Fig. 3. Stereoscopic view of the crystal structure. The axial directions are $a\rightarrow$, $b\uparrow$, and c out of the plane of the paper.

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1,5-Diphenylcarbonohydrazide (*sym*-Diphenylcarbazide)

BY C. J. DE RANTER, N. M. BLATON AND O. M. PEETERS

Laboratorium voor Analytische Scheikunde, Instituut voor Farmaceutische Wetenschappen, Katholieke Universiteit te Leuven, 4 Van Evenstraat, B-3000 Leuven, Belgium

Abstract. $C_{13}H_{14}N_4O$, $M_r = 242\cdot28$, orthorhombic, *Pbnm* (a non-standard setting of space group *Pnma*), $a = 5\cdot7171$ (5), $b = 8\cdot4121$ (13), $c = 25\cdot6982$ (23) Å, $V = 1235\cdot9$ Å^3, $Z = 4$, $D_c = 1\cdot309$ Mg m^{-3}, μ(Cu $K\alpha$) = $0\cdot718$ mm^{-1}. The structure was determined by direct methods and refined to an R of $0\cdot050$ for 784 unique reflections with $I > 3\sigma(I)$. The two phenylhydrazide groups lie on either side of a crystallographic symmetry plane passing along the bond direction of the carbonyl group. Hydrogen bonds form between the hydrazo H(1) atoms and a symmetry-related carbonyl O atom, giving rise to a herring-bone bond structure with the ureylene groups forming the column and the anilino groups as the bones.

Introduction. The title compound and phenyldiazene-carboxylic acid 2-phenylhydrazide (diphenylcarba-zone) are frequently used in analytical chemistry for the colorimetric determination of Cr and as sensitive reagents for metal ions (Hg,Cd). As part of a program to study the interaction of Cr^{VI}, Cr^{III} and Cr^{II} with diphenylcarbazide (DPCI) (I), diphenylcarbazone (DPCO) and diphenylcarbodiazone (DPCDO) (Willems, Blaton, Peeters & De Ranter, 1977) the crystal structures of the three organic substances have been solved.*

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* The crystal structure of DPCDO has been solved by Blaton, Peeters, Willems & De Ranter (1977). The crystal data of DPCO will be published in this journal (Blaton, Peeters, De Ranter & Willems, 1979).

$$O = C \begin{cases} NH-NH-C_6H_5 \\ NH-NH-C_6H_5 \end{cases}$$

(I)
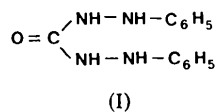
A single crystal of the title compound was prepared by slow cooling of a saturated solution in a methanol–carbon tetrachloride mixture. To record the X-ray data, a Nonius CAD-4 automatic four-circle diffractometer was used, employing graphite-monochromatized Cu $K\alpha$ radiation. The cell parameters were determined by a least-squares fit to the settings for the four angles of 16 reflections. The intensities of 1281 independent reflections up to a 2θ of $130°$ were measured and those 784 with $I > 3\sigma(I)$ were considered significant. The θ–2θ scan technique was used. The net intensities were corrected for Lorentz and polarization effects, but not for absorption. The systematic absences in the original intensity data (for $0kl$, $k = 2n + 1$, and for $h0l$, $h + l = 2n + 1$) indicated the space group *Pbnm* or *Pbn2$_1$*. The structure was solved in space group *Pbn2$_1$* with *SIMPEL* (Schenk, Overbeek & van der Putten, 1976). The E map obtained from the most probable set contained all non-hydrogen atoms among the 18 highest peaks. The O and C positions of the carbonyl group came out at $z = 0\cdot26100$, but the rest of the molecule lay so symmetrically astride a mirror plane that the space group was assumed to be *Pbnm* and the subsequent refinement confirmed this.

