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Structural and spectroscopic investigation of 1-Amino-2,4-dinitrobenzenes

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ABSTRACT: The crystal structures of 1-pyrrolidino-2,4-dinitrobenzene (**3**) and 1-morpholino-2,4-dinitrobenzene (**4**) were determined by single-crystal x-ray diffraction and the structures in solution were investigated by UV–visible spectrophotometry and ^{13}C and ^{1}H NMR spectrosccopy. Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with one independent molecule per asymmetric unit and **3** crystallizes in triclinic *P*-1 with three independent molecules per asymmetric unit. Rotation of the *o*-nitro group and of the amino group out of the aromatic plane was observed in both the solid state and in solution for both compounds. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: 1-amino-2,4-dinitrobenzenes; structures; single-crystal x-ray diffraction; UV–visible spectrophotometry; NMR spectroscopy

INTRODUCTION

Alkylamines have a pyramidal structure with C—N bond lengths of *ca* 1.50 Å and bond angles centered on nitrogen of *ca* 107.9°. The hybridization of nitrogen is almost sp^3 with a non-shared pair of electrons. Amines having an aryl group bound to N are flatter, owing to the interaction of the lone pair of electrons of N with the π system of the aromatic ring.[1]

As a consequence of this interaction, amines of type **1** are resistant to substitution of the amino group by a nucleophile. It has been suggested that if this interaction decreases, carbon-1 can be attacked as readily as when substituted by other groups, and the amine is displaced.[2] The interaction between the aromatic ring and the amine decreases if the amine is rotated out of the aromatic plane.

In enamines, the pyramidality of the N atom varies depending on the amine bound to the C—C double bond and the differences in chemical reactivity between pyrrolidine enamines and piperidine or open-chain enamines seem to reflect these structural differences.[3]

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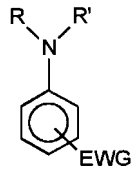

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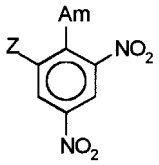

2

EWG = electron withdrawing group

We have found that several aromatic amines of type **2** (Z = H or NO_2; Am = imidazole, pyrrolidine, piperidine or morpholine) yield the corresponding substitution product when they react with hydroxide ions or other amines.[4] When Am was pyrrolidine, piperidine or morpholine, a mechanism involving the formation of σ complexes by addition of nucleophiles to the unsubstituted positions of the aromatic ring was proposed.[2,4d,e] This addition favors the displacement of the amino group due to rotation of the amine from the mean ring plane, reducing the interaction between the nitrogen and the aromatic ring and increasing the C—N bond length.[4c]

In the kinetic study of the hydrolysis reactions of 1-pyrrolidino-2,4-dinitrobenzene (**3**), 1-morpholino-2,4-dinitrobenzene (**4**), and 1-piperidino-2,4-dinitrobenzene (**5**), we found differences in the reactivities[4e] that could be due to structural differences as was observed for the corresponding 2,4,6-trinitrobenzene derivatives.[4d,5,6]

In order to explain the reactivity of compounds **3**, **4** and **5**, we have undertaken an investigation of the structure in solution and in the solid state of compounds **3** and **4**

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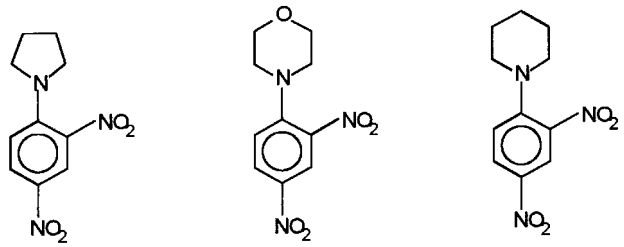


3 **4** **5**

which supports results reported previously for **5.**[7] These results are reported here.

EXPERIMENTAL

Compounds **3** and **4** were prepared from 1-chloro-2,4-dinitrobenzene and the corresponding amine as previously described.[4e]. They were crystallized by slow evaporation from acetone until crystals suitable for x-ray diffraction were obtained.

