.007 Å) may be considered as a weak hydrogen bond, but its influence on the crystal packing is negligible (Llewellyn & Whitmore, 1948; Turley, 1968). In the primary nitramines of the pyridine series, containing an additional basic centre in the aza-aromatic ring, the proton transfer is almost complete. The molecules exist in the nitramino tautomeric forms, bonded by strong hydrogen bonds (Krygowski *et al.*, 1996; Angelova *et al.*, 1998).

We wish to report on the crystal and molecular structure of a primary nitramine of a benzene series in comparison with its secondary analogue and the aforementioned primary nitra-

mines. The crystal and molecular structure of *N*-methyl-*N*,4-dinitroaniline (1) is known (Anulewicz *et al.*, 1993), therefore, we have prepared its primary counterpart *N*,4-dinitroaniline (2).



2. Experimental

2.1. Synthesis

N,4-Dinitroaniline: to a solution of 4-nitroaniline (2.76 g, 0.02 mol) in sulfolane (20 ml), absolute nitric acid (1.0 ml, 0.024 mol) dissolved in acetic anhydride (4.0 ml) was added. The mixture was maintained for 1 h at room temperature and poured on ice and water (600 g). The solution was extracted with ethyl ether (2 × 50 ml), and the extract was diluted with an equal volume of *n*-hexane and dried over anhydrous magnesium sulfate. The product was adsorbed on silica gel (Kieselgel 60, E. Merck) and chromatographed on a column using the benzene–*n*-hexane mixture as the eluent to remove the excess sulfolane. The main product was eluted with benzene and the solution was concentrated and cooled. The nitramine–sulfolane 2:1 complex was obtained as yellow crystals (m.p. 350–351 K) suitable for X-ray diffraction studies. IR (KBr): 3242, 3218, 3159, 3138 cm⁻¹ (nitramide proton); 1520 (asymmetric stretch of nitro groups); 1315, 1293 (envelopes including stretching vibrations of the nitro and sulfonyl groups); 1254 (symmetric stretch of SO₂ group). ¹H NMR (DMSO-*d*₆): 8.32, d, 2H and 7.70, d, ³*J* = 9.4 Hz, 2H (aromatic protons); 3.01–3.09, m, 4H and 2.02–2.17, m, 4H (sulfolane ring).

Repeated crystallization from methylene chloride gave *N*-(4-nitrophenyl)nitramine free of sulfolane; m.p. 384–385 K. The same compound was obtained in 58% yield when nitration with mixed anhydride was carried out in nitromethane. Crystals suitable for X-ray diffraction studies were grown from methylene chloride solutions by slow cooling. MS, *m/z* (int): 183 (*M*⁺, 6), 137 (100), 121 (6), 107 (7), 91 (30), 79 (15), 64 (65), 63 (73). IR (KBr): 3331, 3272, 3184, 3120 cm⁻¹ (nitramide proton); 1511, 1494, 1457, 1392, 1329 and 1292 cm⁻¹ (strong bands in the region of the nitro group stretching vibrations). ¹H NMR (acetone-*d*₆): 13.06, s (broad), 1H (proton on heteroatom); 8.34, d, 2H (3,5 aromatic protons); 7.80, d, ³*J* = 9.4 Hz, 2H (2,6-aromatic protons). ¹³C NMR (DMSO-*d*₆): 144.2 (C4); 141.6 (C1); 124.9 (C3); 119.9 (C2).

2.2. X-ray data collection

Data for structure determination were collected on a Kuma KM4 diffractometer with Mo *K*α radiation (λ = 0.71073 Å, graphite monochromator). The diffractometer was equipped

Table 2

Bond lengths in *N*,4-dinitroaniline and in its complex with sulfolane.

