

cis-1,3-Diphenyl-1,3-dihydroisobenzofuran-1,3-dicarboxylic Acid

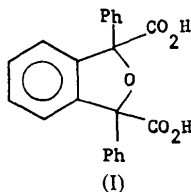
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Abstract. $C_{22}H_{16}O_5$, $M_r = 360.4$, monoclinic, $P2_1/c$, $a = 10.050$ (1), $b = 10.923$ (1), $c = 16.258$ (2) Å, $\beta = 99.72$ (1)°, $V = 1759.1$ Å³, $Z = 4$, $D_c = 1.36$ Mg m⁻³, $F(000) = 752$; systematic absences: $h0l$ if $l = 2n + 1$, $0k0$ if $k = 2n + 1$; Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 0.104$ mm⁻¹. The structure was solved by direct methods and refined by full-matrix least-squares calculations; $R = 0.042$ for 2936 reflections with $I > 3\sigma(I)$. The molecule is shown to be the *cis* isomer with an O–H...O intramolecular hydrogen bond (2.827 Å); in the crystal structure the molecules are linked in chains by O–H...O hydrogen bonds [2.703 (2) Å].

Introduction. In the course of synthetic studies involving alkali-metal derivatives of 1,3-diphenylisobenzofuran the dicarboxylic acid derivative (I) of melting point 496–497 K was prepared (Smith & McCall, 1978).



It proved impossible to decide from spectroscopic studies if the material produced was the *cis* or *trans* isomer. Our X-ray analysis of (I) unambiguously identifies it as the *cis* isomer.

Initial photographic work established the space group and gave approximate values for the unit-cell parameters. Least-squares refinement of the setting angles of 12 reflections with θ (Mo $K\alpha$) between 10 and 20° led to precise values of the cell dimensions. Intensities for 3827 unique reflections with $2 < \theta < 27^\circ$ were collected from a small portion of a needle crystal on a computer-controlled Hilger & Watts Y290 four-circle diffractometer as described previously (Ferguson & Roberts, 1978). The data were corrected for Lorentz and polarization effects but not for absorption which was insignificant. The 2936 independent reflections with $I > 3\sigma(I)$ were used in the refinement calculations.

The structure was solved by direct methods using the SHELX crystallographic program (Sheldrick, 1977)

Table 1. Final fractional coordinates for *cis*-1,3-diphenyl-1,3-dihydroisobenzofuran-1,3-dicarboxylic acid ($\times 10^4$ for O and C, $\times 10^3$ for H) with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	4593 (1)	1833 (2)	2057 (1)
O(2)	4114 (1)	1327 (1)	735 (1)
O(3)	4795 (1)	1717 (1)	-861 (1)
O(4)	6221 (1)	2858 (1)	-1455 (1)
O(5)	6614 (1)	1322 (1)	495 (1)
C(1)	6445 (1)	1863 (1)	1282 (1)
C(2)	4970 (2)	1649 (2)	1398 (1)
C(3)	6988 (1)	2218 (1)	-77 (1)
C(4)	5869 (2)	2210 (2)	-849 (1)
C(11)	6618 (1)	3219 (1)	1157 (1)
C(12)	6920 (1)	3425 (1)	368 (1)
C(13)	7100 (2)	4605 (2)	93 (1)
C(14)	6977 (2)	5567 (2)	625 (1)
C(15)	6693 (2)	5358 (2)	1422 (1)
C(16)	6502 (2)	4187 (2)	1693 (1)
C(21)	7430 (1)	1267 (1)	1985 (1)
C(22)	8587 (2)	1866 (2)	2360 (1)
C(23)	9501 (2)	1284 (2)	2973 (1)
C(24)	9270 (2)	116 (2)	3210 (1)
C(25)	8131 (3)	-490 (2)	2838 (1)
C(26)	7208 (2)	78 (2)	2221 (1)
C(31)	8366 (1)	1892 (1)	-286 (1)
C(32)	8499 (2)	1038 (2)	-895 (1)
C(33)	9775 (2)	703 (2)	-1040 (1)
C(34)	10916 (2)	1197 (2)	-567 (1)
C(35)	10796 (2)	2025 (2)	46 (1)
C(36)	9526 (2)	2375 (2)	184 (1)
H(1)	453 (3)	129 (3)	29 (2)
H(2)	556 (3)	286 (3)	-189 (2)
H(13)	731	475	-45
H(14)	708	638	45
H(15)	663	603	178
H(16)	630	404	223
H(22)	876	268	220
H(23)	1029	170	323
H(24)	990	-28	363
H(25)	797	-130	300
H(26)	642	-35	196
H(32)	772	68	-121
H(33)	986	13	-147
H(34)	1179	96	-67
H(35)	1158	236	38
H(36)	945	295	61