Two cycles of full-matrix least-squares refinement of the atomic coordinates and isotropic thermal param-

eters in space group $Pbn2_1$ reduced R to 0·160, but some of the atoms showed negative temperature factors and parameter shifts of more than 9·0 times their estimated standard deviations. Two refinement cycles in space group $Pbnm$ with the z parameters of O and C(1) restricted at 0·25 showed no abnormalities (maximum shift/error of 3·7 and average shift/error of 0·79) and $R = 0·138$. After two cycles of full-matrix refinement with anisotropic temperature factors ($R = 0·098$) all H atoms were found in a difference Fourier map. Further refinement with the hydrogens included as isotropic atoms at restricted positions resulted in $R = 0·050$ and $R_w = 0·049$, where $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$ with $w = 1/\sigma$.

Table 1. Final atomic coordinates ($\times 10^4$; for H $\times 10^3$) with e.s.d.'s for the non-hydrogen atoms

	x	y	z
O	9134 (5)	2331 (3)	2500 (0)
C(1)	8033 (7)	1067 (4)	2500 (0)
N(1)	7333 (4)	302 (2)	2938 (1)
N(2)	7898 (4)	915 (3)	3420 (1)
C(2)	6265 (5)	1810 (2)	3694 (1)
C(3)	6792 (4)	2222 (3)	4201 (1)
C(4)	5292 (5)	3156 (3)	4487 (1)
C(5)	3236 (5)	3699 (3)	4275 (1)
C(6)	2691 (5)	3282 (3)	3774 (1)
C(7)	4182 (5)	2334 (3)	3476 (1)
H(1)	655	78	287
H(2)	924	38	357
H(3)	828	185	436
H(4)	584	340	485
H(5)	205	439	452
H(6)	116	361	361
H(7)	385	208	311

Table 2. Interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses

O—C(1)	1·235 (4)		
C(1)—N(1)	1·358 (3)	N(1)—H(1)	1·03
N(1)—N(2)	1·377 (3)	N(2)—H(2)	0·98
N(2)—C(2)	1·392 (3)	C(3)—H(3)	1·00
C(2)—C(3)	1·381 (3)	C(4)—H(4)	1·02
C(3)—C(4)	1·375 (4)	C(5)—H(5)	1·10
C(4)—C(5)	1·373 (4)	C(6)—H(6)	1·01
C(5)—C(6)	1·371 (4)	C(7)—H(7)	0·98
C(6)—C(7)	1·395 (4)		
C(7)—C(2)	1·388 (3)		

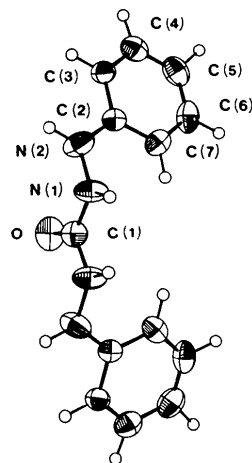| O—C(1)—N(1)	123·8 (1)	C(6)—C(7)—C(2)	118·9 (2)
C(1)—N(1)—N(2)	119·9 (2)	C(7)—C(2)—N(2)	122·8 (2)
N(1)—N(2)—C(2)	120·0 (2)	C(7)—C(2)—C(3)	119·2 (2)
N(2)—C(2)—C(3)	117·8 (2)	N(1)—C(1)—N(1')	112·2 (3)
C(2)—C(3)—C(4)	120·7 (2)		
C(3)—C(4)—C(5)	120·7 (2)	C(1)—N(1)—H(1)	114
C(4)—C(5)—C(6)	118·8 (2)	N(2)—N(1)—H(1)	125
C(5)—C(6)—C(7)	121·4 (2)	N(1)—N(2)—H(2)	112
		C(2)—N(2)—H(2)	125

Fig. 1. ORTEP plot (Johnson, 1965) of the asymmetric unit with atomic numbering. The thermal ellipsoids correspond to the 50% probability limit.

