

| | |
|--------------------------------|---|
| $P2_1/c$ | Cell parameters from 25 reflections |
| $a = 12.9862 (5) \text{ \AA}$ | $\theta = 25\text{--}30^\circ$ |
| $b = 6.4062 (5) \text{ \AA}$ | $\mu = 0.86 \text{ mm}^{-1}$ |
| $c = 14.0857 (12) \text{ \AA}$ | $T = 298 \text{ K}$ |
| $\beta = 116.275 (6)^\circ$ | Lath fragment |
| $V = 1050.7 (3) \text{ \AA}^3$ | $0.47 \times 0.32 \times 0.22 \text{ mm}$ |
| $Z = 4$ | Colorless |

Data collection

| | |
|--|----------------------------------|
| Enraf-Nonius CAD-4 diffractometer | $R_{\text{int}} = 0.014$ |
| ω -2 θ scans | $\theta_{\text{max}} = 75^\circ$ |
| Absorption correction: empirical | $h = 0 \rightarrow 16$ |
| $T_{\text{min}} = 0.94, T_{\text{max}} = 1.00$ | $k = 0 \rightarrow 8$ |
| 2445 measured reflections | $l = -17 \rightarrow 15$ |
| 2152 independent reflections | 3 standard reflections |
| 1685 observed reflections | frequency: 167 min |
| $[I > 3\sigma(I)]$ | intensity variation: 2.1% |

Refinement

| | |
|--|--|
| Refinement on F^2 | $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$ |
| Final $R = 0.041$ | $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$ |
| $wR = 0.054$ | Extinction correction: |
| $S = 2.565$ | $(1 + gI)^{-1}$ |
| 1685 reflections | Extinction coefficient: |
| 182 parameters | $8.6 (4) \times 10^6$ |
| All H-atom parameters refined | Atomic scattering factors |
| $w = 4F^2[\sigma^2(I) + (0.02F^2)^2]^{-1}$ | from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV) |
| $(\Delta/\sigma)_{\text{max}} = 0.03$ | |

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

| | $B_{\text{eq}} = \frac{8\pi^2}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$ | | | |
|-----|---|------------|-------------|-----------------|
| | x | y | z | B_{eq} |
| O1 | 0.6261 (1) | 0.6607 (2) | 0.4472 (1) | 6.12 (3) |
| O2 | 0.8413 (1) | 0.0411 (2) | 0.56066 (9) | 0.565 (3) |
| O3 | 0.8233 (1) | 0.4696 (3) | 0.6762 (1) | 7.41 (4) |
| O4 | 0.6731 (1) | 0.3341 (4) | 0.6724 (1) | 9.66 (6) |
| N | 0.7328 (1) | 0.3784 (3) | 0.6310 (1) | 5.05 (4) |
| C1 | 0.6908 (1) | 0.5212 (3) | 0.4563 (1) | 3.87 (3) |
| C2 | 0.7741 (1) | 0.5042 (3) | 0.4118 (1) | 3.63 (3) |
| C3 | 0.7933 (2) | 0.6440 (3) | 0.3462 (1) | 4.88 (4) |
| C4 | 0.8762 (2) | 0.5912 (4) | 0.3142 (1) | 5.78 (5) |
| C5 | 0.9374 (1) | 0.4071 (4) | 0.3460 (1) | 5.52 (5) |
| C6 | 0.9192 (1) | 0.2695 (3) | 0.4113 (1) | 4.46 (4) |
| C7 | 0.8360 (1) | 0.3201 (3) | 0.4442 (1) | 3.56 (3) |
| C8 | 0.8009 (1) | 0.2010 (3) | 0.5142 (1) | 3.76 (3) |
| C9 | 0.6981 (1) | 0.3162 (3) | 0.5176 (1) | 3.62 (3) |
| C10 | 0.5881 (1) | 0.1902 (3) | 0.4721 (1) | 4.55 (4) |
| C11 | 0.5439 (2) | 0.1452 (3) | 0.3559 (2) | 5.79 (5) |

Table 2. Geometric parameters ($\text{\AA}, ^\circ$)

| | | | |
|-------|-----------|---------|-----------|
| O1—C1 | 1.194 (2) | C3—C4 | 1.380 (3) |
| O2—C8 | 1.204 (2) | C4—C5 | 1.381 (3) |
| O3—N | 1.211 (2) | C5—C6 | 1.369 (3) |
| O4—N | 1.194 (3) | C6—C7 | 1.390 (3) |
| N—C9 | 1.509 (2) | C7—C8 | 1.469 (3) |
| C1—C2 | 1.475 (3) | C8—C9 | 1.545 (2) |
| C1—C9 | 1.551 (2) | C9—C10 | 1.514 (2) |
| C2—C3 | 1.387 (3) | C10—C11 | 1.504 (3) |
| C2—C7 | 1.386 (2) | | |

| | | | |
|----------|-----------|------------|-----------|
| O3—N—O4 | 123.2 (2) | C2—C1—C9 | 107.3 (1) |
| C7—C8—C9 | 107.5 (1) | N—C9—C10 | 111.8 (2) |
| C1—C9—C8 | 103.2 (1) | C9—C10—C11 | 113.3 (2) |

The crystal was sealed in a capillary to prevent sublimation. The *MolEN* (Fair, 1990) package was used for computations.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71037 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1038]

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Structure of 1-Phenylsemicarbazide

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Abstract

The semicarbazide moiety of the title compound is fairly planar (torsion angle -0.8°). The phenyl ring is nearly perpendicular to the plane of the semicarbazide group and intermolecular hydrogen bonds are formed between the N and O atoms of the semicarbazide groups.

