

Acta Cryst. (1997). **C53**, 1930–1932

2,4-Dinitro-*N,N*-methylphenylaniline

JAVIER ELLENA,^a GRACIELA PUNTE^a AND NORMA S. NUDELMAN^b

^aPROFIMO, Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 67, (1900) La Plata, Argentina, and ^bDepartamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires, Ciudad Universitaria, Pabellón 2, Buenos Aires, Argentina. E-mail: ellena@ayelen.fisica.unlp.edu.ar

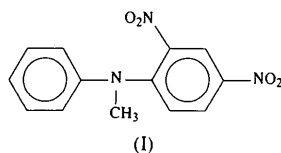
(Received 19 December 1996; accepted 16 May 1997)

Abstract

In the title compound, C₁₃H₁₁N₃O₄, the substituted aromatic ring has a slightly deformed chair conformation and the unsubstituted ring a deformed boat conformation. The dihedral angle between the mean planes of the rings is 62.9 (1)°. The *o*-nitro group is twisted out of the plane of the phenyl ring. Short C—H...O intermolecular contacts stabilize the three-dimensional structure.

Comment

This report is part of a general study on the molecular organization of substituted 2,4-dinitrobenzenes and nitroanilines (Punte, Rivero, Socolovsky & Nudelman, 1987, 1989, 1991; Punte & Rivero, 1991; Ellena *et al.*, 1995; Ellena, Punte & Rivero, 1996*a,b*). In particular, the title compound, (I), was chosen to investigate the ability of the methyl group to sterically hinder the conjugation of the amino group with the aromatic rings, especially with the dinitro-substituted ring.



Analysis of the molecular geometry shows that both phenyl groups have slight deformations. In the substituted phenyl ring, the total puckering amplitude (Cremer & Pople, 1975), Q_T is 0.054 (3) Å. Atoms C1 and C5 are out of the plane defined by the remaining four ring C atoms by 0.065 (3) and -0.040 (3) Å, respectively. The *o*-nitro group is rotated 42.4 (2)° out of that plane, while the *p*-nitro group is only slightly twisted, by 1.6 (2)°. The methyl group and the *o*-nitro group are mutually *anti* and thereby reduce steric hindrance. In the unsub-

stituted aromatic ring, atoms C9 and C12 are out of the mean ring plane by -0.020 (3) and -0.015 (3) Å, respectively, and $Q_T = 0.020$ (3) Å. The amino group is rotated 33.3 (1)° from the plane of the substituted aromatic ring, consistent with the pyramidal arrangement of N1 which is 0.158 (2) Å out of the plane defined by C1, C7 and C8.

The bond length C7—N1, 1.464 (4) Å, is similar to the value found in *N,N*-dimethyl-2,4-dinitro-3-toluidine (Maurin & Krygowski, 1986), 1.458 (3) Å, for the C—N bond length between the N atom of the NR₂ group and the C atom of the methyl group located *anti* to the *o*-nitro group. The bonds between the N—CH₃ group and the rings are not symmetrical: the C8—N1 bond, 1.428 (3) Å, is longer than the C1—N1 bond, 1.359 (3) Å. The latter reveals some degree of conjugation between the amino N atom and the dinitro-substituted ring. In fact, this bond length is similar to those in 2-methyl-4-nitroaniline [1.353 (3) Å; Lipscomb, Garito & Narang, 1981], 2,4-dinitroaniline [1.352 (5) Å; Prasad, Gabe, & Le Page, 1981] and other conjugated 4-nitroanilines like *p*-nitroaniline [1.356 (3) Å; Calopietro, Domenicano, Marciante & Portalone, 1981] and *N,N*-dimethyl-*p*-nitroaniline [1.358 (16) Å; Mak & Trotter, 1965]. The C4—N3 bond length, 1.443 (4) Å, is similar to that in 2,4-dinitroaniline (Prasad, Gabe & Le Page, 1981), 1.442 (5) Å. Therefore, in spite of the pyramidal character of N1 mentioned above, the length of the C1—N1 and C4—N3 bonds confirm conjugation between the amino and the *p*-nitro groups through the aromatic ring. This indication is reinforced by the small dihedral angle observed between the *p*-nitro group and the mean ring plane.