Bond length (Å)	Nitramine (2)		Nitramine–sulfolane complex	
	(2a)	(2b)	(2a)	(2b)
C1–C2	1.398 (2)	1.400 (2)	1.398 (5)	1.398 (5)
C2–C3	1.381 (2)	1.380 (2)	1.378 (5)	1.374 (5)
C3–C4	1.387 (2)	1.382 (2)	1.381 (5)	1.392 (5)
C4–C5	1.389 (2)	1.388 (2)	1.381 (5)	1.383 (5)
C5–C6	1.381 (2)	1.381 (2)	1.390 (5)	1.379 (5)
C6–C1	1.396 (2)	1.398 (2)	1.394 (5)	1.399 (5)
C1–N7	1.408 (2)	1.401 (2)	1.409 (4)	1.405 (4)
N7–N8	1.366 (1)	1.358 (1)	1.345 (4)	1.354 (4)
N8–O9	1.221 (1)	1.222 (1)	1.229 (4)	1.230 (4)
N8–O10	1.229 (1)	1.232 (1)	1.232 (4)	1.230 (4)
C4–N11	1.457 (2)	1.458 (8)	1.466 (4)	1.461 (4)
N11–O12	1.241 (1)	1.224 (1)	1.225 (4)	1.226 (4)
N11–O13	1.222 (1)	1.236 (1)	1.232 (4)	1.234 (4)

with an Oxford cryosystem cooler (dry nitrogen gas stream, temperature stability ±0.1 K). Selected crystallographic data are shown in Table 1.¹ The reflection intensities were collected using the ω–θ scan technique (scan speed 0.3–0.15 s⁻¹, scan width 1°). Two control reflections measured after an interval of 50 reflections showed that the intensity variation was negligible. Lorentz–polarization corrections were applied. The *SHELXTL* (Sheldrick, 1990) set of programs was used for structure solution (direct methods) and refinement (full-matrix least-squares method), whereas the *SHELXL* (Sheldrick, 1997) program was used for drawings.

3. Results and discussion

The synthesis was carried out according to the procedure employed previously in *N*-nitration of 5-nitroindazole (Zaleski *et al.*, 1998). Sulfolane was used as an inert solvent to prevent acetylation with the nitric acid–acetic anhydride mixture. To our surprise, we have obtained a molecular 2:1 complex of the nitramine and the solvent. Nitramines display a tendency to form some complexes with solvents like acetone, dioxane or *N,N*-dimethylformamide (Cobbledick & Small, 1973), but in this case it should be expected that the binding force is of a different nature. The nitramine free of sulfolane was obtained by crystallization from methylene chloride or by nitration in nitromethane solution.

In both crystals, there are two *N*,4-dinitroaniline molecules in an independent part of the unit cell (Fig. 1). The differences in bond lengths, aromatic rings and functional groups are not large. Valence angles are more sensitive to the intermolecular interactions in the crystal lattice, but the most significant variations are observed in the values of torsion angles (see Tables 2–4). Three bonds of the amide nitrogen N7 are arranged in a plane, as in typical secondary nitramines, indicating trigonal hybridization of this atom. The whole nitramino group in (1) is almost planar; the torsion angle along the N7–N8 bond being ~2° only (Anulewicz *et al.*, 1993), while in

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: LC0040). Services for accessing these data are described at the back of the journal.

Table 3
Selected valence angles of *N*,4-dinitroaniline and its complex with sulfolane.

Bond angles (°)	Nitramine (2)		Nitramine-sulfolane complex	
	(2a)	(2b)	(2a)	(2b)
C6–C1–C2	121.0 (1)	120.8 (1)	121.3 (3)	120.3 (3)
C1–C2–C3	119.8 (1)	120.0 (1)	119.5 (3)	120.7 (3)
C4–C3–C2	118.4 (1)	118.5 (1)	118.8 (3)	118.2 (3)
C5–C4–C3	122.5 (1)	122.5 (1)	122.6 (3)	122.0 (3)
C6–C5–C4	119.0 (1)	119.2 (1)	119.1 (3)	119.6 (3)
C5–C6–C1	119.2 (1)	119.1 (1)	118.7 (3)	119.2 (3)
C6–C1–N7	122.7 (1)	124.8 (1)	124.1 (3)	126.2 (3)
C2–C1–N7	116.1 (1)	114.4 (1)	114.5 (3)	113.5 (3)
C1–N7–N8	123.5 (1)	126.9 (1)	126.4 (3)	127.9 (3)
N7–N8–O9	119.4 (1)	120.0 (1)	119.9 (3)	119.0 (3)
N7–N8–O10	115.2 (1)	114.6 (1)	116.0 (3)	116.0 (3)
O9–N8–O10	125.4 (1)	125.4 (1)	124.1 (3)	125.0 (3)
C3–C4–N11	118.9 (1)	118.3 (1)	119.0 (3)	118.2 (3)
C5–C4–N11	118.6 (1)	119.2 (1)	118.4 (3)	119.7 (3)
C4–N11–O12	117.7 (1)	118.6 (1)	118.2 (3)	118.6 (3)
C4–N11–O13	119.2 (1)	118.0 (1)	118.1 (3)	118.3 (3)
O12–N11–O13	123.1 (1)	123.4 (1)	123.7 (3)	123.1 (3)

