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Key indicators

Single-crystal X-ray study
 T = 120 K
 Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
 Disorder in main residue
 R factor = 0.054
 wR factor = 0.126
 Data-to-parameter ratio = 13.7

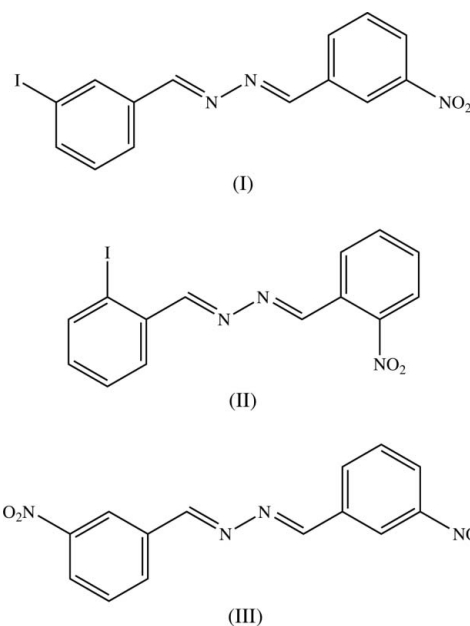
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

(*E,E*)-1-(3-Iodophenyl)-4-(3-nitrophenyl)-2,3-diazabuta-1,3-diene

Molecules of the title compound, $\text{C}_{14}\text{H}_{10}\text{INO}_2$, apparently containing a small proportion of the compound with a second nitro group replacing iodo, are disordered across centres of inversion. The molecules are linked into ordered chains by a two-centre iodo–nitro interaction and these chains are linked into sheets by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Comment

We have recently reported the molecular and supramolecular structures of three isomeric (*E,E*)-1-(2-iodophenyl)-4-(nitrophenyl)-2,3-diazabuta-1,3-dienes (Glidewell *et al.*, 2005). We report here the structure of a further isomer in this series, namely the title compound, (I). Compound (I) crystallizes in the space group $P2_1/c$ with $Z' = 0.5$; the molecules are disordered across centres of inversion and, for the sake of convenience, the reference molecule is selected as that lying across $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 1).



The central $-\text{CH}=\text{N}-\text{N}=\text{CH}-$ unit is strictly planar in (I) and the substituents at each of the $\text{C}=\text{N}$ bonds adopt *E* configurations; the aryl groups are only slightly twisted away from the plane of the central spacer, as shown by the relevant torsion angle (Table 1) and, similarly, the nitro group is almost coplanar with the adjacent aryl ring. The occupancy of the nitro group was found to be greater than that of the iodo substituent with site-occupancy factors of 0.587 (4) and 0.413 (4), respectively. A similar phenomenon was found in the isomeric compound (*E,E*)-1-(2-iodophenyl)-4-(2-nitro-

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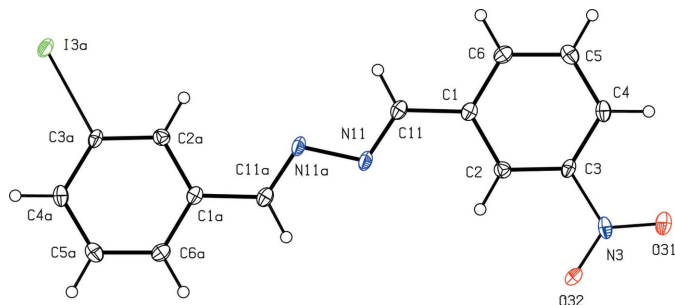


Figure 1

The molecule of (I), showing the atom-labelling scheme. Atoms marked with an 'a' are at the symmetry position $(1 - x, 1 - y, 1 - z)$. Displacement ellipsoids are drawn at the 30% probability level.

phenyl)-2,3-diazabuta-1,3-diene, (II), where the molecules are disordered across inversion centres in the space group $C2/c$. In (II), however, the population of the nitro sites was smaller than that of the iodo site. As in (II), we conclude that some reorganization of the substituted aryl groups has occurred in (I), either during the synthesis or the crystallization, and that a small proportion of (*E,E*)-1,4-bis(3-nitrophenyl)-2,3-diazabuta-1,3-diene, (III), has cocrystallized with (I).

Atom I3 at (x, y, z) , which is part of the molecule centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, can make two intermolecular contacts of possible significance, either with another atom I3 or with nitro atom O32, both at $(1 - x, 2 - y, 1 - z)$, *i.e.* forming parts of the molecule centred at $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$. The key dimensions for these intermolecular contacts are $I \cdots I^i = 3.148(2)$ Å and $C-I \cdots I^i = 168.2(2)^\circ$, and $I \cdots O^i = 3.317(8)$ Å and $C-I \cdots O^i = 166.0(2)^\circ$ [symmetry code: (i) $1 - x, 2 - y, 1 - z$]. If adjacent molecules along [010] are consistently aligned in a head-to-tail fashion, then the two-centre iodo–nitro interaction generates a $C(13)$ chain (Starbuck *et al.*, 1999). However, if adjacent molecules are aligned in a head-to-head fashion, then the $I \cdots I$ contact can only link the molecules in pairs.