Table 2. *Interatomic distances (Å) and angles (°)*

(a) Bond lengths

C(1)–C(2)	1.543 (2)	C(11)–C(12)	1.384 (2)
C(1)–C(11)	1.510 (2)	C(11)–C(16)	1.387 (2)
C(1)–C(21)	1.526 (2)	C(12)–C(13)	1.386 (2)
C(1)–O(5)	1.444 (1)	C(13)–C(14)	1.380 (2)
C(2)–O(1)	1.212 (2)	C(14)–C(15)	1.392 (3)
C(2)–O(2)	1.309 (2)	C(15)–C(16)	1.376 (2)
C(3)–C(4)	1.538 (2)	C(21)–C(22)	1.383 (2)
C(3)–C(12)	1.511 (2)	C(21)–C(26)	1.383 (2)
C(3)–C(31)	1.523 (2)	C(22)–C(23)	1.391 (2)
C(3)–O(5)	1.443 (2)	C(23)–C(24)	1.363 (3)
C(4)–O(3)	1.203 (2)	C(24)–C(25)	1.371 (3)
C(4)–O(4)	1.308 (2)	C(25)–C(26)	1.392 (3)
O(2)–H(1)	0.90 (3)	C(31)–C(32)	1.382 (2)
O(4)–H(2)	0.89 (3)	C(31)–C(36)	1.386 (2)
		C(32)–C(33)	1.392 (3)
		C(33)–C(34)	1.379 (3)
		C(34)–C(35)	1.366 (3)
		C(35)–C(36)	1.387 (2)

(b) Angles

C(2)–C(1)–C(11)	107.5 (1)	C(16)–C(15)–C(14)	120.8 (2)
C(2)–C(1)–C(21)	111.0 (1)	C(11)–C(16)–C(15)	118.4 (1)
C(2)–C(1)–O(5)	107.8 (1)	C(1)–C(21)–C(22)	121.3 (1)
C(11)–C(1)–C(21)	116.4 (1)	C(1)–C(21)–C(26)	119.6 (1)
C(11)–C(1)–O(5)	104.4 (1)	C(22)–C(21)–C(26)	119.0 (1)
C(21)–C(1)–O(5)	109.3 (1)	C(21)–C(22)–C(23)	120.3 (2)
C(1)–C(2)–O(1)	122.3 (1)	C(22)–C(23)–C(24)	120.5 (2)
C(1)–C(2)–O(2)	116.8 (1)	C(23)–C(24)–C(25)	119.8 (2)
O(1)–C(2)–O(2)	120.8 (1)	C(24)–C(25)–C(26)	120.5 (2)
C(4)–C(3)–C(12)	108.1 (1)	C(25)–C(26)–C(21)	119.9 (2)
C(4)–C(3)–C(31)	112.5 (1)	C(3)–C(31)–C(32)	121.3 (1)
C(4)–C(3)–O(5)	106.8 (1)	C(3)–C(31)–C(36)	119.9 (1)
C(12)–C(3)–C(31)	115.3 (1)	C(32)–C(31)–C(36)	118.5 (1)
C(12)–C(3)–O(5)	104.2 (1)	C(31)–C(32)–C(33)	120.2 (1)
C(31)–C(3)–O(5)	109.4 (1)	C(32)–C(33)–C(34)	120.4 (2)
C(3)–C(4)–O(3)	123.1 (1)	C(33)–C(34)–C(35)	119.9 (2)
C(3)–C(4)–O(4)	111.0 (1)	C(34)–C(35)–C(36)	120.1 (1)
O(3)–C(4)–O(4)	125.8 (1)	C(35)–C(36)–C(31)	121.1 (2)
C(1)–C(11)–C(12)	109.4 (1)	C(1)–O(5)–C(3)	112.1 (1)
C(1)–C(11)–C(16)	129.7 (1)	C(2)–O(2)–H(1)	110.0 (2)
C(12)–C(11)–C(16)	120.8 (1)	C(4)–O(4)–H(2)	110.0 (2)
C(3)–C(12)–C(11)	109.7 (1)		
C(3)–C(12)–C(13)	129.6 (1)		
C(11)–C(12)–C(13)	120.8 (1)		
C(12)–C(13)–C(14)	118.4 (2)		
C(13)–C(14)–C(15)	120.8 (2)		