molecule (2) it varies from ~ 1 to 15° . The differences result from the distinct nature of the intermolecular forces and conformations of molecules (1) and (2), and do not reflect any distinction in the charge distribution within the primary and secondary nitramino groups. Three atoms, N7, N8 and O9, of

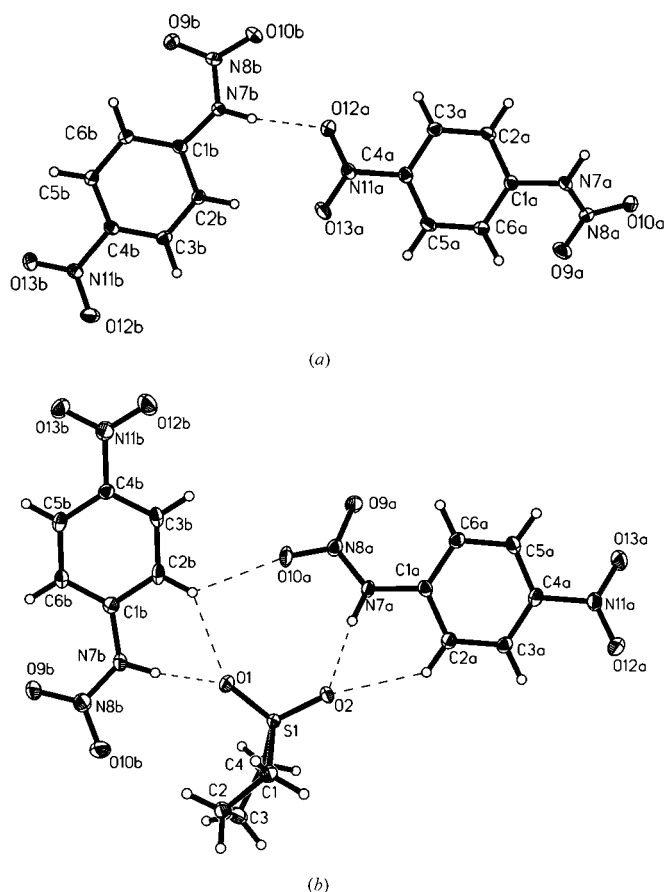


Figure 1
Molecular structure of (a) *N*,4-dinitroaniline and (b) its complex with sulfolane showing 50% probability ellipsoids.

Table 4
Selected torsion angles in *N*,4-dinitroaniline (2) and its complex with sulfolane.

Torsion angles (°)	Nitramine (2)		Nitramine-sulfolane complex	
	(2a)	(2b)	(2a)	(2b)
C6–C1–N7–N8	44.8 (2)	–23.8 (2)	18.2 (5)	14.3 (6)
C2–C1–N7–N8	–139.7 (1)	159.9 (1)	–163.4 (3)	–167.5 (3)
C1–N7–N8–O9	–16.2 (2)	6.7 (2)	–1.5 (5)	–7.3 (5)
C1–N7–N8–O10	–165.8 (1)	–174.3 (1)	179.8 (3)	172.9 (3)
C3–C4–N11–O13	–167.2 (1)	–162.8 (1)	168.3 (3)	179.8 (3)
C3–C4–N11–O12	14.2 (2)	17.8 (2)	–11.4 (5)	0.0 (5)
C5–C4–N11–O13	14.1 (2)	19.0 (2)	–11.1 (5)	–1.8 (5)
C5–C4–N11–O12	–164.6 (1)	–160.4 (1)	169.2 (3)	178.4 (3)