Data collection was carried out on a Siemens P4 four-circle diffractometer with graphite monocromatized Mo Kα radiation. Crystal data and experimental details are summarized in Table 1. Owing to the negligible effect of absorption, no such correction was applied to the data.

Structures were primarily solved by direct methods and completed through difference Fourier maps. Refinement was performed by full matrix least-squares on F^2 using the whole data set. H atoms were included at their expected positions and allowed to ride on to their host atoms with fixed isotropic temperature parameters. Non-H atoms were anisotropically refined until convergence was reached. Final R indices and related parameters are also given in Table 1. Table 2 lists selected interatomic bond lengths, bond angles and torsion angles. Relevant features regarding the description of the rings in the structures are given later in Table 3.

All the calculations were performed using the programs SHELXS86[8] and SHELXL93.[9] PARST95,[10] XP[11] and CIFTAB[9] were used to prepare material for publication.

UV–visible spectra in methanol (HPLC grade) were recorded on a Shimadzu UV 2101 spectrophotometer.

^{13}C and ^{1}H NMR spectra in Cl_3CD were obtained on a Bruker ACE 200 spectrometer and chemical shifts are referred to TMS.

Table 1. Crystal data and structure refinement details for 1-pyrrolidino-2,4-dinitrobenzene (**3**) and 1-morpholino-2,4-dinitrobenzene (**4**)[a]

Parameter	**3**	**4**
Compound	$C_{10}H_{11}N_3O_4$	$C_{10}H_{11}N_3O_5$
Formula weight	237.22	253.22
Crystal system	Triclinic	Monoclinic
Space group	P-1 (no 2)	$P2_1/n$ (no 14)
Crystal size (mm)	0.40 × 0.20 × 0.15	0.50 × 0.15 × 0.15
Color	Colorless	Colorless
Shape	Needles	Needles
a (Å)	7.273(2)	11.204(2)
b (Å)	15.286(4)	9.763(1)
c (Å)	15.472(4)	11.271(1)
α (°)	95.96(1)	90
β (°)	91.65(1)	113.05
γ (°)	103.43(1)	90
V (Å^3)	1661.5(8)	1134.4(3)
Z	6	4
D_c (g cm^{-3})	1.42	1.48
μ (mm^{-1})	0.11	0.12
Temperature (K)	295(2)	295(2)
Wavelength Mo Kα (Å)	0.71073	0.71073
θ range (°)	None	2.17 to 22.55
Index ranges	$-7 \le h \le 0$	$0 \le h \le 12$
	$-16 \le k \le 16$	$0 \le k \le 10$
	$-16 \le l \le 16$	$-12 \le l \le 11$
Absorption correction	None	None
F (000)	744	528
Number of reflections		
Collected	4762	1574
Independent, R_{int}	4348, 0.033	1487, 0.013
Observed [$I > 2\sigma(I)$]	2021	1167
Average $I/\sigma(I)$	5.6	7.8
Data, parameters	4348, 471	1487, 165
Goodness-of-fit on F^2	1.058	1.025
R_1, wR_2 [$I > 2\sigma(I)$]	0.066, 0.117	0.037, 0.094
R_1, wR_2 (all data)	0.169, 0.162	0.051, 0.107
Max., min. $\Delta\rho$ (e Å^{-3})	0.18, −0.18	0.14, −0.13

[a] Data collection was carried out on a Siemens P4 four-circle diffractometer with graphite monocromatized Mo Kα radiation, using the $\omega/2\theta$ scan mode. Structures were primarily solved by direct methods using SHELXS86,[8] and completed through difference Fourier maps. Refinement was performed by full matrix least-squares on F^2 with SHELXL93.[9] The weighting scheme used was $w = 1/[s^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$ and $a = 0.0524/0.0$, $b = 0.0572/0.26$ for **3**/**4**. PARST95,[10] XP[11] and CIFTAB[9] were used to prepare material for publication.

RESULTS AND DISCUSSION

Molecular structure in the solid state

Figures 1 and 2 show schematic views of the molecules with the atomic labeling used. For the sake of clarity, only one independent moiety of **3** (see below) is shown. Figures 3 and 4 provide a view of the packing arrangements in the solid.

