Refinement

Refinement on *F*
Final *R* = 0.033
wR = 0.033
S = 0.67
1230 reflections
202 parameters
All H-atom parameters refined
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	*y*	*z*	U_{eq}
Cl	0.0915 (1)	0.9981 (1)	0.1893 (1)	0.0542 (2)
O1	0.0568 (3)	0.5231 (2)	0.2830 (2)	0.0546 (7)
O16	−0.0222 (3)	0.7998 (2)	0.3073 (2)	0.0569 (7)
N9	−0.1629 (3)	0.6327 (2)	0.3870 (2)	0.0434 (8)
C2	−0.0112 (3)	0.4334 (2)	0.3213 (2)	0.0425 (9)
C3	0.0471 (4)	0.3338 (3)	0.2957 (3)	0.0505 (10)
C4	−0.0275 (4)	0.2459 (3)	0.3379 (3)	0.0563 (11)
C5	−0.1564 (4)	0.2540 (3)	0.4047 (3)	0.0593 (12)
C6	−0.2160 (4)	0.3520 (3)	0.4299 (3)	0.0522 (11)
C7	−0.1439 (3)	0.4435 (2)	0.3874 (2)	0.0406 (9)
C8	−0.2129 (4)	0.5418 (2)	0.4188 (3)	0.0437 (9)
C10	−0.2210 (3)	0.7340 (2)	0.4219 (2)	0.0399 (8)
C11	−0.3412 (4)	0.7466 (3)	0.4960 (3)	0.0496 (10)
C12	−0.3831 (4)	0.8468 (3)	0.5310 (3)	0.0579 (11)
C13	−0.3028 (4)	0.9331 (3)	0.4899 (3)	0.0576 (11)
C14	−0.1836 (4)	0.9211 (2)	0.4147 (3)	0.0510 (10)
C15	−0.1407 (3)	0.8205 (2)	0.3787 (2)	0.0431 (9)

Table 2. *Geometric parameters* (Å, °)

O1—C2	1.356 (4)	C10—C11	1.368 (4)
O16—C15	1.353 (4)	C10—C15	1.393 (4)
N9—C8	1.286 (4)	C11—C12	1.382 (5)
N9—C10	1.438 (4)	C12—C13	1.382 (5)
C2—C3	1.391 (5)	C13—C14	1.369 (5)
C2—C7	1.394 (4)	C14—C15	1.392 (4)
C3—C4	1.380 (5)	Cl···H1^{i}	2.02 (3)
C4—C5	1.370 (5)	Cl···H16	2.18 (4)
C5—C6	1.376 (5)	O1—H1	1.00 (3)
C6—C7	1.409 (5)	O16—H16	0.86 (4)
C7—C8	1.429 (4)		
O1—C2—C7	117.8 (2)	C2—C7—C6	119.3 (3)
O1—C2—C3	122.0 (3)	C6—C7—C8	116.0 (3)
O16—C15—C14	124.7 (2)	C2—C7—C8	124.7 (2)
O16—C15—C10	117.0 (2)	C11—C10—C15	121.4 (3)
N9—C10—C15	114.9 (2)	C10—C11—C12	119.8 (3)
N9—C10—C11	123.6 (3)	C11—C12—C13	119.3 (3)
C8—N9—C10	126.6 (3)	C12—C13—C14	121.2 (3)
C7—C8—N9	124.2 (3)	C13—C14—C15	120.0 (3)
C3—C2—C7	120.2 (3)	C10—C15—C14	118.3 (2)
C2—C3—C4	118.9 (3)	H1^{i}···Cl···H16	106.1 (14)
C3—C4—C5	121.9 (4)	Cl···H1^{i}—O1^{i}	162 (2)
C4—C5—C6	119.8 (3)	Cl···H16—O16	171 (4)
C5—C6—C7	119.9 (3)		

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

Equimolar amounts of salicylaldehyde and *o*-aminophenol in ethanol were mixed as described by Haegele (1992) from which red needle crystals of *o*-(salicylideneamino)phenol were precipitated. Olive-green crystals of the hydrochloride were obtained by recrystallization from 95% methanol after acidifying with 10% hydrochloric acid.