(c) Hydrogen-bond geometry

O(2)···O(3)	2.827 (2)	H(1)···O(3)	1.99 (3)
O(2)–H(1)···O(3)	154 (2)		
O(4)···O(1) ⁱ	2.703 (2)	H(2)···O(1) ⁱ	1.85 (3)
O(4)–H(2)···O(1) ⁱ	160 (2)		

The superscript (i) refers to the equivalent position $x, \frac{1}{2} - y, -\frac{1}{2} + z$.

and refined by full-matrix least-squares calculations minimizing $\sum w(|F_o| - |F_c|)^2$, with weights derived from counting statistics. After initial anisotropic refinement of the non-hydrogen atoms, a difference synthesis at $R = 0.07$ revealed electron density maxima in positions consistent with all H atoms. In subsequent calculations the carboxylic H atoms were allowed to refine isotropically; the remaining H atoms bonded to aromatic C atoms were constrained to idealized geometry with C–H 0.95 Å and only an overall isotropic thermal parameter U was refined for those atoms. The scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968) and

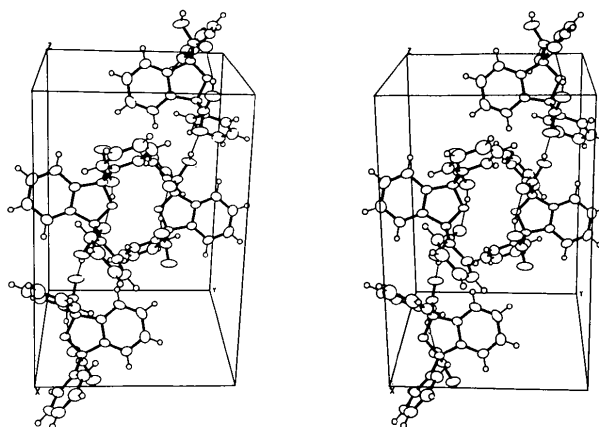


Fig. 1. Stereoview of part of the unit cell. Hydrogen bonds are indicated by thin lines.

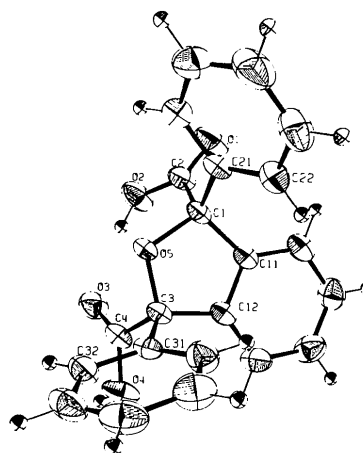


Fig. 2. A view of the molecule with an indication of the numbering scheme. The aromatic ring C atoms are numbered C(1)···C(16) sequentially around each ring.

those for H from Stewart, Davidson & Simpson (1965). In the final cycles of calculation a weighting scheme of the form $w^{1/2} = [1/(\sigma^2 F + pF^2)]^{1/2}$ was employed; the final p value is 0.0041. In the last cycle the maximum shift/error ratio was 0.35 for the y coordinate of H(1) and a final difference map was devoid of any significant features.

