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Acta Cryst. (1997). C53, 1930–1932

2,4-Dinitro-N,N-methylphenylaniline

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

[a]*PROFIMO, Departamento de Física, Facultad de Ciencias
Exactas, Universidad Nacional de La Plata, CC 67, (1900)
La Plata, Argentina, and [b]Departamento 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*

Abstract

In the title compound, $C_{13}H_{11}N_3O_4$, 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.

(I)
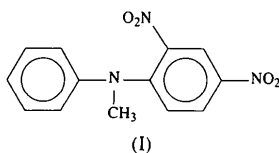
Analysis of the molecular geometry shows that both phenyl groups have slight deformations. In the substituted phenyl ring, the total puckering amplitude (Cremer & Pople, 1975), Q_T is 0.054 (3) Å. Atoms C1 and C5 are out of the plane defined by the remaining four ring C atoms by 0.065 (3) and −0.040 (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 NR_2 group and the C atom of the methyl group located *anti* to the o-nitro group. The bonds between the N—CH_3 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
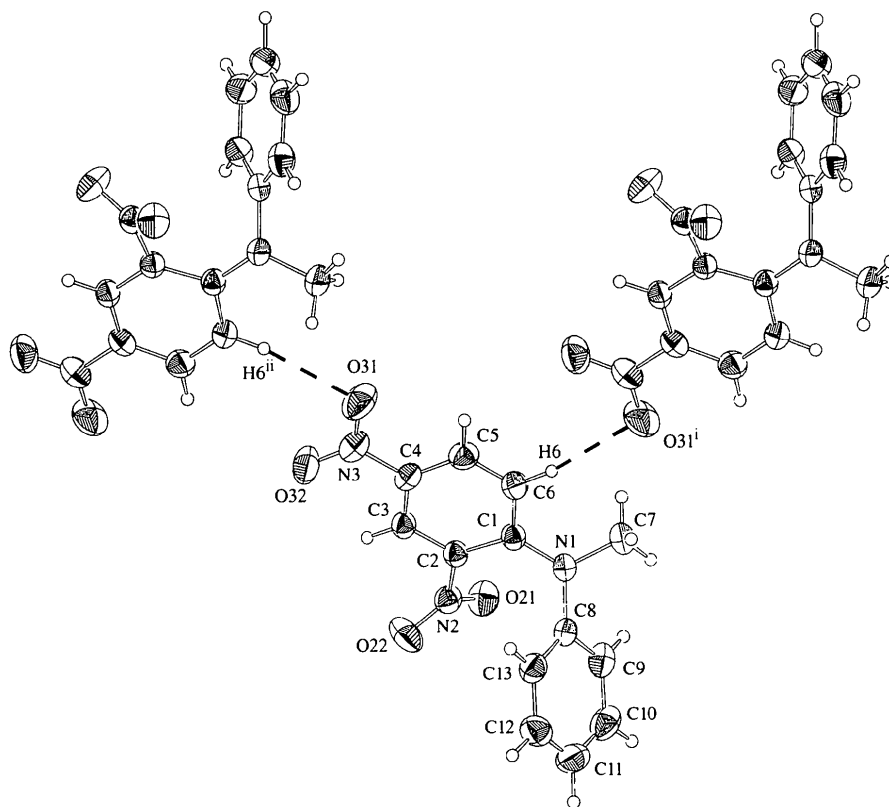
Fig. 1. An *ORTEP*II (Johnson, 1976) view of the molecule showing the atom labelling, 50% probability ellipsoids and the crystal packing. [Symmetry codes: (i) $-x - \frac{1}{2}, y - \frac{1}{2}, 1 - z$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, 1 - z$.]

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$\cdots$O31^i: H$\cdots$O 2.46 Å and C—H$\cdots$O 172°; symmetry code: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, 1 - x$].

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

$C_{13}H_{11}N_3O_4$
$M_r = 273.25$
Monoclinic
$P2_1/a$
$a = 7.027 (4)$ Å
$b = 12.436 (3)$ Å
$c = 14.390 (4)$ Å
$\beta = 93.95 (4)°$
$V = 1254.6 (9)$ Å^3
$Z = 4$
$D_x = 1.447$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 8.00-17.64°$
$\mu = 0.110$ mm^{-1}
$T = 293 (2)$ K
Rectangular prism
$0.20 \times 0.15 \times 0.08$ 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 $I > 2\sigma(I)$

$R_{int} = 0.046$
$\theta_{max} = 26.96°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 18$
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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*93
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: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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α-Phase p-Dichlorobenzene at 293 K

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

[a]*Unitat de Cristal·lografia i Mineralogia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain, and* [b]*Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, 08028 Barcelona, Spain. E-mail: geneta@santiuste.uab.es*

Abstract

The α-phase structure of the title compound, $C_6H_4Cl_2$, 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—C_6H_4—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