Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# (*E*)-5-[(4-Nitrophenylhydrazono)-phenylacetyl]-3-phenylisoxazole

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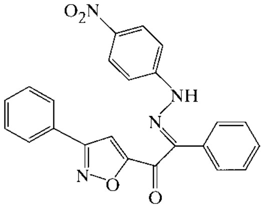
Received 26 October 1999
Accepted 12 November 1999

The title compound, $C_{23}H_{16}N_4O_4$, can be considered as consisting of two connected fragments: a nitrophenylhydrazone moiety, which assumes an *E* configuration, and an isoxazole moiety. In this latter fragment, the weak $\pi$-electron delocalization shortens the carbonyl–isoxazole O···O distance [2.643 (2) Å] to less than the van der Waals radii sum.

## Comment

As part of our investigation into the participation of vicinal groups in the bromination reaction of isoxazole compounds to form bis-heterocyclic spirans, we succeeded in obtaining single crystals, suitable for X-ray crystallography, of the title compound, (I). This compound was formed during the electrophilic bromination of 3-phenyl-*p*-nitrophenylhydrazone-5-phenacylisoxazole in chloroform. The formation of (I) can be ascribed to a hydrolytic process resulting from the presence of moisture in the reaction medium.



(I)

The structure of (I) is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. In the following discussion, the molecule will be considered as two fragments, *i.e.* the nitrophenylhydrazone moiety and the isoxazole moiety.

It is remarkable that the *E* isomer of the nitrophenylhydrazone derivative was formed preferentially over the *Z* isomer since the latter would almost certainly feature an NH···OC intramolecular hydrogen bond. In (I), the *E* isomer is stabilized by an intermolecular hydrogen bond involving atoms N2, C23 and C2. The geometric parameters are listed in Table 2. Atoms N3 and O2 are involved in two intermolecular hydrogen-bond interactions that stabilize the molecular packing, N3 with O4$^{i}$ and C7 with O2$^{ii}$; the geometric parameters are listed in Table 2 [symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $x-1, y, z$].

The phenylhydrazone fragment is almost planar; geometric calculations show that the maximum distance from the mean plane is 0.077 (2) Å for O4. All geometric parameters concerning the nitrophenylhydrazone fragment of the mol-

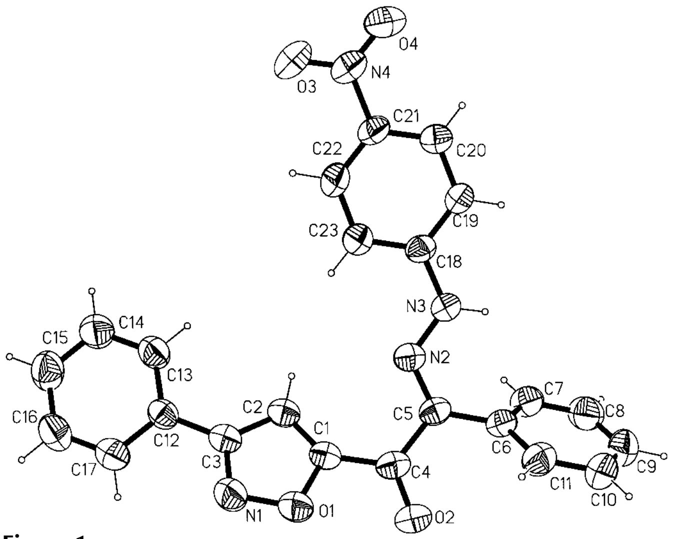


**Figure 1**
A view of (I) showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are drawn as circles of arbitrary radii.

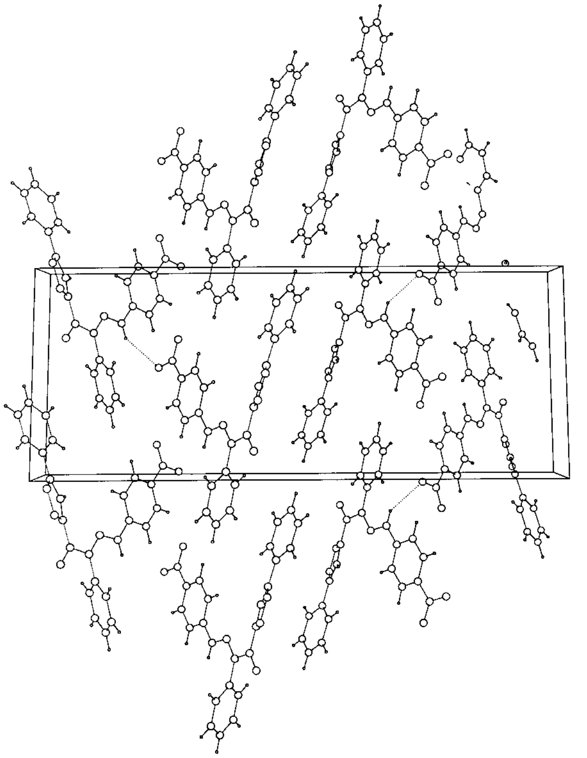


**Figure 2**
A view of the molecular packing in (I) along the *a* axis.

ecule agree with the values found in the literature for similar compounds (Willey & Drew, 1983; Drew & Willey, 1982; Stanković *et al.*, 1991; Whitaker & Walker, 1987) without an intramolecular hydrogen bond (NH···OC).