Comment

1-Phenylsemicarbazide, also known as cryogenin, has anti-inflammatory activity (Kaplan, Wolke &

Malone, 1967). The *in vivo* DNA-damaging activity of the title compound and other hydrazine derivatives has been examined (Parodi *et al.*, 1981). The title compound is also the starting material in the synthesis of a number of novel and stable cyclic bicoordinated phosphorus compounds (Rodi, Lopez, Malavaud, Boisdon & Barrans, 1991). The structure determination of the title compound was undertaken in order to understand its function and to compare its bonding system with that of the related 1-phenylthiosemicarbazide (Czugler, Kálmán & Argay, 1973).

The semicarbazide moiety is fairly planar as seen by the N(1)—N(2)—C(7)—N(3) torsion angle of $-0.8(5)^\circ$. The torsion angles N(2)—N(1)—C(1)—C(6) and C(1)—N(1)—N(2)—C(7) are $-23.6(5)$ and $122.8(4)^\circ$, respectively. This means that the phenyl ring is nearly perpendicular to the plane of the semicarbazide group. The overall conformation of 1-phenylsemicarbazide resembles that of 1-phenylthiosemicarbazide, in which the O atom is substituted by an S atom.

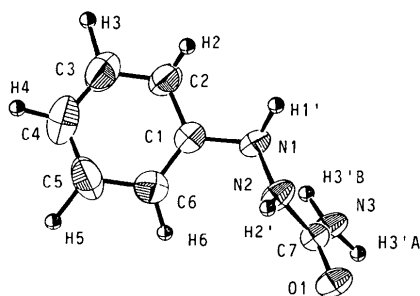


Fig. 1. Perspective view of 1-phenylsemicarbazide with the atomic numbering used.

Experimental

Crystal data

$C_7H_9N_3O$

$M_r = 151.17$

Monoclinic

$P2_1/a$

$a = 9.609(2) \text{ \AA}$

$b = 5.087(1) \text{ \AA}$

$c = 15.923(2) \text{ \AA}$

$\beta = 91.74(1)^\circ$

$V = 778.0(3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.291 \text{ Mg m}^{-3}$

$D_m = 1.291(2) \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 24 reflections

$\theta = 30.0\text{--}44.2^\circ$

$\mu = 0.085 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate

$0.30 \times 0.30 \times 0.10 \text{ mm}$

Light orange

Crystal source: 50% ethanol

Data collection

Rigaku AFC-5R diffractometer

$R_{int} = 0.037$

$\theta_{max} = 27.5^\circ$

$\omega/2\theta$ scans

Absorption correction:

DIFABS (Walker & Stuart, 1983)

$T_{min} = 0.84$, $T_{max} = 1.09$

2108 measured reflections

1995 independent reflections

764 observed reflections

$[I > 3\sigma(I)]$

Refinement

Refinement on F

Final $R = 0.034$

$wR = 0.06$

$S = 1.96$

764 reflections

100 parameters

H-atom parameters not refined

$w = 4F_o^2/\sigma^2(F_o^2)$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 6$

$l = -19 \rightarrow 19$

3 standard reflections

monitored every 150

reflections

intensity variation:

-0.60%

$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.131 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.108 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{eq} = (4/3)[B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac(\cos \beta)].$$

| | <i>x</i> | <i>y</i> | <i>z</i> | B_{eq} |
|------|------------|------------|------------|----------|
| O(1) | 0.8612 (2) | 0.0185 (5) | 0.0633 (2) | 3.8 (1) |
| N(1) | 1.0997 (3) | 0.4641 (6) | 0.1587 (2) | 3.5 (2) |
| N(2) | 1.0353 (3) | 0.2313 (6) | 0.1312 (2) | 3.8 (2) |
| N(3) | 0.8534 (3) | 0.4634 (6) | 0.0707 (2) | 3.7 (2) |
| C(1) | 1.1257 (4) | 0.4803 (8) | 0.2467 (2) | 3.5 (2) |
| C(2) | 1.2282 (4) | 0.652 (1) | 0.2754 (3) | 4.6 (2) |
| C(3) | 1.2558 (5) | 0.679 (1) | 0.3598 (4) | 6.2 (3) |
| C(4) | 1.1826 (6) | 0.540 (1) | 0.4174 (3) | 6.8 (3) |
| C(5) | 1.0798 (6) | 0.368 (1) | 0.3896 (3) | 6.3 (3) |
| C(6) | 1.0511 (4) | 0.338 (1) | 0.3036 (3) | 4.8 (2) |
| C(7) | 0.9133 (3) | 0.2312 (8) | 0.0870 (2) | 2.8 (2) |