The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1986) and refined anisotropically by block-diagonal least squares in three blocks (*SHELX*76; Sheldrick, 1976). H atoms were located from a $\Delta\rho$ map and expected geometry. All H atoms were refined isotropically. Other computer programs used: *SDP-Plus* (B. A. Frenz & Associates, Inc., 1984); *PARST* (Nardelli, 1991).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71267 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1045]

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Structure of Diphenanthro[1,2-*b*;2′,1′-*d*]-furan at 191 K

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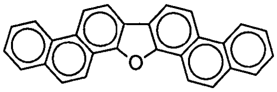
Abstract

Diphenanthro[1,2-*b*;2′,1′-*d*]furan crystallizes in space group *Pnma* (No. 62) with the mirror plane bisecting the molecule and passing through the furan O atom. Although exhibiting packing similar to that of dibenzofuran, this diphenanthrofuran showed no disorder of the sort found in that close molecular analog. The C atoms of the individual phenanthrene rings of the title compound have a mean deviation of 0.027 (21) Å from the best least-squares plane describing the rings. The configuration and conformation of the individual phenanthrene rings in this

diphenanthrofuran closely match the theoretical and experimental results for phenanthrene itself. Overall, this diphenanthrofuran molecule adopts a distinct V shape, the dihedral angle between the least-squares best-fit planes of the phenanthrene rings being 11.0 (1.2)°.

Comment

The structures of dibenzofuran (Reppart, Gallucci, Lundstedt & Gerkin, 1984) and dibenzofuran-d_8 (Fitzgerald, Gallucci & Gerkin, 1993) were found to manifest a type of disorder such that approximately 10% of the molecules adopted an alternative orientation. This alternative orientation is such that disordered molecules are related to ordered molecules by a 180° rotation about an axis passing through the molecular center of mass and perpendicular to the furan ring. The structures of the related compounds fluorene (Gerkin, Lundstedt & Reppart, 1984) and carbazole (Gerkin & Reppart, 1986) were found to be isomorphic with dibenzofuran, although no disorder was observed. Dinaphtho[1,2-*b*;2′,1′-*d*]furan, a third compound related to dibenzofuran, was found to be neither isomorphic nor disordered (Gerkin & Reppart, 1985). The present study of diphenanthro[1,2-*b*;2′,1′-*d*]furan (I) was undertaken to determine whether this molecule would crystallize in a structure showing dibenzofuran-like disorder. Since this substance has not been described previously, its synthesis is outlined.



(I)

A unit-cell drawing is shown in Fig. 1. The space group was found to be *Pnma*, the same as for the isomorphic structures of dibenzofuran, fluorene and carbazole. Also, as in those structures, the mirror plane passes through the furan oxygen and bisects the diphenanthrofuran molecule. While the *a* and *c* cell edges are similar in length to the respective *c* and *a* cell edges of the isomorphic structures above, the *b* cell edge is considerably longer in the present structure in order to accommodate the longer molecule. There was no evidence in the present structure of the type of disorder found in the structures of dibenzofuran and dibenzofuran-d_8. Indeed, such disorder in the diphenanthrofuran structure described here would result in disordered H(3) and H(9) positions 2.26–2.55 Å away from ordered C-atom positions, distances considerably less than the sum of the corresponding van der Waals radii, 2.94 Å (Bondi, 1964). The closest approaches as determined for the present structure are listed in Table 2. The approaches for which the difference between the observed separations and the sums of the relevant van der Waals radii are most negative are C···C interactions in the **a** and **c** directions. In the **b** direction the closest approaches involve C(6)···C(6^{iii}) and C(6)···H(6^{iii}). None of these closest approaches involves H···H interactions.