Table 3. Torsion angles (°) of important groups

| O—C(1)—N(1)—N(2)	−1·6 (5)
C(1)—N(1)—N(2)—C(2)	98·6 (3)
N(1)—N(2)—C(2)—C(3)	171·7 (2)
N(1)—N(2)—C(2)—C(7)	−10·1 (4)
O—C(1)—N(1)—H(1)	−175·0 (3)
C(1)—N(1)—H(1)—O"	22·3 (5)

A final difference electron density synthesis did not show any peaks greater than 0·25 e Å^{-3}. The scattering factors of Cromer & Mann (1968) were used for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for H. All refinement calculations were performed on the K. U. Leuven IBM 370/158 computer with the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The refined coordinates are given in Table 1, and the resulting inter-atomic distances and angles in Table 2.* Torsion angles are given in Table 3. A drawing of the molecule with the atomic-numbering scheme is shown in Fig. 1.

Discussion. As could be expected from the chemical formula the molecule has a crystallographic mirror plane through the carboxyl group [O and C(1) at the special positions $z = 0·25$ or 0·75], so that both phenylhydrazide groups are crystallographically completely equivalent to each other. The most important feature of this structure is the hydrogen-bond network (Fig. 2) built up between the H atoms of the ureylene

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34228 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

group [H(1)—N(1)—C(1)O—N(1^i)—H(1^i)] and the O^{ii} atom of a neighboring molecule, as a result of the twofold screw axis along the *b* axis.* The whole structure consists of parallel chains with the hexagonal unit

(II)
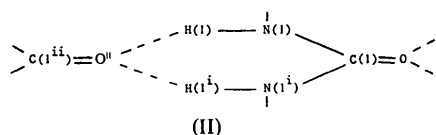
forming the links of a herring-bone bond structure. The anilino groups are the bones and the acute angle between a plane defined by the atoms of the hexagon and the phenyl groups is 82·1°. The hexagon itself is

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* Symmetry code

(i) $x, y, \frac{1}{2} - z$ (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z$

Equivalent positions for *Pbnm*, a non-standard setting of *Pnma* (D_{2h}^{16}, No. 62)

x, y, z $\bar{x}, \bar{y}, \bar{z}$
$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
$\bar{x}, \bar{y}, \frac{1}{2} + z$ $x, y, \frac{1}{2} - z$
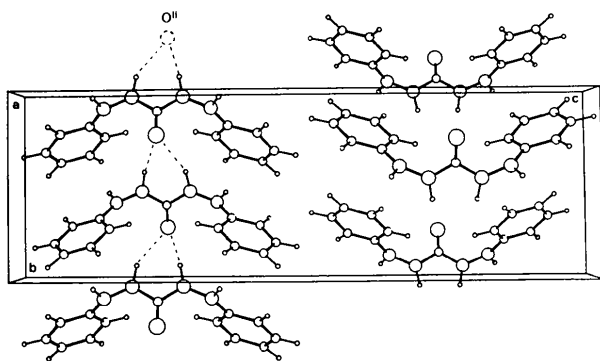$\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$ $\frac{1}{2} - x, \frac{1}{2} + y, z$

Fig. 2. *ORTEP* plot (Johnson, 1965) of the unit cell showing the packing and the hydrogen-bonding scheme.

perpendicular to the mirror plane at $z = 0.25$ and the acute angle between the phenyl plane and the mirror plane is 70·6°. All bond lengths and angles in the phenyl group are normal and the observed N—H···O geometry is regular [N(1)···O^{ii} 2·870 (2) Å, H(1)··· O^{ii} 1·89 Å, N(1)—H(1)—O^{ii} 156°]. In the hydrazo chain [C(1)—N(1)—N(2)—C(2)] a marked bond delocalization is apparent [C(1)—N(1) 1·358 (3), N(1)—N(2) 1·377 (3), N(2)—C(2) 1·392 (3) Å]; the same effect has been reported by Burke-Laing & Laing (1976) in nitrogen-containing compounds and is also found in the hydrazo chain of phenyldiazenecarboxylic acid 2-phenylhydrazide (DPCO).

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