The C2—N2 bond length, 1.464 (3) Å, is larger than the previously mentioned C—N bond lengths, and is similar to the mean value, 1.471 (2) Å, observed by Domenicano *et al.* (1989) for the C—N bond length in nitrobenzene derivatives for which the substituents were chosen to avoid conjugation. The C2—N2 and C4—N3 bond lengths are in agreement with the values found in other heavily amino-substituted 2,4-dinitrobenzenes such as *N,N*-diisopropyl-2,4-dinitroaniline (Punte, Rivero, Socolovsky & Nudelman, 1989), where the bond lengths are 1.466 (4) and 1.450 (3) Å, respectively, and in 1-piperidine-2,4-dinitrobenzene (Ellena *et al.*, 1995), where the bond lengths are 1.465 (2) and 1.453 (2) Å, respectively.

The N—O bonds are compatible with the mean value obtained from 1762 nitrobenzene fragments retrieved from the Cambridge Structural Database (CSD System version 5.12 as released on October 1996; Allen & Kennard, 1993), 1.217 (1) Å. The values of the O—N—O bond angles [O21—N2—O22 123.9 (2) and O31—N3—O32 122.9 (3)°] are consistent with the mean value obtained from the same search, 123.55 (4)°.

The crystal packing of the title compound is shown in Fig. 1. The three-dimensional structure is stabilized by

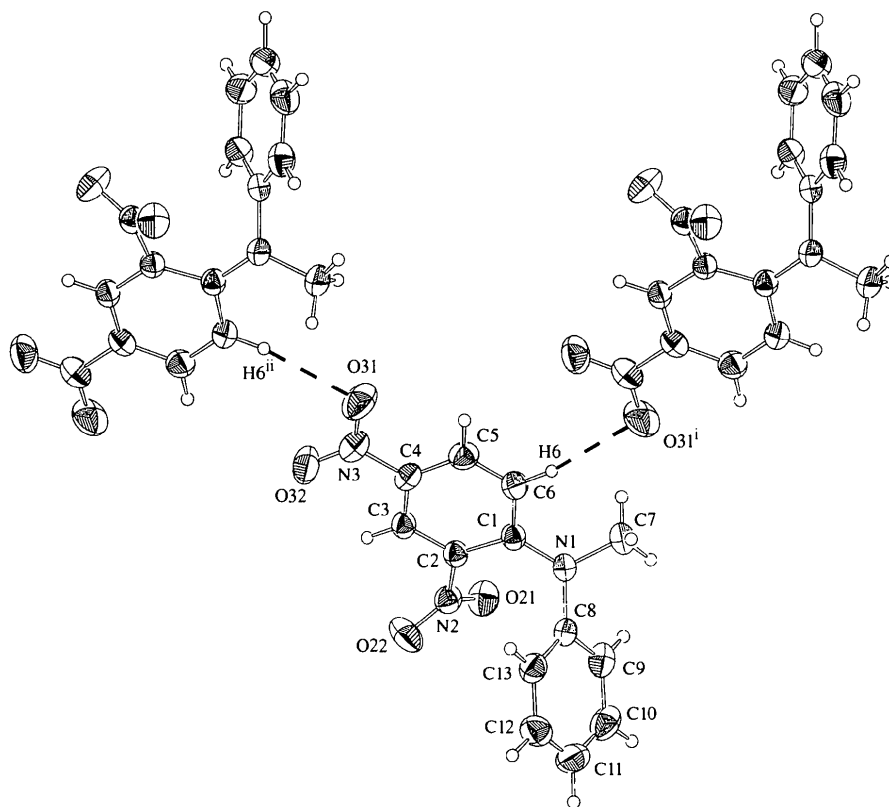


Fig. 1. An ORTEP (Johnson, 1976) view of the molecule showing the atom labelling, 50% probability ellipsoids and the crystal packing. [Symmetry codes: (i) $-x - \frac{1}{2}, y - \frac{1}{2}, 1 - z$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, 1 - z$.]