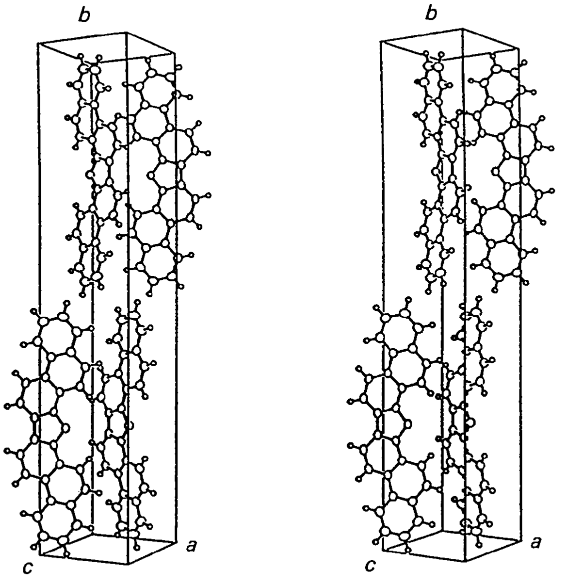


Fig. 1. A stereoview of a unit cell of diphenanthro[1,2-*b*;2′,1′-*d*]-furan drawn using *ORTEP*II (Johnson, 1976). Displacement ellipsoids have been drawn at 50% probability for all atoms except H, for which they have been set artificially small.

Fig. 2(*a*) shows a diphenanthrofuran molecule with bond lengths specified on one asymmetric unit and bond angles on another. The C atoms of the phenanthrene rings in the present structure have a mean deviation of 0.027 (21) Å from the best least-squares plane describing these atoms. The corresponding value for phenanthrene, as calculated from the data of Kay, Okaya & Cox (1971), is 0.019 (10) Å. In the present study, H(4) and H(5) are found to be twisted in opposite directions by 0.08 (3) and 0.10 (3) Å, respectively, out of the plane of the phenanthrene rings and are 2.07 (3) Å apart. This result is in agreement with results for phenanthrene (Kay *et al.*, 1971). The C—C bond lengths for the phenanthrene rings found in diphenanthrofuran demonstrate a pattern of values that agrees well with the theoretical values calculated by Cioslowski, O'Connor & Fleischmann (1991) for phenanthrene, as well as with the observed values of Kay *et al.* (1971). The longest bond of the phenanthrene rings in the present study is C(12)—C(13) of 1.450 (4) Å;

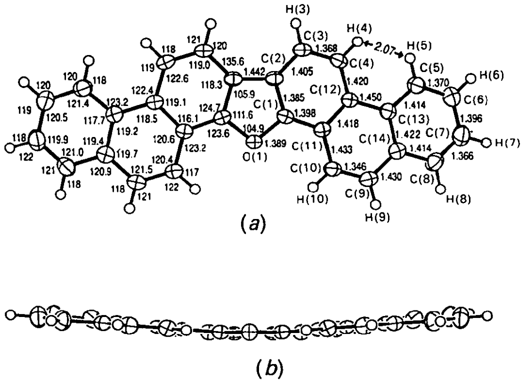


Fig. 2. (*a*) An *ORTEP*II drawing of diphenanthro[1,2-*b*;2′,1′-*d*]-furan showing the atom-numbering scheme. Bond lengths (Å) are given on one asymmetric unit and bond angles (°) on the other. The maximum e.s.d. for bond lengths involving non-H atoms is 0.004 Å; for bond lengths involving H atoms, 0.03 Å. The maximum e.s.d. for bond angles involving non-H atoms is 0.3°; for angles involving H atoms, 2.0°. (*b*) An *ORTEP*II drawing of the title molecule viewed from a direction close to the line of intersection of the furan ring plane and the mirror plane containing the furan O atom.

the shortest is C(9)—C(10) of 1.346 (4) Å. The corresponding values for phenanthrene reported by Kay *et al.* (1971) are 1.464 (5) and 1.341 (7) Å, while the corresponding values calculated by Cioslowski *et al.* (1991) are 1.461 and 1.339 Å.

Overall, this diphenanthrofuran molecule assumes a distinct V shape, as shown in Fig. 2(*b*). The dihedral angle between the least-squares plane of the phenanthrene rings and the furan ring [C(1), C(2), C(1^{i}), C(2^{i}), O(1)] is 5.5 (6)°. This can be compared to 1.5° for dibenzofuran and dibenzofuran-d_8 (Reppart *et al.*, 1984; Fitzgerald *et al.*, 1993) and 0.5° for dinaphthofuran (Gerkin & Reppart, 1985). The bond lengths for C(1)—O(1) and C(2)—C(2^{i}) agree well with those reported for dibenzofuran [C—O 1.384 (2), C—C 1.438 (2) Å] and dinaphthofuran [C—O 1.381 (2), C—C 1.438 (3) Å].