Compound **4** crystallizes in the monoclinic space group $P2_1/n$, with one independent molecule per asymmetric unit. Compound **3**, in contrast, crystallizes in triclinic P-1 with three independent molecules (hereafter labeled **a**, **b** and **c**) per asymmetric unit. It can be seen by inspection of the list of torsion angles in Table 2 that these independent units are very similar to each other. This initially suggested the existence of an extra hidden symmetry, missed by both the diffractometer and by the preliminary precession photographs taken, which only

Table 2. Selected bond lengths (Å), angles (°) and torsion angles (°) for 1-pyrrolidino-2,4-dinitrobenzene (**3**) and 1-morpholino-2,4-dinitrobenzene (**4**).

Bond	**3a**	**3b**	**3c**	**4**
C(1)—N(3)	1.358(6)	1.355(6)	1.343(5)	1.373(3)
C(1)—C(2)	1.417(6)	1.408(6)	1.416(6)	1.414(3)
C(1)—C(6)	1.419(6)	1.413(6)	1.423(6)	1.407(3)
C(2)—C(3)	1.381(6)	1.378(6)	1.377(6)	1.377(3)
C(2)—N(1)	1.457(6)	1.469(6)	1.478(6)	1.463(3)
C(3)—C(4)	1.369(6)	1.376(6)	1.370(6)	1.375(3)
C(4)—C(5)	1.382(6)	1.382(6)	1.392(7)	1.374(3)
C(4)—N(2)	1.456(6)	1.456(7)	1.451(6)	1.459(3)
C(5)—C(6)	1.362(6)	1.363(6)	1.362(6)	1.370(3)
N(3)—C(1)—C(2)	125.8(5)	125.1(5)	125.8(5)	123.4(2)
N(3)—C(1)—C(6)	118.9(5)	119.9(5)	119.2(5)	121.6(2)
C(2)—C(1)—C(6)	115.3(5)	115.0(5)	114.8(5)	115.0(2)
C(3)—C(2)—C(1)	121.9(4)	122.8(5)	123.0(5)	123.1(2)
C(3)—C(2)—N(1)	114.1(5)	113.7(5)	114.2(4)	114.8(2)
C(4)—C(3)—C(2)	119.8(5)	119.2(5)	119.6(5)	118.7(2)
C(3)—C(4)—C(5)	120.6(5)	120.4(5)	119.7(5)	120.8(2)
C(5)—C(4)—N(2)	119.5(5)	119.8(6)	120.5(6)	120.2(2)
C(6)—C(5)—C(4)	119.8(5)	119.8(5)	120.8(5)	120.1(2)
C(5)—C(6)—C(1)	122.5(5)	122.7(5)	121.8(5)	122.2(2)
O(1)—N(1)—C(2)	117.9(6)	117.0(6)	116.6(5)	118.0(2)
C(1)—N(3)—C(10)	127.1(4)	126.0(5)	122.1(4)	121.0(2)
C(1)—N(3)—C(7)	121.3(4)	121.6(5)	125.9(4)	119.5(2)
C(10)—N(3)—C(7)	109.7(4)	110.9(5)	110.1(4)	109.8(2)
N(3)—C(1)—C(2)—C(3)	175.8(5)	175.7(5)	171.7(5)	−177.7(2)
C(6)—C(1)—C(2)—C(3)	−2.1(8)	−3.2(8)	−4.5(8)	3.7(3)
C(1)—C(2)—C(3)—C(4)	1.7(8)	1.8(9)	2.8(8)	−1.3(3)
C(2)—C(3)—C(4)—C(5)	−0.8(8)	0.3(9)	0.6(8)	−1.9(3)
C(3)—C(4)—C(5)—C(6)	0.3(9)	−0.9(9)	−2.1(9)	2.3(3)
C(4)—C(5)—C(6)—C(1)	−0.8(9)	−0.7(9)	0.3(9)	0.4(3)
C(2)—C(1)—C(6)—C(5)	1.6(6)	2.6(8)	2.9(8)	−3.2(3)
C(3)—C(2)—N(1)—O(1)	135.6(6)	126.3(8)	131.5(5)	−132.4(2)
C(3)—C(2)—N(1)—O(2)	−40.3(7)	−57.9(6)	−45.1(7)	45.2(3)
C(3)—C(4)—N(2)—O(4)	177.1(6)	−179.0(6)	−178.4(5)	−170.1(2)
C(3)—C(4)—N(2)—O(3)	−2.1(8)	1.2(9)	2.4(8)	8.7(3)
C(6)—C(1)—N(3)—C(10)	158.7(5)	163.8(5)	159.7(5)	−131.8(2)
C(6)—C(1)—N(3)—C(7)	−3.8(8)	−0.9(8)	−3.1(8)	10.8(3)
C(8)—C(7)—N(3)—C(1)	176.5(6)	−177.9(5)	−151.8(5)	158.6(2)
C(9)—C(10)—N(3)—C(1)	−150.1(6)	−156.1(5)	178.4(5)	−158.8(2)

