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Key indicators

Single-crystal X-ray study
 $T = 297$ K
Mean $\sigma(C-C) = 0.007$ Å
 R factor = 0.086
 wR factor = 0.250
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

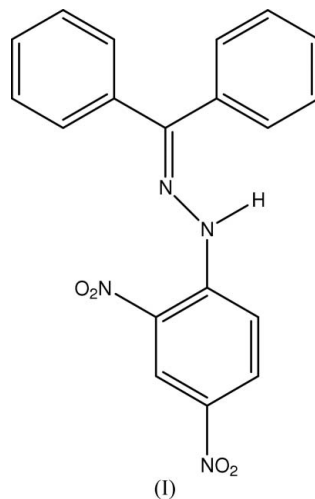
Benzophenone 2,4-dinitrophenylhydrazone

In the title structure, $C_{19}H_{14}N_4O_4$, there are two crystallographically independent molecules in the asymmetric unit. The nitro groups are coplanar with the attached benzene rings. The crystal structure is stabilized by weak intermolecular C—H \cdots O and π – π interactions.

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Comment

Benzophenone-2,4-dinitrophenylhydrazone, (I), was reported by Shriner & Brown (1938) as a by-product in their studies of the interaction of organosilver salts with nitro compounds. Recently, this compound was prepared *via* protection of the carbonyl group with a Dowex polymer (Niknam *et al.*, 2005). It was also found that dinitrophenylhydrazones are better stabilizers than phenylhydrazones for the detection, characterization and protection of carbonyl compounds (Niknam *et al.*, 2005). They also exhibit good nonlinear optical (NLO) crystalline properties (Baughman *et al.*, 2004) as a result of their significant molecular nonlinearities and remarkable ability to crystallize in non-centrosymmetric crystal systems (Zare *et al.*, 2005; El-Seify & El-Dossoki, 2006; Kim & Yoon, 1998). Many X-ray structural studies of benzophenone-2,4-dinitrophenylhydrazone derivatives have been reported (Tabata *et al.*, 1972; Takada *et al.*, 1975). Recently, some derivatives of (I) were investigated and used as an anticancer agent (Klein *et al.*, 1993; Morgan *et al.*, 2002, 2003). We present here the structure of (I), which crystallizes with two unique molecules, *A* and *B*, in the asymmetric unit (Fig. 1).



The bond lengths and angles in the two molecules are similar, show normal values (Allen *et al.*, 1987) and are comparable to those in related structures (Shan *et al.*, 2003;

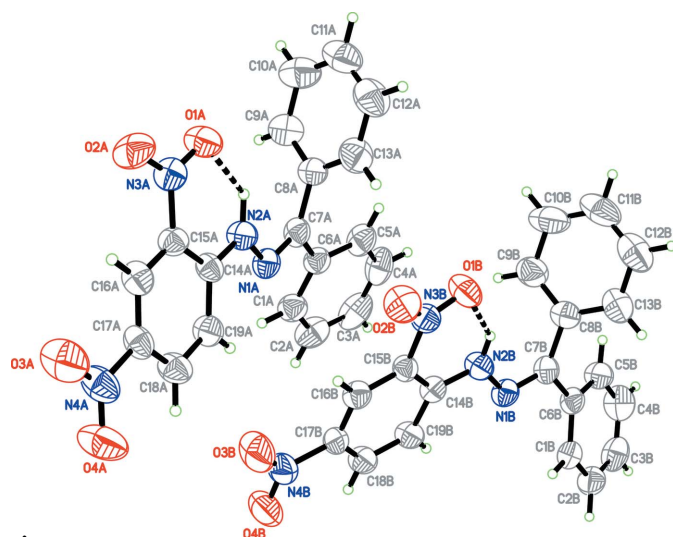


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering. The dashed lines indicate intramolecular hydrogen bonds.

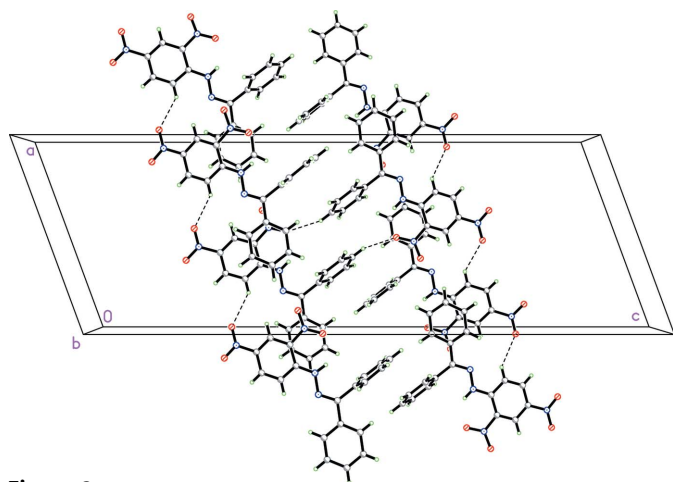


Figure 2
The crystal packing of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