Experimental

Crystal data

$C_{28}H_{16}O$
M_r = 368.43
Orthorhombic
Pnma
a = 6.806 (3) Å
b = 34.693 (4) Å
c = 7.678 (2) Å
V = 1812.9 (8) Å^3
Z = 4
D_x = 1.35 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 13.5–15°
μ = 0.0748 mm^{-1}
T = 191 K
Rectangular chunk, clear
0.38 × 0.35 × 0.23 mm
Pale yellow
Crystal source: slow evaporation of solvent at room temperature

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
3092 measured reflections
3092 independent reflections
1320 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max}$ = 30°
h = 0 → 10
k = 0 → 48
l = 0 → 9
6 standard reflections monitored every 150 reflections intensity variation: ±3.2%

Refinement

Refinement on F
Final R = 0.047
wR = 0.049
S = 1.59
1320 reflections
165 parameters
All H-atom parameters refined
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max}$ = 0.22 e Å^{-3}
$\Delta\rho_{\min}$ = −0.23 e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974) for C, O and Stewart, Davidson & Simpson (1965) for H

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	0.2629 (3)	0.250000	0.9357 (2)	2.5 (1)
C(1)	0.1495 (3)	0.28175 (6)	0.9810 (3)	2.3 (1)
C(2)	−0.0312 (3)	0.27078 (6)	1.0476 (2)	2.4 (1)
C(3)	−0.1599 (3)	0.29972 (6)	1.1056 (3)	2.7 (1)
C(4)	−0.1004 (3)	0.33735 (6)	1.0987 (3)	2.6 (1)
C(5)	0.0359 (4)	0.41912 (7)	1.0954 (3)	3.2 (1)
C(6)	0.0995 (4)	0.45654 (7)	1.0858 (4)	3.9 (1)
C(7)	0.2779 (4)	0.46543 (7)	1.0057 (4)	4.0 (1)
C(8)	0.3929 (4)	0.43660 (7)	0.9401 (3)	3.5 (1)
C(9)	0.4579 (3)	0.36738 (6)	0.8889 (3)	2.9 (1)
C(10)	0.4027 (3)	0.33015 (6)	0.8972 (3)	2.6 (1)
C(11)	0.2152 (3)	0.31983 (6)	0.9680 (3)	2.3 (1)
C(12)	0.0860 (3)	0.34852 (6)	1.0327 (2)	2.3 (1)
C(13)	0.1492 (3)	0.38843 (6)	1.0274 (3)	2.6 (1)
C(14)	0.3342 (3)	0.39760 (6)	0.9522 (3)	2.7 (1)

Table 2. *Intermolecular closest approaches* (Å) *in the title structure with e.s.d.'s in parentheses*

The van der Waals sums are based upon Bondi (1964).

	Observed separation	Observed separation minus van der Waals sum
C(1)···C(3^{i})	3.48 (1)	−0.06
C(1)···H(3^{i})	2.92 (2)	−0.02
C(3)···C(11^{ii})	3.45 (1)	−0.09
C(4)···C(12^{ii})	3.56 (1)	0.02
C(6)···C(6^{iii})	3.56 (1)	0.02
C(6)···H(6^{iii})	2.96 (2)	0.02
C(9)···C(12^{iv})	3.42 (1)	−0.12
C(10)···C(11^{iv})	3.54 (1)	−0.00
C(11)···H(10^{iv})	2.96 (2)	0.02
C(12)···H(4^{i})	2.95 (2)	0.01
C(13)···H(9^{v})	2.91 (2)	−0.03
C(14)···H(9^{v})	2.94 (2)	0.00

