

Benzaldehyde 2,4-dinitrophenyl-
hydrazoneShang Shan,^a Duan-Jun Xu,^{b*} Chen-Hsiung Hung,^c
Jing-Yun Wu^d and Michael Y. Chiang^d^aCollege of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang, People's Republic of China, ^bDepartment of Chemistry, Zhejiang University, Hangzhou, Zhejiang, People's Republic of China, ^cDepartment of Chemistry, National Changhua University of Education, Changhua, Taiwan, and ^dDepartment of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan
Correspondence e-mail: xudj@mail.hz.zj.cn

Received 9 December 2002

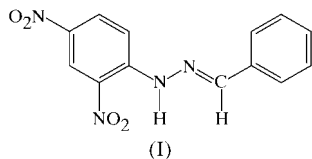
Accepted 28 January 2003

Online 18 February 2003

Crystals of the title compound, C₁₃H₁₀N₄O₄, were obtained from a condensation reaction of benzaldehyde and 2,4-dinitrophenylhydrazine. The molecule assumes an approximately planar *E* configuration. Within the dinitrophenyl moiety, the average distance for the aromatic C—C bonds close to the imino group [1.417 (3) Å] is appreciably longer than the average distance for the other aromatic C—C bonds in the same phenyl ring [1.373 (3) Å]. This increased distance may be a result of the overlap of the non-bonding orbital of the imino N atom with the π orbitals of the arene. It is likely that π - π stacking exists in the crystal structure.

Comment

As some phenylhydrazone derivatives have been shown to be potential DNA-damaging or mutagenic agents (Okabe *et al.*, 1993), a series of new phenylhydrazone derivatives has been synthesized in our laboratory in order to investigate their structure–bioactivity relationship. The structure of the title compound, (I), is reported here as an early result in our study of this new series of compounds.



The molecular structure of (I) is shown in Fig. 1. The molecule assumes a flat planar structure, with a maximum deviation of 0.066 (3) Å for atom O2.

The title molecule crystallizes in the *E* conformation, with the C8-phenyl group and the dinitrophenyl group on opposite sides of the C7=N4 double bond. This configuration agrees with that commonly found in phenylhydrazone derivatives

(Bolte & Dill, 1998). The N3—N4 bond distance of 1.374 (2) Å is appreciably shorter than a typical N—N single bond, such as that found in free 2,4-dinitrophenylhydrazine [1.405 (6) Å; Okabe *et al.*, 1993], which suggests the existence of a delocalized double bond in the hydrazone moiety.

The N3—C1 bond distance of 1.350 (2) Å (Table 1) suggests a partial double bond between the amine group and the phenyl ring. It is notable that the C1—C2 [1.420 (3) Å] and C1—C6 [1.414 (3) Å] bonds are appreciably longer than the average distance of 1.373 (3) Å for the other C—C bonds in the same phenyl ring [range 1.356 (3)–1.387 (3) Å]. The differences in ring bond lengths in (I) are comparable to the situation in several derivatives of 2,4-dinitrophenylhydrazone reported previously (Bolte & Dill, 1998; Ohba, 1996; Borwick *et al.*, 1997; Naidu *et al.*, 1996; Shan *et al.*, 2002) and are presumably due to the overlap of the non-bonding orbital of the imino N atom with the π orbitals of the arene. This overlap contributes to the iminocyclohexadiene resonance structure.

Both intra- and intermolecular hydrogen bonding exists between the imino and nitro groups (as shown in Fig. 1 and Table 2), which results in a short contact of 2.757 (3) Å between atoms O4 and O4(1 - x, -y, 1 - z).

As the planar molecules are packed nearly perpendicular to the crystallographic *b* axis, the molecules related by a screw axis are nearly coplanar, with a dihedral angle of 5.03 (3)°. The nearly coplanar molecules form a parallel-layered supramolecular structure *via* the hydrogen bonding.

Fig. 2 shows the overlap arrangement of neighboring molecules. The distances from atoms C2(1 - x, 1/2 + y, 1/2 - z) and C9(1 - x, 1/2 + y, 1/2 - z) to the molecular plane that includes

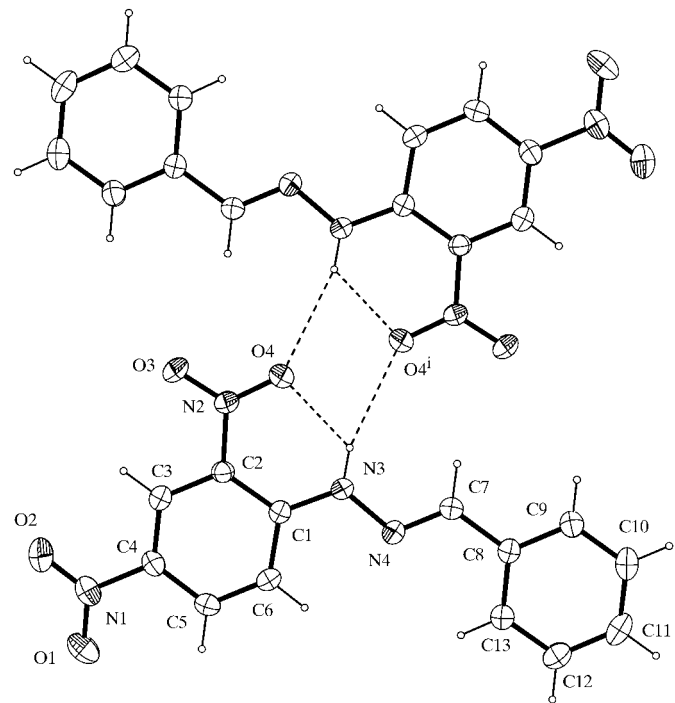


Figure 1

The structure of (I) shown with 30% probability displacement ellipsoids. Dashed lines show the hydrogen bonding. The symmetry code is as in Table 2.