In the second fragment, the isoxazole ring is nearly planar; the maximum deviation from the mean plane is 0.010 (2) Å for N1. The angle between the nitrophenylhydrazone plane and the isoxazole plane is 32.94 (6)°, and the phenyl ring is twisted a further 20.48 (8)° from the isoxazole plane. The mutual orientation of the aromatic ring and the isoxazole moiety is due to the presence of an intramolecular hydrogen bond interaction involving N1 and C17 (see Table 2). The values of the C2—C1, C1—C4 and C4—O2 bond lengths (Table 1) show a weak $\pi$-electron delocalization with respect to the compound reported by Sundaralingam & Jeffrey (1962). Other geometric parameters are in good agreement with those reported in the literature (Staskun *et al.*, 1991; Smith *et al.*, 1991).

The packing is mainly determined by normal van der Waals interactions and two intermolecular hydrogen bonds involving the N3 and O2 atoms, as discussed above. As can be seen in Fig. 2, the molecules are packed in a head-to-tail fashion along the *a* axis.

## Experimental

3-Phenyl-*p*-nitrophenylhydrazone-5-phenacylisoxazole (1 mmol) was dissolved in hot chloroform (40 ml). $Br_2$ (2 mmol) was added with continuous stirring and the mixture refluxed for 4 h. During the reaction a powder began to precipitate. The solid was removed by filtration and the organic phase was separated and evaporated to dryness. The residue, (I), was crystallized from acetone at room temperature (m.p. 422–424 K). Single crystals of (I) suitable for X-ray diffraction analysis were grown from a dichloromethane–methanol mixture (~ 1:2 *v*/*v*).

*Crystal data*

$C_{23}H_{16}N_4O_4$
$M_r = 412.40$
Monoclinic, $P2_1/n$
$a = 5.7870$ (10) Å
$b = 29.089$ (3) Å
$c = 11.8810$ (10) Å
$\beta = 100.490$ (10)°
$V = 1966.6$ (4) Å$^3$
$Z = 4$
$D_x = 1.393$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 41 reflections
$\theta = 12$–28°
$\mu = 0.098$ mm$^{-1}$
$T = 293$ (2) K
Prismatic, colourless
0.25 × 0.18 × 0.12 mm

*Data collection*

Siemens *R3m/V* diffractometer
$\omega/2\theta$ scans
3739 measured reflections
3301 independent reflections
1899 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\rm max} = 24.5°$
$h = -1 \rightarrow 6$
$k = -7 \rightarrow 34$
$l = -13 \rightarrow 13$
3 standard reflections every 197 reflections intensity decay: 1.31%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.079$
$S = 0.835$
3301 reflections
282 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1383P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.230$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.186$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.085 (7)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C1 | 1.354 (2) | C4—C5 | 1.476 (2) |
| O1—N1 | 1.400 (2) | C5—N2 | 1.302 (2) |
| N1—C3 | 1.316 (2) | C5—C6 | 1.489 (2) |
| C3—C2 | 1.421 (2) | N2—N3 | 1.343 (2) |
| C3—C12 | 1.475 (2) | N3—C18 | 1.386 (2) |
| C2—C1 | 1.347 (2) | C21—N4 | 1.449 (2) |
| C1—C4 | 1.491 (2) | N4—O3 | 1.222 (2) |
| C4—O2 | 1.219 (2) | N4—O4 | 1.229 (2) |
| | | | |
| C1—O1—N1 | 108.5 (1) | C5—N2—N3 | 118.3 (2) |
| C3—N1—O1 | 106.1 (2) | N2—N3—C18 | 120.2 (2) |
| N1—C3—C2 | 110.8 (2) | C23—C18—N3 | 122.0 (2) |
| N1—C3—C12 | 119.2 (2) | N3—C18—C19 | 118.5 (2) |
| C2—C1—O1 | 109.7 (2) | C22—C21—N4 | 119.8 (2) |
| O1—C1—C4 | 112.4 (2) | C20—C21—N4 | 119.1 (2) |
| O2—C4—C5 | 120.9 (2) | O3—N4—O4 | 122.6 (2) |
| O2—C4—C1 | 118.7 (2) | O3—N4—C21 | 118.3 (2) |
| N2—C5—C4 | 115.6 (2) | O4—N4—C21 | 119.1 (2) |
| N2—C5—C6 | 125.8 (2) | | |

**Table 2**
Hydrogen-bonding and short-contact geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2···N2 | 0.93 | 2.75 | 3.024 (2) | 98 |
| C23—H23···N2 | 0.93 | 2.51 | 2.796 (2) | 98 |
| C11—H11···O2 | 0.93 | 2.81 | 3.028 (2) | 94 |
| C17—H17···N1 | 0.93 | 2.55 | 2.842 (3) | 99 |
| C20—H20···O4 | 0.93 | 2.44 | 2.718 (2) | 98 |
| N3—H3···O4$^{\rm i}$ | 0.86 | 2.43 | 3.183 (2) | 147 |
| C7—H7···O2$^{\rm ii}$ | 0.93 | 2.48 | 3.382 (2) | 163 |

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

Data collection: *P*3/*V* (Siemens, 1989); cell refinement: *P*3/*V*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XPW* (Siemens, 1996); software used to prepare material for publication: locally modified *PARST*97 (Nardelli, 1995) and *SHELXL*97.

We would like to express our gratitude, for support and aid, to the Italian MURST and to the Centro Interdipartimentale di Servizi per la Diffrattometria a Raggi X of the University of Messina.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1439). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (2000). C**56**, 254–255 Giuseppe Bruno *et al.* • $C_{23}H_{16}N_4O_4$ **255**