the nitramino group and three others, C1, C6 and hydrogen on the latter, form an irregular hexagon. Its internal angles, centred on C1, N7 and N8, are significantly greater than in (1); their sum varies from 365.6 to 373.1° and is the lowest in the molecule, in which the torsion angles along C1–N7 and N7–N8 are the largest. The aforementioned valence angles in (1) do not exceed 120° , but in this molecule the nitramino group is nearly perpendicular to the aromatic ring. It is inferred that in aryl nitramines, the NNO_2 group can accommodate a conformation without a sterical interaction between the nitramino group and *ortho*-H atoms in two ways: either by rotation along the Ar–N bond or enhancement of the appropriate valence angles in the nitramino group. Deformations of the aromatic ring, which can be interpreted as the result of the mesomeric interaction between the nitro and nitramino groups, are not observed. In (2) the C6–C1–N7 and C1–N7–N8 angles are larger than 120° . The C1–N7–N8 angle is slightly easier to deform (from 0.8 to 2.3°) than C6–C1–N7. The C1–N7–N8 angle in both crystals is between 123.5 (1) and 127.9 (3) $^\circ$, whereas the C6–C1–N7 angle is between 122.7 (1) and 126.2 (3) $^\circ$. The characteristic feature of the NNO_2 group is the increased O–N–O angle to $\sim 125^\circ$, followed by the decrease of N–N–O angles. In this case also the intramolecular repulsion between H6 and O9 leads to a decrease in the O10–N8–N7 angle to $\sim 115^\circ$, whereas the O9–N8–N7 angle remains close to 120° . The nitramino group is rotated with respect to the phenyl ring by increasing the C–C–N–N and C–N–N–O torsion angles. The deformation is much smaller for the (2) complex with sulfolane in comparison to the pure crystals of (2). In the sulfolane complex the nitramino group is rotated for ~ 17 and 13° around the C1–N7 bond for two independent molecules, whereas the rotation around the N7–N8 bond is smaller, ~ 1 and 7° , respectively. In the case of pure *N*,4-dinitroaniline, deformations are even higher; the rotation around C1–N7 amounts to ~ 42 and 22° , whereas around the N7–N8 bond it is equal to ~ 15 and 6° . This is probably associated with the more difficult planar packing of *N*,4-dinitroaniline molecules in comparison to the packing of (2) molecules together with sulfolane.

The benzene ring retains its hexagonal shape and deformations of the internal valence angles are explicable as the result of the inductive effect of N atoms. The aromatic ring in the title compound is not a regular hexagon,

however, the deviations from its regular shape do not exceed 3° . As can be expected (Domenicano & Hargittai, 1992), the presence of the nitro group, a strong electron-withdrawing substituent, increases the valence angle centred on C4 for ~ 2.0 – 2.6° . The analogous effect on C1 is much smaller, ~ 0.3 – 1.3° , indicating that the nitramino group is only a weak electron-withdrawing substituent.

In the FTIR spectra of a series of ring-substituted *N*-methyl-*N*-phenylnitramines, absorption characteristic of the *N*-nitro group appears in the narrow regions of 1517 – 1524 and 1252 – 1289 cm^{-1} , without any relationship with the electron-donating or -releasing properties of the second substituent (Daszkiewicz *et al.*, 1995). The frequencies assigned to the asymmetric stretching vibrations of the *N*-nitro group in the primary *N*-phenylnitramines decrease from 1607 to 1585 cm^{-1} in a regular way, parallel to Hammett's σ constant. It may be indicative of some type of interaction between the nitramino group and another substituent bound to the aromatic ring.

Another interesting region of the FTIR spectra is that characteristic of protons on heteroatoms; we have observed a strong and broad absorption, with several sub-maxima, in the

region of 2930 – 3200 cm^{-1} , indicative of hydrogen bonds. The situation seems to be intermediary between those mentioned above: no hydrogen bonds in aliphatic nitramines and complete proton transfer in pyridylnitramines, but such an interpretation contradicts the experimental results. In the FTIR spectrum of (2), registered in diluted (0.13 M) solution in deuterated methylene chloride, stretching vibrations of the *N*–H bond give rise to the strong band at 3367 cm^{-1} . In the solid state (KBr pellets), a broad band has four sub-maxima between 3331 and 3120 cm^{-1} ; there is no enhancement of the absorption and the shift towards lower wavenumbers is small (Fig. 2). In fact, the hydrogen bond in the crystal network is weak and electrostatic in nature (Fig. 3).