The final coordinates and standard deviations are in Table 1 and details of molecular dimensions are in Table 2. Fig. 1 is a stereoview of the crystal structure and Fig. 2 shows our crystallographic numbering scheme. Final values of $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R' = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$ are 0.042 and 0.054 respectively.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34343 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The crystal structure contains discrete molecules of the *cis* isomer linked in chains parallel to *c* by intermolecular O(4)—H...O(1) (2.703 Å) hydrogen bonds (Fig. 1). The conformation of the carboxyl groups allows the formation of an intramolecular hydrogen bond [O(2)—H...O(3) 2.827 Å]. In each aromatic ring the atoms are close to coplanar (r.m.s. deviation 0.003–0.006 Å). The furan ring is slightly distorted from planarity towards a very shallow envelope conformation with O(5) 0.031 Å from the five-membered-ring plane; the dihedral angle between the furan- and benzene-ring planes in the isobenzofuran moiety is 2.0°. The orientations of the phenyl and carboxylic groups are defined by the torsion angles C(11)—C(1)—C(21)—C(22) –13.8, C(12)—C(3)—C(31)—C(36) 25.4, C(11)—C(1)—C(2)—O(1) –79.8, and C(12)—C(3)—C(4)—O(3) –98.4°. The bond lengths in the molecule are in accord with expected values; mean distances are C(sp²)—C(sp²) aromatic

1.382, C(sp²)—C(sp³) 1.525, C(sp³)—O 1.444, C=O 1.208, C(sp²)—O 1.309 Å.

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References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 FERGUSON, G. & ROBERTS, P. J. (1978). *Acta Cryst.* **B34**, 3083–3086.
 SHELDRIK, G. M. (1977). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.
 SMITH, J. G. & MCCALL, R. B. (1978). Personal communication.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1979). **B35**, 1722–1724

Benzo[*b*][1,4]diazabicyclo[3.2.1]octane, a Molecule Containing a \dot{N} —C(sp²) Single Bond

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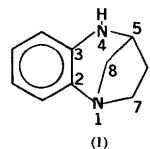
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Abstract. C₁₀H₁₂N₂, *M_r* = 160.2, monoclinic, *P*2₁/*n*, *a* = 9.764 (6), *b* = 10.528 (2), *c* = 8.698 (2) Å, β = 106.31 (2)°, *Z* = 4, *D_c* = 1.24 Mg m⁻³. The structure was solved with direct methods. The final *R* index was 0.037 for 1041 reflections. The two benzene— \dot{N} bonds are, respectively, 1.387 and 1.452 Å. The first is typical of anilines and reflects some double-bond character, whereas the geometry of the nitrogen involved in the 1.452 Å bond indicates that it is essentially a single \dot{N} —C(sp²) linkage.

Introduction. Our initial interest in the title compound (I) was as a bridgehead N-containing substrate for lanthanide shift reagent—nuclear magnetic resonance experiments. Its structural details were of interest because the orientations of the secondary [N(4)] and tertiary [N(1)] nitrogen atoms relative to the aromatic ring suggest that two quite different amine—C(sp²) bonds are present in the molecule. In particular, N(1)'s non-bonding electron-pair orbital should be approximately parallel to the adjacent benzene ring, resulting in

a situation in which the N(1)—C(2) bond should be essentially free of bond-shortening π-type conjugation effects.



(I) was prepared according to the procedure of Cunningham (1969) and Cunningham & Day (1973) with modifications: colorless solid, m.p. 407–408 K (literature m.p. 404–407 K). Recrystallization from petroleum ether (333–383 K) gave suitable diffraction samples. All X-ray measurements were made with a 0.2 × 0.2 × 0.4 mm specimen mounted parallel to the long crystal axis (*b*) on a Picker FACS-I diffractometer with Mo radiation (graphite monochromator, *K*α, λ = 0.71069 Å). The unit-cell parameters were obtained by least squares from the Bragg angles of 13 reflections manually centered at ±2θ (average of |2θ_o – 2θ_c| = 0.004°).

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