a weak attractive interaction between one O atom of the *p*-nitro group and one H atom of the substituted aromatic ring in a symmetry-related molecule [C6—H6···O31ⁱ: H···O 2.46 Å and C—H···O 172°; symmetry code: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$].

Experimental

A solution of 1.0 g (5 mmol) of 2,4-dinitrochlorobenzene in ethanol (20 ml) was added at room temperature at a stirred solution of 2.0 g (0.02 mol) of aniline in ethanol (10 ml); the yellow product crystallized readily. Crystals were purified by recrystallization from ethanol (m.p. 439 K).

Crystal data

C₁₃H₁₁N₃O₄
M_r = 273.25
 Monoclinic
*P*2₁/*a*
a = 7.027 (4) Å
b = 12.436 (3) Å
c = 14.390 (4) Å
 β = 93.95 (4)°
V = 1254.6 (9) Å³
Z = 4
D_x = 1.447 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 20 reflections
 θ = 8.00–17.64°
 μ = 0.110 mm⁻¹
T = 293 (2) K
 Rectangular prism
 0.20 × 0.15 × 0.08 mm
 Yellow

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 2822 measured reflections
 2720 independent reflections
 1426 reflections with
 $I > 2\sigma(I)$

*R*_{int} = 0.046
 θ_{\max} = 26.96°
h = -8 → 8
k = 0 → 15
l = 0 → 18
 1 standard reflection
 frequency: 100 min
 intensity variation: 2%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.157$
 $S = 1.102$
 2141 reflections
 220 parameters
 All H-atom parameters
 refined except H6 and H9
 which were refined as part
 of a riding model
 $w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.391P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.03$
 $\Delta\rho_{\max} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL93
 Extinction coefficient:
 0.012 (2)
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N1—C1	1.359 (3)	N2—C2	1.464 (3)
N1—C8	1.428 (3)	N3—O32	1.224 (3)
N1—C7	1.464 (4)	N3—O31	1.229 (3)

N2—O21	1.217 (3)	N3—C4	1.443 (3)
N2—O22	1.218 (3)		
C1—N1—C8	122.0 (2)	N1—C1—C2	123.6 (2)
C1—N1—C7	118.6 (2)	C6—C1—C2	115.3 (2)
C8—N1—C7	115.7 (2)	C13—C8—C9	119.2 (3)
O21—N2—O22	123.9 (2)	C13—C8—N1	120.4 (2)
O32—N3—O31	122.9 (3)	C9—C8—N1	120.3 (3)
N1—C1—C6	121.1 (2)		

All H atoms were found on successive Fourier difference maps. All non-H atoms were refined anisotropically. Atoms H6 and H9 were refined riding on their parent C atoms.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