displayed *P*-1 symmetry. Careful checks performed with PARST95[10] on the fully refined model revealed the existence of three pseudo centers of inversion at (0.18, 0.18, −0.15), (−0.18, −0.18, −0.35) and (−0.36, −0.36, −0.20) as the only possible extra symmetry elements, not consistent with the eventual existence of any lattice of higher symmetry. Similar negative results were obtained throughout the use of MYSSYM.[12]

All the information regarding the aromatic ring system is given in Table 3(a). The structure of the 2,4-dinitrobenzene core is similar in both compounds, with the planar aromatic ring exhibiting maximum deviations from the least-squares plane of 0.009(6), 0.016(6), 0.022(5) and 0.021(2) Å for molecules **3a**, **3b**, **3c** and **4**, respectively. In **5**, the aromatic ring presents a slight boat distortion with a maximum deviation of 0.085(1) Å.[7]

The nitro groups display similar orientations in the two compounds. The one bound to C(4) is almost coplanar with the aromatic plane, while the other at C(2) is considerably twisted around the C—N bond, so as to minimize steric interactions with the substituent at C(1). This effect is accompanied by a significant out-of-the-plane angle subtended by the C(2)—N(1) bond, which amounts to 6.0(4), 6.8(4), 10.0(3) and 7.0(1)° for **3a**, **3b**, **3c** and **4**, respectively. These results are in agreement with those reported for the homologous trinitro structures[6] and for compound **5**.[7] On the other hand, there is not a well defined relationship between the rotation angle of the *o*-nitro group and the size of the substituent in C(1) for compounds **3** and **4**.

In 2,4-dinitroaniline and 2,4,6-trinitroaniline, the amino group is coplanar with the aromatic ring while rotation of the *o*-nitro groups is found in the compound with two *o*-nitro groups.[13] Rotation of the amino group is observed in compounds where N is substituted with alkyl groups due to steric hindrance.[14] A similar effect is observed in the structures of 2,4-dinitroanisole and 2,6-dinitroanisole, where the presence of a second *o*-nitro

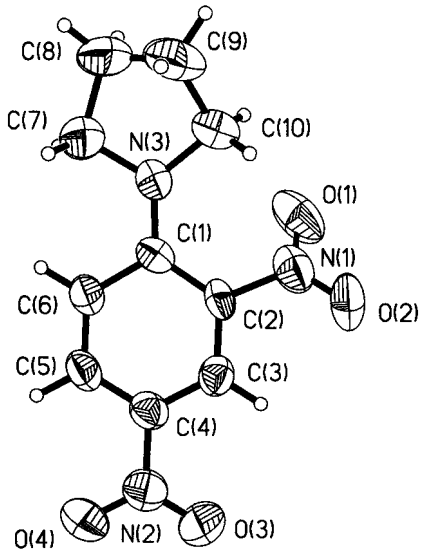


Figure 1. Schematic diagram of one of the independent moieties of **3**, showing the numbering scheme used. Ellipsoids drawn at 50% level