The angular properties of the $C-I \cdots I$ interaction here are consistent with generalizations proposed (Ramasubbu *et al.*, 1986) from the results of database analysis, namely that in structures where $X \cdots X$ distances ($X = \text{halogen}$) are significantly less than the van der Waals sum, the observed $C-X \cdots X$ angles are clustered around either 180 or 90° . The short $I \cdots I$ distance found in (I) is well below the conventional van der Waals sum for an $I \cdots I$ contact (3.90 Å; Bondi, 1964) and still well below the revised value (3.52 Å) established from the polar-flattening model (Nyburg & Faerman, 1985). This may point to an avoidance of such contacts in (I) wherever possible; such contacts are readily avoided if the molecules within each [010] chain are aligned in a head-to-tail fashion, so that the disorder of the molecules is correlated within each [010] chain; however, this correlation neither requires nor implies any correlation of disorder between adjacent chains. Thus we conclude that the molecules of (I) are linked into [010] chains by a two-centre iodo–nitro interaction, and that short $I \cdots I$ contacts are, in fact, absent from this structure.

There are two possible $C-H \cdots O$ hydrogen bonds within the structure (Table 2), whose structural influence is intimately

bound up with the orientational disorder of the molecules. Atoms C5 and C6 at (x, y, z) , which are components of the molecule centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, itself part of the chain along $(\frac{1}{2}, y, \frac{1}{2})$, act as hydrogen-bond donors, respectively, to atoms O32 at $(1 + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and O31 at $(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, which themselves are components of the molecules centred across $(\frac{3}{2}, 1, 1)$ and $(\frac{3}{2}, 0, 1)$, respectively, which are components of the chain lying along $(\frac{3}{2}, y, 1)$. A given aryl ring can act only as a single donor of hydrogen bonds, and which of these is actually formed by this pair of $C-H$ bonds in a given aryl ring depends only upon the relative orientation of the [010] chains containing the potential donors and acceptors. If the chains along $(\frac{1}{2}, y, \frac{1}{2})$ and $(\frac{3}{2}, y, 1)$ are aligned in a parallel fashion, they will be linked by the hydrogen bond formed by C6, but if they are aligned antiparallel they will be linked by the hydrogen bond formed by C5. However, there will always be exactly one such interaction present for each aryl ring. Regardless of the local connectivity, the overall effect of the hydrogen bonds is to link [010] chains into a $(10\bar{2})$ sheet.

By contrast with the occurrence of $C-H \cdots O$ hydrogen bonds in compound (I), no such bonds occur in the isomer (II). We note without comment that in both of these disordered structures, (I) and (II), the unit cells are of markedly tabular shape, with a short *a* dimension in (I) and a short *b* dimension of 3.7952 (3) Å in (II).

Experimental

An equimolar mixture of 3-iodobenzaldehyde and 3-nitrobenzaldehyde hydrazone (3 mmol of each) in methanol (20 ml) was heated under reflux for 20 min; the mixture was cooled and the resulting solid product, (I), was collected by filtration. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in 1,2-dichloroethane.

Crystal data

$C_{14}H_{10}I_{0.82}N_{3.18}O_{2.34}$
 $M_r = 365.08$
 Monoclinic, $P2_1/c$
 $a = 3.8044(2)$ Å
 $b = 15.0015(11)$ Å
 $c = 11.6159(8)$ Å
 $\beta = 90.658(4)^\circ$
 $V = 662.90(8)$ Å³
 $Z = 2$

$D_x = 1.829$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1503 reflections
 $\theta = 3.5\text{--}27.5^\circ$
 $\mu = 2.02$ mm⁻¹
 $T = 120(2)$ K
 Block, yellow
 $0.22 \times 0.10 \times 0.08$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.665$, $T_{\max} = 0.855$
 7368 measured reflections

1503 independent reflections
 1229 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -4 \rightarrow 4$
 $k = -19 \rightarrow 17$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.126$
 $S = 1.32$
 1503 reflections
 110 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2)P^2 + 2.587P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.93$ e Å⁻³

Table 1

Selected torsion angles (°).

C2—C1—C11—N11	-5.9 (7)	C2—C3—N3—O31	177.5 (7)
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Table 2

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>
C5—H5···O32 ⁱ	0.95	2.51	3.279 (9)	138
C6—H6···O31 ⁱⁱ	0.95	2.55	3.414 (8)	152

Symmetry codes: (i) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$.

All H atoms were located in a difference Fourier map and then treated as riding atoms, with C—H distances of 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The refined values of the site-occupancy factors for the nitro group and the I atom were 0.587 (4) and 0.413 (4), respectively.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); soft-

ware used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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