The authors thank to E. E. Castellano for helpful discussion, the Instituto de Quimica e Fisica de Sao Carlos, Brazil, for experimental facilities and CONICET, Argentina, for financial support. GP and NSN are members of the Carrera del Investigador Científico del CONICET. JAE would like to thank CONICET for a research grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1140). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 131–136.
- Calopietro, M., Domenicano, A., Marciante, C. & Portalone, G. (1981). *Acta Cryst.* **A37**, C-199.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Domenicano, A., Schultz, G., Hargittai, I., Colapietro, M., Portalone, G., George, P. & Bock, C. W. (1989). *Struct. Chem.* **1**, 107–122.
- Ellena, J., Punte, G., Rivero, B. E., Remedi, M. V., de Vargas, E. B. & de Rossi, R. H. (1995). *J. Chem. Crystallogr.* **25**, 801–805.
- Ellena, J., Punte, G. & Rivero, B. E. (1996a). *J. Chem. Crystallogr.* **26**, 319–324.
- Ellena, J., Punte, G. & Rivero, B. E. (1996b). *Acta Cryst.* **C52**, 2074–2076.
- Enraf–Nonius (1993). *CAD-4-PC*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lipscomb, G. F., Garito, A. F. & Narang, R. S. (1981). *J. Chem. Phys.* **75**, 1509–1516.
- Mak, T. C. W. & Trotter, J. (1965). *Acta Cryst.* **18**, 68–74.
- Maurin, J. K. & Krygowski, T. M. (1986). *Acta Cryst.* **C43**, 64–66.
- Prasad, L., Gabe, E. J. & Le Page, Y. (1981). *Acta Cryst.* **B38**, 674–675.
- Punte, G. & Rivero, B. E. (1991). *Acta Cryst.* **C47**, 2118–2122.
- Punte, G., Rivero, B. E., Socolovsky, S. E. & Nudelman, N. S. (1987). *Acta Cryst.* **A43**, C-169.
- Punte, G., Rivero, B. E., Socolovsky, S. E. & Nudelman, N. S. (1989). *Acta Cryst.* **C45**, 1952–1957.
- Punte, G., Rivero, B. E., Socolovsky, S. E. & Nudelman, N. S. (1991). *Acta Cryst.* **C47**, 1222–1227.

- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). **C53**, 1932–1935

α -Phase *p*-Dichlorobenzene at 293 K

EUGÈNIA ESTOP,^a ANGEL ALVAREZ-LARENA,^a ABDESSELAM BELAARAJ,^a XAVIER SOLANS^b AND MANUEL LABRADOR^b

^aUnitat de Cristal·lografia i Mineralogia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain, and
^bDepartament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, 08028 Barcelona, Spain.
E-mail: geneta@santiuste.uab.es

(Received 4 March 1997; accepted 23 May 1997)

Abstract

The α -phase structure of the title compound, C₆H₄Cl₂, has been accurately redetermined at room temperature. Comparison with 100 K data shows that all different shortest intermolecular contacts (Cl···Cl, Cl···C, Cl···H, C···C, C···H, H···H) undergo thermal expansion. A three-centred hydrogen-bonding geometry is considered for some Cl···H contacts.

Comment

As a part of a study on molecular miscibility, some temperature–composition phase diagrams of *para*-disubstituted benzenes X—C₆H₄—Y (X, Y = Cl, Br, I, Me) have been studied (Haget *et al.*, 1984; Bonpunt *et al.*, 1991; Calvet *et al.*, 1995). In order to define the factors determining the existence of mixed crystals, it is important to know the crystal structure (packing) of the components. Some of them have been known for a long time: *p*-dichlorobenzene (α -phase at room temperature: Croatto, Bezzi & Bua, 1952; α -phase at 133 K, metastable: Frasson, Garbuglio & Bezzi, 1959; α -phase at 100 K, metastable: Wheeler & Colson, 1976; β -phase: Housty & Clastre, 1957; β -phase at 100 and 300 K, metastable: Wheeler & Colson, 1976; γ -phase at 100 K: Wheeler & Colson, 1975; high-pressure phase: Sankaran, Sharma, Sikka & Chidambaram, 1986); *p*-dibromobenzene (Bezzi & Croatto, 1942; Croatto & Bezzi, 1949); *p*-diiodobenzene (α -phase: Hendricks, Maxwell, Mosley & Jefferson, 1933; Struchkov & Dun-Chai, 1959; Hinchliffe, Munn, Pritchard & Sunpicer, 1985; Alcobé *et al.*, 1994; β -phase at 333 K: Alcobé *et al.*, 1994); *p*-bromochlorobenzene (Hendricks, 1933; Klug, 1947); and *p*-iodotoluene (Ahn, Soled & Carpenter, 1972). We present here a more precise determination