The packing diagram of the *N*,4-dinitroaniline complex with sulfolane is presented in Fig. 4. Molecules of (2) are situated parallel to each other in the *xz* plane. Two *N*,4-dinitroaniline molecules are connected with sulfolane by *N*–H \cdots O hydrogen bonds with *N* \cdots O distances of 2.776 (4) and 2.786 (4) Å (Table 5). These motifs are connected with others by much weaker C–H \cdots O hydrogen bonds with C \cdots O distances of 3.180 (4)– 3.302 (4) Å. In crystals of pure (2) the

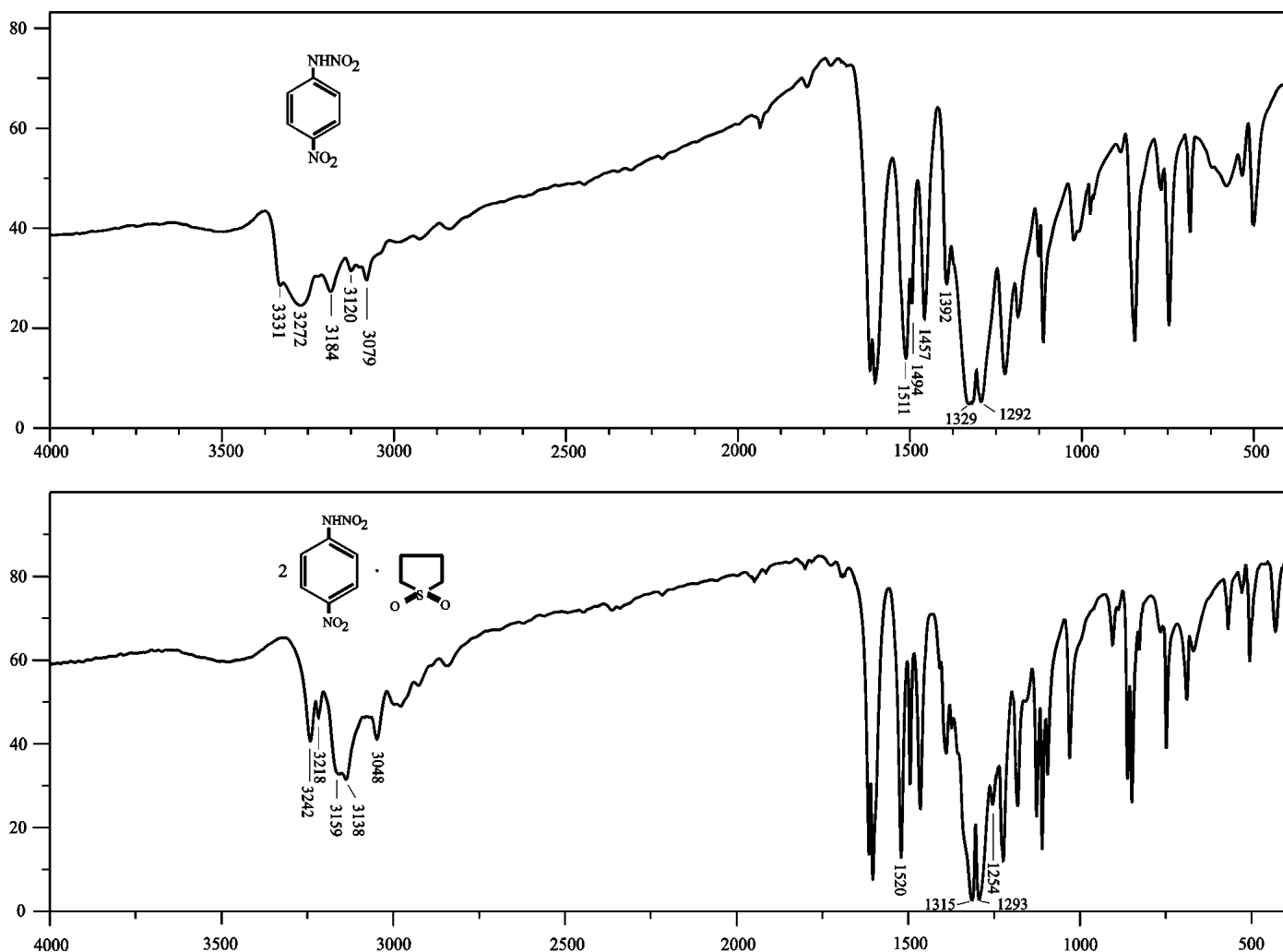


Figure 2
IR spectra of the title compounds.

