

one of which was the hydrazone starting material. Proton NMR also showed the hydrazone. Column chromatography on silica gel, eluting with methylene chloride, yielded 130 mg (7.9% overall yield) of mixed azine (1) as a crystalline yellow solid. The triclinic crystal was obtained by slow diffusion of hexane into a solution of (1) in chloroform.

Crystal data

C₁₅H₉F₅N₂O $M_r = 328.24$

Triclinic

 $P\bar{1}$ $a = 6.8822(8) \text{ \AA}$ $b = 8.9557(10) \text{ \AA}$ $c = 11.0364(12) \text{ \AA}$ $\alpha = 98.765(2)^\circ$ $\beta = 92.365(2)^\circ$ $\gamma = 98.660(2)^\circ$ $V = 663.18(13) \text{ \AA}^3$ $Z = 2$ $D_x = 1.644 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.70930 \text{ \AA}$

Cell parameters from 1647 reflections

 $\theta = 5.0\text{--}25.0^\circ$ $\mu = 0.15 \text{ mm}^{-1}$ $T = 293 \text{ K}$

Prism

 $0.30 \times 0.20 \times 0.15 \text{ mm}$

Yellow

Data collection

Siemens SMART CCD area-detector diffractometer

 ω scans

Absorption correction:

multi-scan (SADABS;

Blessing, 1995)

 $T_{\min} = 0.954$, $T_{\max} = 0.977$

3918 measured reflections

2720 independent reflections

1776 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.017$ $\theta_{\text{max}} = 27^\circ$ $h = -8 \rightarrow 8$ $k = -11 \rightarrow 11$ $l = 8 \rightarrow 14$ Intensity decay: $< 2\%$

Refinement

Refinement on F $R = 0.058$ $wR = 0.075$ $S = 1.19$

1776 reflections

208 parameters

H-atom parameters

constrained

 $w = 1/[\sigma^2(F) + 0.002F^2]$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *Inter-**national Tables for X-ray**Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

F1—C3	1.344 (3)	O1—C15	1.447 (4)
F2—C4	1.343 (3)	N1—N2	1.407 (3)
F3—C5	1.335 (3)	N1—C1	1.282 (4)
F4—C6	1.346 (3)	N2—C8	1.291 (4)
F5—C7	1.346 (3)	C1—C2	1.463 (4)
O1—C12	1.356 (3)	C2—C3	1.398 (4)
N2—N1—C1	111.5 (3)	N1—C1—C2	121.9 (3)
N1—N2—C8	111.3 (3)	N2—C8—C9	121.5 (3)
C1—N1—N2—C8	174.8 (6)	N2—N1—C1—C2	-180.0 (5)
N1—N2—C8—C9	179.0 (5)	N1—C1—C2—C3	178.4 (6)
N1—C1—C2—C7	0.4 (3)	N2—C8—C9—C10	178.8 (6)
N2—C8—C9—C14	-2.6 (3)		

H atoms were placed in calculated positions with C—H 1.08 \AA and $U(\text{H}) = U(\text{C}) + 0.01$, and treated as riding during refinement.

Data collection: SMART (Siemens, 1995). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Pro-

gram(s) used to refine structure: NRCVAX (Gabe *et al.*, 1989). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: NRCVAX.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1178). Services for accessing these data are described at the back of the journal.

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Naphthalene-2,3-dicarbaldehyde

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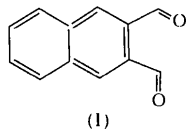
Abstract

The molecular structure of the title compound, C₁₂H₈O₂, is normal. The two CHO groups are rotated 7.2(1) and 22.7(1)° out of the mean plane of the naphthalene

fragment. The H atom in one CHO group is 2.30 Å from the O atom in the adjacent group in an intramolecular C—H...O hydrogen bond. There are no intermolecular hydrogen bonds.

Comment

The intermolecular C—H...O—C arrangements found in 4-formyl benzoic acid (Haisa *et al.*, 1976), *p*-chloro- and *p*-bromobenzaldehyde (Britton, 1994) and terephthalaldehyde (Britton, 1998) all appear to involve C—H...O hydrogen bonding. Although the H...O distances (2.58–2.75 Å) are about what would be expected from the usual van der Waals radii, the C—H...O angles are all near 180° and the H...O angles are near 120°. For general discussions of this type of hydrogen bond, see Taylor & Kennard (1982), Berkovitch-Yellin & Leiserowitz (1984), and Desiraju (1991). To look for another example of this type and also to look for an intramolecular C—H...O bond, the structure of the title compound, (I), has been determined.



The anisotropic displacement ellipsoids and the atom-labeling scheme for (I) are shown in Fig. 1. The bond lengths and angles are normal. The H-atom positions were all refined. The C—H distances ranged from 0.94(2) to 1.01(2) Å, with *U* values in the range 0.029(4)–0.051(5) Å². The CHO group at C1 is rotated 7.2(1)° out of the mean plane of the naphthalene fragment, while that at C2 is rotated 22.7(1)°. Both rotations are in a direction to increase the O1...H12 distance.