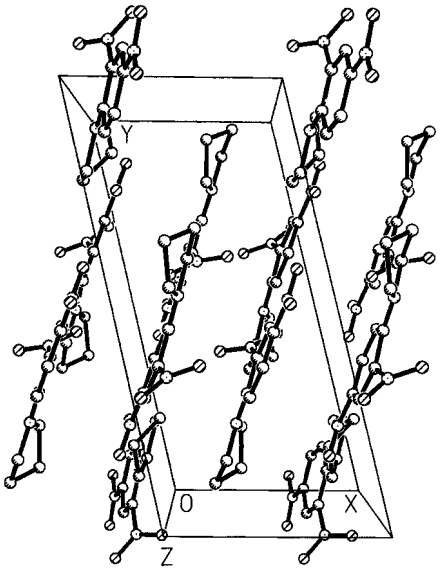


Figure 3. Packing diagram of **3**, viewed along *c*. H atoms not shown

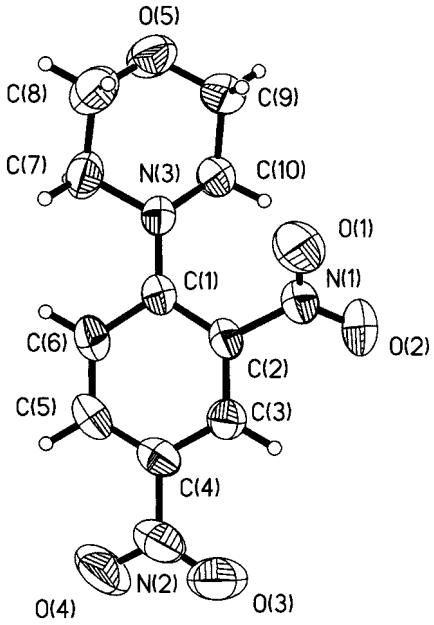


Figure 2. Schematic diagram of **4** showing the numbering scheme used. Ellipsoids drawn at 50% level

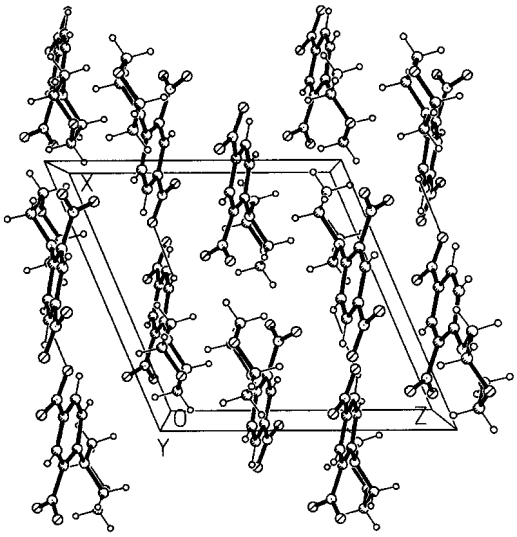


Figure 4. Packing diagram of **4**, viewed along *b*.

group in the latter causes the rotation of both the *o*-nitro groups and the substituent on C(1).[15]

Conformational details of non-aromatic rings are summarized in Table 3(b), where the displacement deformation parameters[16] and the corresponding puckering parameters,[17] as calculated by PARST95,[10] are shown. Analysis of the pyrrolidine group in **3** yields values mainly compatible with a twofold axis through N(3), thus defining a conformational state biased towards a twist. Similar results can be attained when the puckering parameters are inspected. In turn, the six-membered morpholine ring in **4** shows an unambiguous chair conformation, evidenced by a clear *D*3*h* character. Again, these results are in fair agreement with those found in the homologous trinitro compounds.[6]

The interactions providing the cohesion of the structures are purely of the van der Waals type, in contrast with what has been observed in **5** where some C—H···O distances are shorter than the sum of the van der Waals radii of the involved atoms.[7]

It can be seen from Table 3(a3) that bending of the amino group out of the aromatic plane prevails over

Table 3. Analysis of the ring systems in 1-pyrrolidino-2,4-dinitrobenzene (**3**) and 1-morpholino-2,4-dinitrobenzene (**4**).