Table 5

Geometric parameters of hydrogen bonds in *N*,4-dinitroaniline and its complex with sulfolane.

Hydrogen bond	$R(X-H)$	$d(H\cdots A)$	$d(X\cdots A)$	$\theta(X-H-A)$
C3a—H3a \cdots O10b ⁱ	0.94 (2)	2.52 (2)	3.192 (2)	128 (1)
C3b—H3b \cdots O10a ⁱⁱ	0.98 (2)	2.33 (2)	3.272 (2)	161 (1)
C5a—H5a \cdots O10a ⁱⁱⁱ	0.95 (2)	2.40 (2)	3.217 (2)	145 (1)
C5b—H5b \cdots O10b ⁱⁱⁱ	0.95 (2)	2.55 (2)	3.321 (2)	138 (1)
C6a—H6a \cdots O12b ^{iv}	0.94 (2)	2.53 (2)	3.421 (2)	157 (1)
N7a—H7a \cdots O13b ^v	0.87 (1)	2.20 (1)	3.064 (2)	171 (1)
N7b—H7b \cdots O12a	0.90 (1)	2.05 (1)	2.924 (2)	167 (1)
C2b—H2b \cdots O1 ^{vi}	0.96	2.41	3.196 (4)	139
C2b—H2b \cdots O10a ^{vii}	0.96	2.49	3.180 (4)	129
C5b—H5b \cdots O10b ^{viii}	0.96	2.48	3.424 (4)	169
N7a—H7a \cdots O2 ^{ix}	0.90	1.88	2.776 (4)	164
N7b—H7b \cdots O1 ^{vi}	0.90	1.98	2.786 (4)	151
C2a—H2a \cdots O2 ^{ix}	0.96	2.52	3.302 (4)	138

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, -y, -z+1$; (iii) $x, y+1, z$; (iv) $-x, -y+1, -z+1$; (v) $x+1, y-2, z$; (vi) $x+\frac{3}{2}, -y-\frac{1}{2}, z-\frac{1}{2}$; (vii) $-x+3, -y-1, -z+1$; (viii) $-x+3, -y, -z+1$; (ix) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

molecules are disposed close to the yz plane (Fig. 3). They are connected to each other with the $N-H\cdots O$ hydrogen bonds forming chains. The $N-H\cdots O$ hydrogen bonds are much weaker in comparison to those in the complex with sulfolane. The $N\cdots O$ distances are equal to 2.924 (2) and 3.064 (2) Å. The interaction between the *N*,4-dinitroaniline chains may be considered as weak $C-H\cdots O$ hydrogen bonds with $C\cdots O$ distances of 3.192 (2) to 3.421 (2) Å, comparable to those observed in the sulfolane complex. When predicting the crystal packing, we have expected either multimerization of (2) through the $N-H\cdots N$ hydrogen bonds or dimerization head-to-tail ($N-H\cdots O$) of the nitramino groups, as in carboxylic acids. It seems, however, that nitramines have no basic centre capable of hydrogen-bond formation. The O atoms of the nitro group, attached to N11, act as proton acceptors despite the poor basicity of the nitro groups.

