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## Spiro(2*H*-dibenzo[*f,h*]-3,4-dihydro-1,5-dioxacyclononene-3,1'-cyclopropane)

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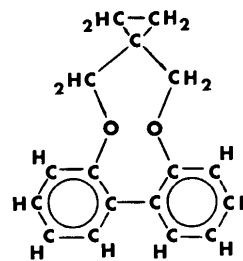
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**Abstract.** C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>, monoclinic,  $P2_1/c$ ,  $a = 9.771$  (1),  $b = 20.381$  (6),  $c = 6.892$  (4) Å,  $\beta = 104.92$  (9)°,  $Z = 4$ ,  $D_c = 1.26$ ,  $D_m = 1.24$  (1) Mg m<sup>-3</sup>. The molecule is asymmetric with a torsion angle of 58° between the linked phenyl rings.

**Introduction.** The title compound (I) was prepared and crystallized by Smolinski & Jamrozik (1974). From systematic absences the space group was determined as  $P2_1/c$ . The cell parameters and their standard deviations were obtained from diffractometer angular settings of 15 centered reflections using Cu  $K\alpha$  radiation for five different crystal samples. The crystal used for data collection was rectangular, of dimensions 0.2 × 0.2 × 0.3 mm. Intensities were collected on an automated Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) and 2494 symmetry-independent reflections ( $2\theta < 140^\circ$ ) were measured in the  $\theta$ – $2\theta$  mode. Lorentz and polarization corrections were made but no absorption corrections were applied [ $\mu(\text{Cu } K\alpha) = 0.64$  mm<sup>-1</sup>]. The phase determination was carried out by the symbolic addition procedure (Karle & Karle, 1966). The structure shown in Fig. 1 was solved by recognizing a significant fragment of the molecule, which was shifted to the correct location by a translation function (Karle, 1972) and developed to the complete structure by using phases based on the fragment as a starting set of phases. The resulting  $E$  map showed all the O and C atoms except one cyclopropane C atom which was subsequently found in a difference map. Subsequently the

structure was easily solved by use of a theory that forms the basis for selecting triplets with essential certainty that their values would be equal to zero or  $\pi$  (Karle, 1979). The approximate coordinates of the C and O atoms were refined by a full-matrix least-squares procedure, with isotropic thermal parameters, followed by two cycles of anisotropic refinement. The difference map showed all the H atoms except one on C(17) for which coordinates were calculated for an ideal position. Refinement was continued on the positional parameters of all the atoms (including the H atoms), anisotropic thermal parameters for the C and O atoms and fixed isotropic thermal parameters for H atoms with  $B = 5.0$  Å<sup>2</sup>. Reflections 100,  $\bar{1}\bar{3}1$ , 002, 564 were omitted from the refinement because of larger than normal differences between the observed and calculated values. The differences in the first three reflections may have been due to extinction and the last one to some misprint. Final refinement for all the observed data resulted in agreement factors  $R(F) = 5.3\%$  and  $R(F^2) = 6.48\%$ . The  $R_w$  factor (weights based on counting statistics) was equal to 5.1%.



(I)

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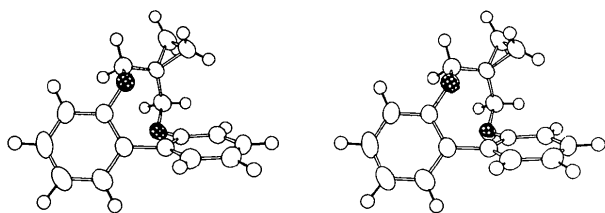


Fig. 1. Stereoscopic view of the molecule C<sub>17</sub>H<sub>16</sub>O<sub>2</sub> drawn by ORTEP (Johnson, 1965). The thermal vibration ellipsoids are at 50% probability.

Table 1. Fractional coordinates

The standard deviations for the O atoms are 0.0001, 0.00006 and 0.0002 for *x*, *y* and *z*. For the C atoms they are 0.0002, 0.0001 and 0.0003 or 0.0004 for *x*, *y* and *z*.

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.6531	0.0487	1.1129
O(2)	0.5610	0.1361	0.7672
C(1)	0.6573	0.1627	1.1746
C(2)	0.7328	0.1042	1.1824
C(3)	0.8771	0.1016	1.2678
C(4)	0.9475	0.1578	1.3508
C(5)	0.8749	0.2157	1.3507
C(6)	0.7303	0.2185	1.2632
C(7)	0.5046	0.1647	1.0713
C(8)	0.4588	0.1475	0.8683
C(9)	0.3163	0.1474	0.7681
C(10)	0.2170	0.1648	0.8703
C(11)	0.2592	0.1831	1.0697
C(12)	0.4028	0.1834	1.1696
C(13)	0.7018	0.0053	0.9779
C(14)	0.7011	0.0379	0.7831
C(15)	0.5663	0.0722	0.6779
C(16)	0.8377	0.0655	0.7543
C(17)	0.7812	0.0011	0.6547

The atomic positional parameters are given in Table 1,\* while the calculated bond lengths, bond angles and torsional angles are shown in Fig. 2(a) and (b).