The intramolecular interaction between H12 and O1 is described in the first entry in Table 1, where

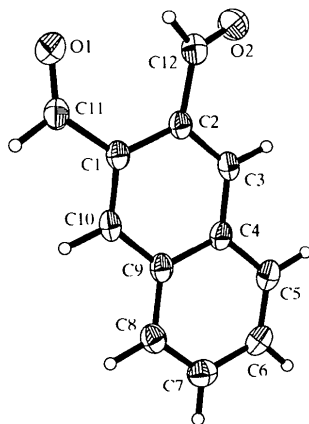


Fig. 1. The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

it is compared with similar interactions in aromatic aldehydes with *ortho* CO or NO₂ groups, and with a variety of 1,2-dialdehydes. While the angle at H12 is far from 180°, the distance is about 0.3 Å shorter than any of the previously mentioned intermolecular distances and is probably an attractive interaction, namely a C—H...O hydrogen bond. The subsequent three entries in Table 1 describe interactions with similar distances, and presumably with similar strengths. Most of the remaining entries do not appear to be much more than ordinary van der Waals interactions.

The intermolecular interactions in the title compound are given in Table 2. There are six of these interactions with H...O less than 2.8 Å. Although the H...O distances are in the same range as those quoted in the introduction, and all of the interactions are presumably energetically favorable, the angles are such that there seems no point in describing any of these as C—H...O hydrogen bonds.

Experimental

The title compound was obtained from Aldrich Chemical Co., and a suitable crystal was present in the original sample.

Crystal data

C₁₂H₈O₂
M_r = 184.18
 Monoclinic
*P*2₁/*c*
a = 3.8724(2) Å
b = 12.0839(5) Å
c = 18.4079(6) Å
 β = 91.412(2)°
V = 861.11(6) Å³
Z = 4
D_x = 1.421(1) Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 2848 reflections
 θ = 2.0–25.1°
 μ = 0.097 mm⁻¹
T = 173(2) K
 Cut from needle
 0.50 × 0.15 × 0.10 mm
 Colorless

Data collection

Siemens SMART area-detector diffractometer
 ω scans
 Absorption correction: multi-scan *SADABS* (Sheldrick, 1996; Blessing, 1995)
 T_{\min} = 0.92, T_{\max} = 0.99
 4396 measured reflections
 1530 independent reflections

1310 reflections with $I > 2\sigma(I)$
 R_{int} = 0.029
 θ_{max} = 25.11°
 h = -4 → 4
 k = -12 → 14
 l = -21 → 19
 209 standard reflections
 intensity decay: < 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.039
 $wR(F^2)$ = 0.108
 S = 1.06
 1530 reflections
 160 parameters
 H atoms: see below

$\Delta\rho_{\text{max}}$ = 0.17 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.19 e Å⁻³
 Extinction correction: *SHELXTL* (Sheldrick, 1995)
 Extinction coefficient: 0.007(4)

$$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.270P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.01$

Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Intramolecular C—H...O—X contacts (C—H...O hydrogen bonds) in CHO—C—C—XO fragments (\AA , °)

X—O	C—H...O	H...O	H...O—X	C...O	Reference
—CHO	116	2.30	100	2.884 (2)	this work
—C=O(—C)	124	2.06	109	2.767	(a)
—C=O(—C)	109	2.27	103	2.769	(a)
—NO ₂	106	2.27	111	2.725	(b)
—NO ₂	78	2.71	88	2.701	(c)
—CHO	122	2.43	101	3.045	(d)
—CHO	92	2.48	87	2.686	(e)
—CHO	86	2.55	87	2.692	(f)
—CHO	85	2.62	88	2.735	(g)
—CHO	84	2.63	85	2.715	(g)

References: (a) Talipov *et al.* (1995); (b) Byrn *et al.* (1993); (c) Coppens & Schmidt (1964); (d) McCague *et al.* (1984); (e) Sterner *et al.* (1990); (f) De Rosa *et al.* (1994); (g) Puliti *et al.* (1995).

Table 2. Intermolecular C—H...O—C' contacts for (I) (\AA , °)

C—H...O—C'	C—H...O	H...O	H...O—C'	C...O
C5—H5...O2—C12 ⁱ	152	2.51	156	3.417 (2)
C7—H7...O1—C11 ⁱⁱ	140	2.58	140	3.361 (2)
C11—H11...O1—C11 ⁱⁱⁱ	129	2.64	107	3.367 (2)
C3—H3...O2—C12 ^{iv}	147	2.65	147	3.486 (2)
C12—H12...O2—C12 ^v	116	2.73	103	3.302 (2)
C8—H8...O2—C12 ^{vi}	129	2.74	98	3.459 (2)

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

The first 209 reflections were remeasured 12 h later at the end of the data collection to monitor crystal decay. H atoms were refined with isotropic displacement parameters.

Data collection: *ASTRO* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1446). Services for accessing these data are described at the back of the journal.

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Two new 2,3-substituted 5-norbornenes

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Abstract

In the bicyclo[2.2.1]heptene (norbornene) moieties of *S*-methyl 3-(4-methylphenyl)bicyclo[2.2.1]hept-5-ene-2-carbothioate, C₁₆H₁₈OS, (*2a*), and *S*-methyl 3-(4-nitrophenyl)bicyclo[2.2.1]hept-5-ene-2-carbothioate, C₁₅H₁₅NO₃S, (*2b*), the five-membered rings are in envelope conformations, while the six-membered rings adopt boat conformations. The dihedral angles between the norbornene six-membered ring moiety and the phenyl substituent are 67.22 (9) and 31.8 (2)°, for (*2a*) and (*2b*), respectively. In both compounds, molecules are joined through C—H...O interactions.

Comment

The Diels–Alder reaction of α,β -unsaturated carbonyl and carboxylic compounds with cyclopentadiene has been extensively investigated (Sauer & Sustmann, 1980; Camilo & Gruber, 1999). When no Lewis acid catalysts