(a) Aromatic rings

(a1) Deviations, d (Å), from weighted least-squares plane through the aromatic ring[a]

Atom	**3a**	**3b**	**3c**	**4**
C(1)	−0.009(6)	−0.016(6)	−0.022(5)	−0.021(2)
C(2)	0.009(6)	0.014(6)	0.021(5)	0.014(2)
C(3)	−0.004(6)	−0.001(6)	−0.004(5)	0.003(2)
C(4)	−0.001(6)	−0.009(6)	−0.014(6)	−0.018(2)
C(5)	0.000(6)	0.005(6)	0.014(6)	0.009(2)
C(6)	0.005(6)	0.008(6)	0.008(6)	0.012(2)

(a2) Lifting of the C—N bonds (°) out of the aromatic plane

Bond	**3a**	**3b**	**3c**	**4**
N(3)—C(1)	2.9(3)	3.0(3)	5.9(3)	1.5(1)
N(1)—C(2)	−6.0(4)	−6.9(4)	−10.0(3)	−7.0(1)
N(2)—C(4)	−1.0(3)	−0.3(4)	0.2(3)	1.5(1)

(a3) Angular deviations (°) of the amino and nitro groups out of the aromatic core

Compound	Group 1	Group 2	Total angle[b]	Rotation[c]	Bending[d]
3a	C(6)—C(1)—C(2)	C(10)—N(3)—C(7)	17.74	10.67	14.23
3b	C(6)—C(1)—C(2)	C(10)—N(3)—C(7)	14.26	7.36	12.24
3c	C(6)—C(1)—C(2)	C(10)—N(3)—C(7)	18.16	9.33	15.62
4	C(6)—C(1)—C(2)	C(10)—N(3)—C(7)	39.52	29.57	−27.69
3a	O(1)—N(1)—O(2)	C(3)—C(2)—C(1)	41.12	40.26	8.57
3b	O(1)—N(1)—O(2)	C(3)—C(2)—C(1)	54.33	53.65	0.84
3c	O(1)—N(1)—O(2)	C(3)—C(2)—C(1)	44.80	43.67	10.37
4	O(1)—N(1)—O(2)	C(3)—C(2)—C(1)	44.64	44.10	−7.22
3a	O(3)—N(2)—O(4)	C(5)—C(4)—C(3)	3.01	3.01	0.09
3b	O(3)—N(2)—O(4)	C(5)—C(4)—C(3)	1.08	0.45	0.99
3c	O(3)—N(2)—O(4)	C(5)—C(4)—C(3)	1.35	1.19	0.64
4	O(3)—N(2)—O(4)	C(5)—C(4)—C(3)	9.70	9.69	0.51

(b) Non-aromatic rings

(b1) Asymmetry parameters for the non-aromatic rings[e]

Parameter	**3a** (C_4H_8N—)	**3b** (C_4H_8N—)	**3c** (C_4H_8N—)	**4** (C_4H_8ON—)
DS[N(3)]	0.316(4)	0.315(3)	0.323(3)	0.001 (1)
DS[C(7)]	0.262(2)	0.242(3)	0.260(3)	0.008 (1)
DS[C(8)]	0.109(4)	0.077(3)	0.098(3)	0.008 (1)
DS[C(9)]	0.086(4)	0.117(3)	0.101(3)	
DS[C(10)]	0.248(4)	0.267(3)	0.262(3)	
*D*2[N(3)]	0.008(3)	0.015(2)	0.001(3)	0.260 (1)
*D*2[C(7)]	0.128(3)	0.147(3)	0.140(3)	0.260 (1)
*D*2[C(8)]	0.216(3)	0.223(3)	0.224(3)	0.259 (1)
*D*2[C(9)]	0.221(3)	0.213(3)	0.224(3)	
*D*2[C(10)]	0.143(3)	0.123(3)	0.138(3)	
DS[O(5)—C(9)]				0.329 (1)
DS[C(8)—O(5)]				0.329 (1)
DS[C(7)—C(8)]				0.328 (1)
*D*2[O(5)—C(9)]				0.004 (1)
*D*2[C(8)—O(5)]				0.004 (1)
*D*2[C(7)—C(8)]				0.007 (1)

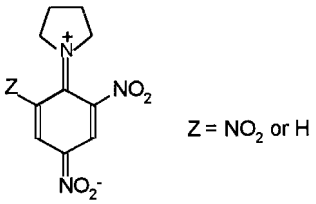
Table 3 (cont.)