**Discussion.** The formula of the investigated molecule is symmetric. A model of the molecule containing a twofold rotation axis through the mid-point of C(1)–C(7) and C(14) becomes increasingly strained as the O(1)···O(2) distance is increased to a van der Waals value. The model showed that only an asymmetric conformation is possible if the O(1)···O(2) separation is made to be 2.8 Å or larger. The crystal structure result showed that the molecule does assume such an asymmetric conformation, Fig. 1. The nine-

\* Lists of structure factors, H atom positional parameters and anisotropic thermal parameters have been deposited with British Library Lending Division as Supplementary Publication No. SUP 34194 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

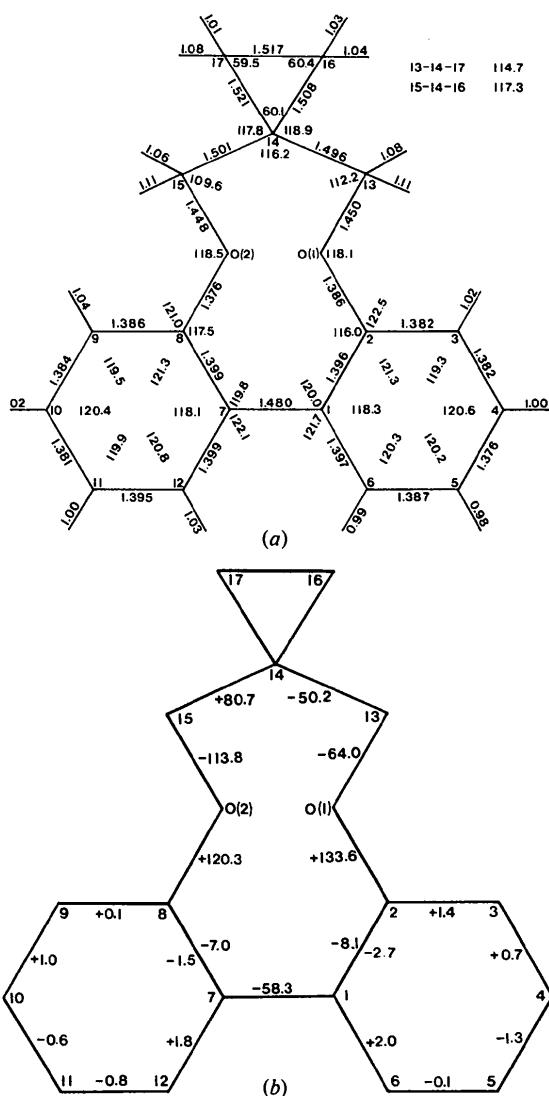


Fig. 2. (a) Bond lengths (Å) and angles (°). E.s.d.'s are not greater than 0.004 Å for all the C–C and C–O bond lengths; for the C–H bond lengths they are less than 0.04 Å. E.s.d.'s for the bond angles not involving H atoms are not higher than 0.3°. (b) Torsional angles. The e.s.d.'s are near 0.6°. Note: The numbering system of the atoms is arbitrary.

membered ring is skewed and has an asymmetric distribution of torsion angles, Fig. 2(b). The torsion angle between phenyl rings is 58° but the C(1)–C(7) bond distance of 1.480 Å still remains shorter than a single-bond value. The intramolecular O(1)···O(2) distance is equal to 2.925 Å. The perpendicular projection of the atom C(14) on the biphenyl bond is displaced from the center of the bond. Furthermore the plane of the cyclopropane group is not perpendicular to the C(1)–C(7) bond. The molecular packing, Fig. 3, is dominated by van der Waals contacts. The shortest intermolecular distances are between O(2) and H(6), 2.411 Å, and O(1) and H(131), 2.683 Å.

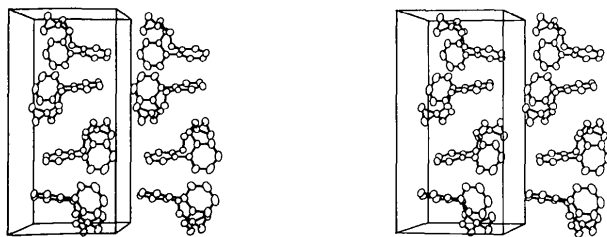


Fig. 3. Stereoscopic view of the crystal structure. The axial directions are  $a \rightarrow$ ,  $b \uparrow$ , and  $c$  out of the plane of the paper.

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## 1,5-Diphenylcarbonohydrazide (*sym*-Diphenylcarbazine)

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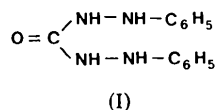
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**Abstract.** C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O,  $M_r = 242.28$ , orthorhombic, *Pbnm* (a non-standard setting of space group *Pnma*),  $a = 5.7171$  (5),  $b = 8.4121$  (13),  $c = 25.6982$  (23) Å,  $V = 1235.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.309$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 0.718$  mm<sup>-1</sup>. The structure was determined by direct methods and refined to an  $R$  of 0.050 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 (diphenylcarbazine) 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<sup>VI</sup>, Cr<sup>III</sup> and Cr<sup>II</sup> with diphenylcarbazine (DPCI) (I), diphenylcarbazono (DPCO) and diphenylcarbodiazone (DPCDO) (Willems, Blaton, Peeters & De Ranter, 1977) the crystal structures of the three organic substances have been solved.\*

\* 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).



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  $2\theta$  of 130° were measured and those 784 with  $I > 3\sigma(I)$  were considered significant. The  $\theta$ - $2\theta$  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<sub>1</sub>*. The structure was solved in space group *Pbn2<sub>1</sub>* 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  $z = 0.26100$ , 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-

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