Table 2. Bond lengths (\AA), angles ($^\circ$) and hydrogen-bond contact distances (\AA)

| | | | |
|----------------------------|-----------|-----------------------------|-----------|
| O(1)—C(7) | 1.264 (4) | C(2)—C(3) | 1.368 (6) |
| N(1)—N(2) | 1.400 (4) | C(3)—C(4) | 1.369 (7) |
| N(1)—C(1) | 1.419 (5) | C(4)—C(5) | 1.383 (7) |
| N(2)—C(7) | 1.349 (4) | C(5)—C(6) | 1.397 (7) |
| N(3)—C(7) | 1.336 (4) | N(1)—O(1) | 2.976 (4) |
| C(1)—C(2) | 1.384 (5) | N(3)—O(1) | 2.827 (4) |
| C(1)—C(6) | 1.378 (6) | N(3)—O(1) | 2.935 (4) |
| N(2)—N(1)—C(1) | 114.9 (3) | C(3)—C(4)—C(5) | 119.3 (5) |
| N(1)—N(2)—C(7) | 122.2 (3) | C(4)—C(5)—C(6) | 120.0 (5) |
| N(1)—C(1)—C(2) | 117.8 (4) | C(1)—C(6)—C(5) | 119.7 (4) |
| N(1)—C(1)—C(6) | 122.6 (4) | O(1)—C(7)—N(2) | 119.5 (4) |
| C(2)—C(1)—C(6) | 119.6 (4) | O(1)—C(7)—N(3) | 122.8 (3) |
| C(1)—C(2)—C(3) | 120.2 (4) | N(2)—C(7)—N(3) | 117.6 (3) |
| C(2)—C(3)—C(4) | 121.1 (5) | | |
| N(1)···O(1 ⁱ) | 2.976 (4) | N(3)···O(1 ⁱⁱⁱ) | 2.935 (4) |
| N(3)···O(1 ⁱⁱ) | 2.827 (4) | | |

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

Data collection scan rate $32^\circ \text{ min}^{-1}$ (in ω), scan width $(1.78 + 0.30\tan\theta)^\circ$. The ratio of peak counting time to background counting time was 2:1. Data collection, cell refinement: *MSC/AFC* software (Rigaku Corporation, 1988). Programs used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). All calculations, including data reduction, were carried out using *TEXSAN* (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71013 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1004]

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Structure of 1,4-Diethyl-3,5-dimethoxy-1,4-dihydrobenzoic Acid†

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Abstract

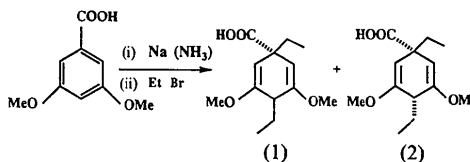
This X-ray diffraction study establishes the molecular structure of the major isomer resulting from the Birch reduction and dialkylation (with EtBr) of 3,5-dimethoxybenzoic acid, according to the procedure

† Contribution No. 1176 of the Instituto de Química, UNAM.

of Guzmán, Castanedo & Maldonado [*Synth. Commun.* (1991), **21**, 1001–1012]. The six-membered ring adopts a conformation intermediate between the envelope ¹E and the half-chair ¹H₆ conformations, defined by $\theta = 59.2(9)^\circ$, $\varphi = -12(9)^\circ$ and $Q = 0.024(3) \text{ \AA}$ [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1358; Boeyens (1978). *J. Crystallogr. Spectrosc. Res.* **8**, 317–320].

Comment

The Birch reduction and dialkylation reaction of aromatic carboxylic acids is a new reaction of current interest (Guzmán, Castanedo & Maldonado, 1991). The reaction, in its original version (excess of Na and alkyl halide in liquid NH₃) is poorly diastereoselective and thus from 3,5-dimethoxybenzoic acid and ethyl bromide, a 3:2 mixture of diastereoisomeric 1,4-reduced and diethylated acids, (1) and (2), is obtained in high yield, from which the major isomer can be isolated by fractional crystallization.



On the other hand, metallation of 1-ethyl-3,5-dimethoxy-1,4-dihydrobenzoic acid with ⁿBuLi in tetrahydrofuran, followed by ethylation (EtBr) is a completely diastereoselective alkylation process, affording as the only product a single isomer identified by this structure determination as (1), the major isomer of the above reaction.

The methoxy groups at C(3) and C(5) are nearly coplanar with the six-membered ring [dihedral angles of $-2.7(3)$ and $2.7(3)^\circ$, respectively], while the ethyl groups at C(1) and C(4) are *cis* to each other and perpendicular to the six-membered ring

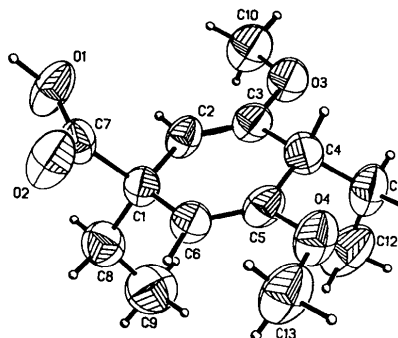


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.