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

Diphenanthro[1,2-*b*;2′,1′-*d*]furan was synthesized by a three-step sequence starting from dibenzofuran (Aldrich Chemical Company). (The experimental details of this synthesis will be published elsewhere in due course.) The 4,6-dilithio derivative of dibenzofuran, obtained from the reaction of dibenzofuran with three equivalents of *sec*-butyllithium, was treated with dimethylformamide to afford dibenzofuran-4,6-dicarboxaldehyde. The Wittig-type reaction of this dialdehyde with diethylbenzylphosphonate and ^{t}BuOK in dry dimethylformamide gave 4,6-(2,2-diphenylethenyl)dibenzofuran in good yield. This stilbenoid was converted to the desired diphenanthro-[1,2-*b*;2′,1′-*d*]furan [m.p. 583-587 K (dec.)] by irradiation with UV light in the presence of air and iodine. The diphenanthrofuran was crystallized from solution in dimethoxyethane to provide the experimental sample.

The sample was mounted on a quartz pin with epoxy cement and a unit cell was determined at room temperature (295 K). The following non-idealized parameters were obtained from a least-squares fitting of the setting angles for 25 centered reflections: a = 6.825 (2), b = 34.842 (4), c = 7.749 (1) Å, α = 90.01 (2), β = 90.01 (2), γ = 90.01 (2)°, V = 1842.8 (6) Å^3. The crystal was then cooled to 191 K utilizing a Molecular Structure Corporation low-temperature apparatus. The stated temperature was measured continuously during data collection in the cold gas flow just upstream of the crystal; the estimated uncertainty of the crystal temperature is ±2 K. Unit-cell parameters for the low-temperature cell were obtained from a symmetry-constrained least-squares fit of the same reflections used to determine the room-temperature cell. The low-temperature unit-cell parameters are given in the *Experimental* section.

Data were collected utilizing graphite-monochromated radiation. Scan widths were (1.4 + 0.35tanθ)° in ω, with a background/scan time ratio of 1:2. No corrections were made for decay or absorption; the data were corrected for Lorentz and polarization effects. Systematic absences (0*kl*, *k*+*l* = odd; *hk*0, *h* = odd) were consistent with two space groups: *Pnma* and *Pna*2$_1$. Since intensity statistics indicated a centrosymmetric space group, *Pnma* (No. 62) was given initial preference; refinement proceeded well and it was adopted.

The direct-methods program *SHELXS*86 (Sheldrick, 1985) was used to generate an *E* map from which the initial positions of the non-H atoms were identified. Fourier difference methods were then used to locate the H atoms. The C and O atoms were refined anisotropically and the H atoms isotropically using full-matrix least squares (*TEXSAN*; Molecular Structure Corporation, 1989). The weighting scheme used was $w = \sigma_F^{-2}$, where $\sigma_F = \sigma_I/2FLp$ and $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$. The maximum peak on the final electron density difference map was located at (−0.04, 0.25, 1.08), approximately at the midpoint of the C(2)—C(2$^{\rm i}$) bond; the minimum peak was located at (0.27, 0.36, 0.95) approximately at the center of the C(9)-C(14) ring.

The support of LJF by PPG Industries and the partial support of this research through purchase of the diffractometer system by an NIH grant are gratefully acknowledged. Various contributions of Dr J. C. Gallucci are also greatly appreciated.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, isotropic displacement parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71246 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1052]

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Redetermination of the Structures of 1-Naphthoic Acid and 2-Naphthoic Acid

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Abstract

The structures of 1-naphthoic acid and 2-naphthoic acid have been investigated in order to determine the degree of disorder of the carboxylic acid groups. 1-Naphthoic acid was found to be completely ordered with C—O bond lengths of 1.214 (3) and 1.312 (3) Å, and C—C—O bond angles of 124.8 (2) and 114.2 (2)°. 2-Naphthoic acid was found to possess a significant degree of disorder with C—O bond lengths of 1.256 (3) and 1.274 (3) Å, and C—C—O bond angles of 117.7 (2) and 119.1 (2)°. In 2-naphthoic acid, the acid H atom was refined at two sites with 0.5 occupancy at each. Analysis of the anisotropic displacement ellipsoids of the acid O atoms for each structure demonstrated that these

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