(b2) Puckering parameters for the non-aromatic rings[f]

Parameter	**3a** (C_4H_8N—)	**3b** (C_4H_8N—)	**3c** (C_4H_8N—)	**4** (C_4H_8ON—)
Q	0.394 (9)	0.395 (7)	0.405 (6)	0.566(3)
θ_2				0.8 (2)
ϕ_2	−88 (1)	−93.6(8)	−90.1 (8)	−1 (2)

[a] Following Ref. 23.
[b] Angle between planes defined by the three atoms of Group 1 and Group 2.
[c] Rotation component of total angle around C—N bond between Group 1 and Group 2.
[d] Bending component of total angle in a direction perpendicular to C—N bond between Group 1 and Group 2.
[e] Following Ref. 16.
[f] Following Ref. 17.

rotation in compound **3**, as observed in 1-pyrrolidino-2,4,6-trinitrobenzene (**6**)[6] and 1-pyrrolidino-2,4-dinitronaphthalene (**7**).[18] In compound **4**, rotation of the morpholino group out of the aromatic plane prevails over bending and both bending and rotation are greater than in **3**. In addition, rotation of the *p*-nitro group is greater in **4** than in **3** while rotation of the *o*-nitro group is similar in both compounds. This phenomenon permits larger stabilization by resonance interaction for compounds with pyrrolidine in C(1) as shown in **8** than for compounds with morpholine or piperidine.



8

Molecular structure in solution

UV spectra. In order to establish the structure in solution of compounds **3** and **4**, and to determine whether there are any conformational changes between the solid state and solution, we analyzed their UV–visible spectra in methanol. Table 4 summarizes the spectral data for **3**, **4** and **5**.

The spectrum of 2,4-dinitroaniline (**9**) in methanol shows two charge-transfer UV bands, one at 336 nm (ε = 14450) and the other at 390 nm (sh, ε = 6460). These bands correspond to the electronic transitions from the amino group to the *p*-nitro (band 1) and *o*-nitro (band 2) groups, respectively.[19] N-Monoalkylation of **9** produces a bathochromic displacement of band 1 as a result of electronic and hydrogen-bonding factors.[19] *N*,*N*-Dialkylation of **9** induces a bathochromic displacement and steric enhancement of the resonance of band 1, while steric inhibition of band 2 is observed.[19] These results indicate that the electron-withdrawing *ortho* substituent is rotated out of the phenyl ring in solution.[19] In order to minimize the steric interactions, the rotation of the *o*-nitro group is accompanied by rotation of the amino group.[19,20] This is evidenced by a reduction in the intensity of band 1.[19]

Table 4. UV–visible data for 1-pyrrolidino-2,4-dinitrobenzene (**3**), 1-morpholino-2,4-dinitrobenzene (**4**) and 1-piperidino-2,4-dinitrobenzene (**5**)

Compound	λ_{max} (nm)	ε ($dm^3\ mol^{-1}\ cm^{-1}$)
3[a]	370.2	7080
4[a]	375.4	12800
5[b]	374.8	11500

[a] This work.
[b] Ref. 7.

These bathochromic displacements are a consequence of destabilization of the ground state of the molecule due to rotation around the C(1)—N bond,[21] or to steric enhancement of resonance caused by rotation around the C(2)—N, or by a combination of both factors.[19,20]

In compounds **3** and **4**, as well as in **5**, we found that band 1 showed a bathochromic displacement as compared with **9** while band 2 disappeared completely, pointing to the rotation of the *o*-nitro group out of the aromatic plane. The rotation of the amino group out of this plane in **3** and **4** is inferred by comparing the value of ε of band 1 with that in **9**.