Baughman *et al.*, 2004). A major difference between the two molecules lies in the orientation of the three benzene rings with respect to the central C7=N1–N2 linkage (Fig. 1). In *A*, the C1–C6, C8–C13 and C14–C19 benzene rings are oriented at angles of 22.19 (4), 78.7 (2) and 10.6 (3)° with respect to the C7=N1–N2 plane; the corresponding angles for *B* are 27.3 (4), 63.4 (2) and 10.9 (3)°. In both molecules, the nitro groups at C15 and C17 are approximately coplanar with the attached ring [O1A–N3A–C15A–C14A = –4.8 (6)° and O3A–N4A–C17A–C16A = 0.5 (6)°; O1B–N3B–C15B–C14B = 7.3 (6)° and O3B–N4B–C17B–C16B = –2.7 (6)°].

In the crystal structure, intramolecular N2–H2···O1 interactions generate *S*(6) ring motifs in both molecules (Bernstein *et al.*, 1995). The intermolecular C19B–H19B···O3Aⁱ and C19A–H19A···O3B interactions (Table 1 and Fig. 2) form infinite chains along the *a* axis. In addition, molecules from adjacent chains form dimers by intermolecular C11B–H11B···O1Bⁱⁱ interactions (Table 1 and Fig. 2). The

crystal packing is further stabilized by weak π – π interactions involving the benzene rings, C1A–C6A (centroid Cg1) at (*x*, *y*, *z*) and the C14B–C19B (centroid Cg6) at (*x*, *y*, *z*) with the centroid–centroid distance 3.712 (3) Å, while the corresponding distance between the C1B–C6B ring (centroid Cg2) at (*x*, *y*, *z*) and the C14A–C19A ring (centroid Cg5) at (1 + *x*, *y*, *z*) is 3.638 (3) Å.

Experimental

The title compound was prepared by the slow addition of 2,4-dinitrophenylhydrazine (400 mg, 2 mmol) dissolved in concentrated sulfuric acid (5 ml) to benzophenone (368 mg, 2 mmol) dissolved in 20 ml of 95% ethanol. The mixture was stirred for 15 min, then left to stand at room temperature for 30 min. The resulting product was filtered; an orange powder was collected and redissolved in 30 ml of ethanol, the solution was boiled, and ethyl acetate (10 ml) was added with continuous stirring for 15 min. The hot mixture was filtered and (I) was collected as an orange powder. Crystals suitable for diffraction analysis were grown by slow evaporation of a saturated solution of (I) in methanol–acetonitrile (1:1).

Crystal data

C₁₉H₁₄N₄O₄
M_r = 362.34
 Monoclinic, *P*2₁/*c*
a = 13.6764 (6) Å
b = 6.9852 (3) Å
c = 37.9306 (18) Å
 β = 110.253 (3)°
V = 3399.6 (3) Å³

Z = 8
D_x = 1.416 Mg m^{–3}
 Mo *K*α radiation
 μ = 0.10 mm^{–1}
T = 297 (2) K
 Plate, light orange
 0.36 × 0.29 × 0.12 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
T_{min} = 0.964, *T_{max}* = 0.988

35803 measured reflections
 6003 independent reflections
 2866 reflections with *I* > 2σ(*I*)
R_{int} = 0.091
 θ_{\max} = 25.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.086
wR (*F*²) = 0.250
S = 1.06
 6003 reflections
 495 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1037P)^2 + 1.1324P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

| <i>D</i> –H··· <i>A</i> | <i>D</i> –H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> –H··· <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| N2A–H2C···O1A | 0.93 (5) | 2.01 (6) | 2.616 (5) | 121 (4) |
| N2B–H2D···O1B | 0.84 (5) | 1.99 (6) | 2.624 (5) | 132 (5) |
| C19A–H19A···O3B | 0.93 | 2.56 | 3.301 (6) | 136 |
| C19B–H19B···O3A ⁱ | 0.93 | 2.53 | 3.290 (6) | 139 |
| C11B–H11B···O1B ⁱⁱ | 0.93 | 2.60 | 3.437 (7) | 150 |

Symmetry codes: (i) *x* + 1, *y*, *z*; (ii) –*x* + 1, –*y* + 1, –*z* + 1.

H atoms on N were located in difference maps and refined isotropically, with N–H distances in the range 0.84 (5)–0.93 (5) Å. The remaining H atoms were positioned geometrically and treated as riding, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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