The term basicity has two different meanings; basicity of a particular compound may be expressed as an equilibrium constant in a proton transfer reaction (pK_A) or as a formation constant (pK_{HB}) of a complex bound with a hydrogen bond. It was shown that the relationship between pK_A and pK_{HB} is limited to the same class of compounds (nitriles, ketones, ethers *etc.*). Two compounds belonging to different classes may display a significant difference in pK_A values, despite the closely related pK_{HB} values (Taft *et al.*, 1969). The *C*-nitro group may be protonated only in a concentrated sulfuric acid solution (March, 1985). However, *C*-nitro compounds form complexes with 4-fluorophenol in which a hydrogen bond is formed between the phenolic and nitro functional groups when dissolved in a non-polar solvent (Laurence *et al.*, 1994). In the crystal network of the nitramine–sulfolane complex the $N-H\cdots O$ hydrogen bond is significantly stronger, as indicated by the shorter distance between the proton donor and acceptor and pronounced shift of the $N-H$ band in the FTIR spectrum. Again, a non-basic sulfone group is a proton acceptor in this interaction. Consequently, the proton affinity

of the nitramino group is lower than that of the nitro and sulfone groups.

4. Conclusions

The results demonstrate that the primary and secondary phenylnitramines have similar electronic structure. They both are rather flexible substituents, susceptible to deformations under the influence of even weak intermolecular interactions. The nitramino group displays no tendency to conjugate with an electron-demanding substituent across the aromatic ring. The primary nitramino group participates in the hydrogen

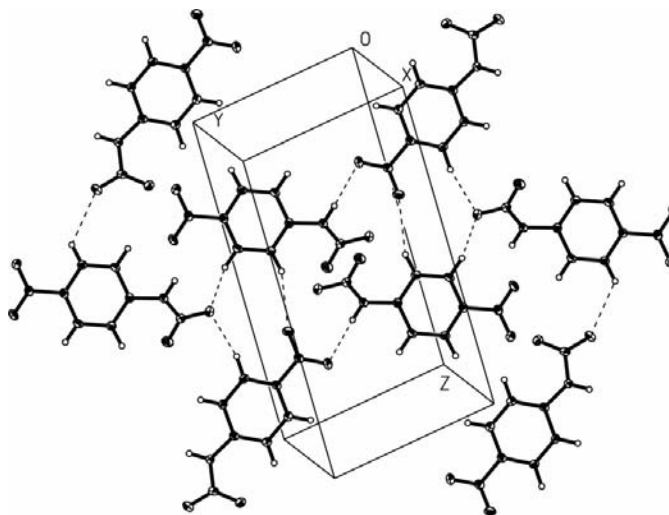


Figure 3
Packing diagram of *N*,4-dinitroaniline showing the hydrogen-bonding scheme. Ellipsoids are at the 50% probability level.

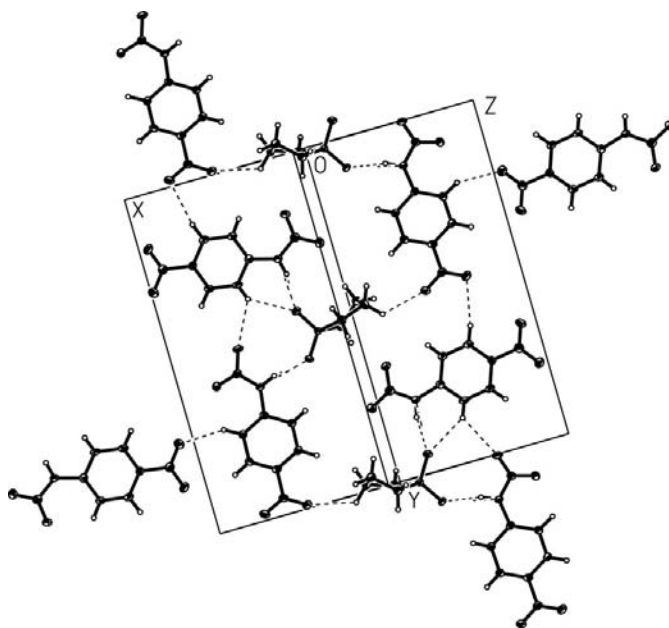


Figure 4
Packing diagram of the *N*,4-dinitroaniline–sulfolane complex showing the hydrogen-bonding scheme. Ellipsoids are at the 50% probability level.

bond as a proton donor only. It does not contain a basic centre, which could act as a proton acceptor, hence nitramines cannot react with diluted, aqueous solutions of mineral acids as bases. In spite of this, the nitramine rearrangement of compounds such as (1) or (2) are catalysed with acids. A simple explanation, involving protonation of a nitramino group as the preliminary step of the rearrangement, is not acceptable as there are discrepancies with the structure of the substrates.

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