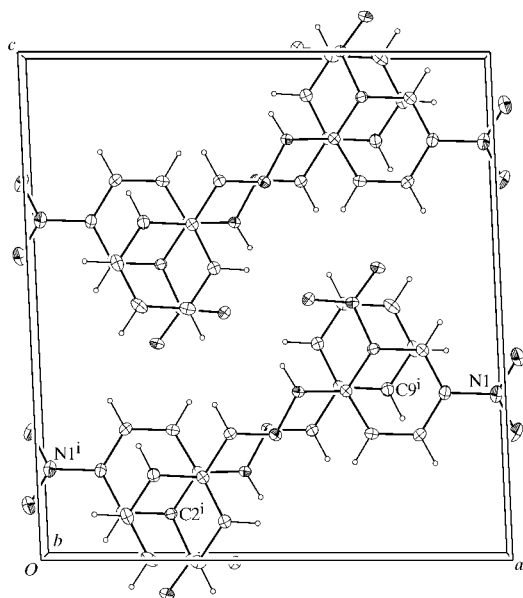


Figure 2
A packing diagram of the unit cell, showing the π - π stacking between neighboring molecules. [Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

atom N1 are 3.372 (3) and 3.351 (3) Å, respectively. These strongly suggest the existence of aromatic π - π -stacking interactions between neighboring molecules in the crystal.

Experimental

2,4-Dinitrophenylhydrazine (0.4 g, 0.2 mmol) was dissolved in ethanol (10 ml), and H_2SO_4 (98%) (0.5 ml) was dropped slowly into this solution with stirring. The resulting solution was heated at about 333 K for several minutes until it became transparent. Benzaldehyde (0.21 g, 0.2 mmol) was dropped slowly into the above solution with continuous stirring, and the resulting mixture was kept at about 333 K for half an hour. When the solution was cooled to room temperature, fine orange crystals appeared. These crystals were separated from the solution and washed with water three times. Recrystallization was performed twice, from chloroform and acetone in turn, to obtain crystals suitable for X-ray analysis.

Crystal data

$\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4$
 $M_r = 286.25$
 Monoclinic, $P2_1/c$
 $a = 13.290$ (3) Å
 $b = 6.825$ (3) Å
 $c = 14.3316$ (18) Å
 $\beta = 92.596$ (15)°
 $V = 1298.6$ (7) Å³
 $Z = 4$

$D_x = 1.464$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 24 reflections
 $\theta = 4.9$ – 10.8°
 $\mu = 0.11$ mm⁻¹
 $T = 298$ (2) K
 Prism, orange
 $0.45 \times 0.40 \times 0.20$ mm

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 2677 measured reflections
 2564 independent reflections
 1258 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$
 $\theta_{\text{max}} = 26.0^\circ$

$h = 0 \rightarrow 16$
 $k = 0 \rightarrow 8$
 $l = -17 \rightarrow 17$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.141$
 $S = 1.00$
 2564 reflections
 191 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2 + 0.0073P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.16$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.016 (2)

Table 1

Selected geometric parameters (Å, °).

N3—C1	1.350 (2)	C1—C6	1.414 (3)
N3—N4	1.374 (2)	C1—C2	1.420 (3)
N4—C7	1.275 (2)	C7—C8	1.461 (3)
C1—N3—N4	118.85 (15)	N4—C7—C8	120.70 (18)
C7—N4—N3	116.55 (16)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N3—H3A \cdots O4	0.86	2.02	2.628 (2)	127
N3—H3A \cdots O4 ⁱ	0.86	2.55	3.331 (2)	151

Symmetry code: (i) $1 - x, -y, 1 - z$.

All H atoms were placed in calculated positions, with C—H distances of 0.93 Å and an N—H distance of 0.86 Å. H atoms were included in the final cycles of refinement in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); structure solution: *SIR92* (Altomare *et al.*, 1993); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the National Natural Science Foundation of China (No. 29973036).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1407). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
 Bolte, M. & Dill, M. (1998). *Acta Cryst.* **C54**, IUC9800065.
 Borwick, S. J., Howard, J. A. K., Lehmann, C. W. & O'Hagan, D. (1997). *Acta Cryst.* **C53**, 124–126.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Molecular Structure Corporation (1985). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. Version 5.32. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Naidu, S. M., Krishnaiah, M., Sivakumar, K. & Sharma, R. P. (1996). *Acta Cryst.* **C52**, 1054–1056.
 Ohba, S. (1996). *Acta Cryst.* **C52**, 2118–2119.
 Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* **C49**, 1678–1680.
 Shan, S., Xu, D., Wu, J. & Chiang, M. Y. (2002). *Acta Cryst.* **E58**, o1333–o1335.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.