NMR spectra. NMR data can be very helpful in obtaining information about the conformation of molecules in solution.[14,15,18,20] Therefore, the ^{13}C NMR spectra of **3** and **4** were measured and the data are reported in Table 5 together with data for the related compounds *N*,*N*-diisopropyl-2,4-dinitroaniline (**10**) and *N*,*N*-diethyl-2,4-dinitroaniline (**11**).

The lack of coplanarity between the *o*-nitro group and the aromatic ring in a series of *N*,*N*-dialkyl-substituted dinitroanilines can be inferred from ^{13}C NMR data.[20] The rotation of the *o*-nitro group induces shielding in the *ipso* [C(2)] and the *para* [C(5)] carbons and deshielding in the *ortho* carbon [C(3)]. On the other hand, rotation of the

Table 5. Experimental and calculated ^{13}C NMR chemical shift of 1-pyrrolidino-2,4-dinitrobenzene (**3**), 1-morpholino,2,4-dinitrobenzene (**4**), 1-piperidino-2,4-dinitrobenzene (**5**), *N,N*-diisopropyl-2,4-dinitroaniline (**10**) and *N,N*-diethyl-2,4-dinitrobenzene (**11**)

Carbon	**3**[a]	**4**[a]	**5**[b]	**10**[c]	**11**[c]	**11**[d]
1	145.5	149.3	149.7	147.9	147.9	148.5
2	135.5	138.4	137.2	138.5	129.7	132.4
3	127.5	123.6	123.9	123.7	123.7	118.5
4	135.5	138.8	137.3	142.6	125.3	135.9
5	127.6	128.3	127.9	126.1	129.9	129.3
6	115.4	119.2	119.1	122.3	113.8	113.6

[a] Experimental values, this work.
[b] Experimental values from Ref. 7.
[c] Experimental values from Ref. 20a.
[d] Calculated values from Ref. 7.

amino group produces deshielding in the *ortho* [C(2) and C(6)] and *para* [C(4)] carbons.[20] Differences observed between experimental and calculated chemical shifts for C(2) and C(3) in **11** are attributed to rotation of the *o*-nitro group.

If we compare the chemical shifts of C(4) and C(6) in **10** and **11**, it can be inferred that in **10** both the *o*-nitro group and the amino group are rotated in order to minimize steric strain. Further, the shift of the signal of C(5) in **10** to higher fields indicates that the rotation of the *o*-nitro group in this compound is greater than that in **11**. Values of the chemical shifts of the aromatic carbons in **3** and **4** range between those of **11** and **10** except for that of C(1). The values for **4** and **5** are close to those for **10** while the values for **3** are close to those for **11**, so we estimate that the rotation of the amino group in **3** is less significant than in **4** and **5**.

We can use the chemical shift of the methylene protons α to N to confirm the rotation of the amino group. We calculated the chemical shift of the α-methylene protons in **3** or **4** as 3.6 ppm using the arguments described previously for **5**.[7] The difference between this value and the observed values (δ = 3.34 and 3.27 ppm for **3** and **4**, respectively) shows a shielding of the protons in pyrrolidine and morpholine that could be attributed to the ring current produced by benzene electrons.[22] Hence the amine moiety must be rotated with respect to the main plane of the aromatic ring.

CONCLUSIONS

Results obtained in the solid state are in good agreement with those obtained in solution. In compounds **3**, **4** and **5**, rotation out of the aromatic plane of the *o*-nitro and of the amino groups is observed. It seems that in solution, **3** is more planar than **4** and **5**, as observed for trinitrobenzenes[6] and naphthalenes[15,18] substituted with the same amines.

The reactivity of **3** with hydroxide ion is less than that of **4** or **5**,[4e] and this is a consequence of a greater stabilization of the ground state of **3** by interaction of the lone pair of electrons of the nitrogen in the amino group with the π system of the aromatic ring due to the greater planarity of this substrate. A similar argument was used to explain the difference in reactivity of 2,4- and 2,6-dinitroanisole in aminolysis reactions.[15]

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