$S = 1.477$
637 reflections
97 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{max} = 0.009$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1 for C, Br, N and O atoms, and Table 6.1.1.2 for H atoms)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Br1	0.19925 (4)	0.08695 (7)	0.1245 (1)	0.0637 (3)
O1	0.0467 (2)	0.0301 (4)	0.2114 (8)	0.059 (2)
N1	0.0351 (4)	1/4	0.179 (1)	0.038 (3)
C1	0.1359 (3)	0.1747 (6)	0.300 (1)	0.042 (2)
C2	0.1510 (3)	0.1425 (7)	0.531 (1)	0.044 (2)
C3	0.0912 (3)	0.1859 (6)	0.650 (1)	0.048 (2)
C4	0.1989 (5)	1/4	0.583 (1)	0.051 (4)
C5	0.0686 (3)	0.1367 (7)	0.225 (1)	0.040 (2)
C6	−0.0326 (5)	1/4	0.100 (2)	0.057 (4)
C7*	−0.0818 (8)	0.199 (2)	0.266 (3)	0.056 (6)
C8*	−0.0896 (9)	0.299 (2)	0.429 (3)	0.066 (7)
C9	−0.1368 (5)	1/4	0.600 (2)	0.071 (5)

* Site occupancy 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Br1—C1	1.942 (6)	C2—C3	1.508 (9)
O1—C5	1.190 (7)	C2—C4	1.513 (9)
N1—C5	1.384 (7)	C3—C3^{i}	1.32 (1)
N1—C6	1.47 (1)	C6—C7	1.56 (2)
C1—C1^{i}	1.55 (1)	C7—C8	1.49 (2)
C1—C2	1.566 (9)	C8—C9	1.55 (2)
C1—C5	1.506 (9)		

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

The molecule has been treated as lying on a crystallographic mirror plane, with a disordered *n*-butyl substituent, in preference to the corresponding ordered space group, $Pn2_1a$, in which refinement became ill-conditioned.

Data collection: *MSC/AFC* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We thank the SERC, UK for funds for the purchase of the Rigaku AFC-5*R* diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1163). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5,15-Diaza-6,16-dihydroxytetrabenzo[*b*,*e*,*k*,*n*]perylene

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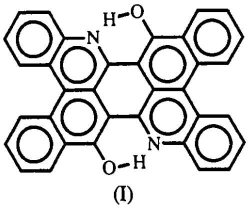
Abstract

The molecule of the title compound, $C_{34}H_{18}N_2O_2$, belongs to point group C_i. The area between the two opposing phenyl rings is overcrowded so that each phenyl ring is bent out of the diazaperylene skeleton in such a way that one ring is above and the other is below the molecular plane. Due to the ring strain thus induced, the C—C bonds in the bent phenyl rings are no longer equal. There are intramolecular hydrogen bonds between the OH groups and N atoms, which stabilize the molecule. The molecules are stacked in a herringbone fashion, with an interplanar distance of 3.43 (1) Å along the *b* axis where there are close interatomic contacts.

Comment

5,15-Diaza-6,16-dihydroxytetrabenzo[*b*,*e*,*k*,*n*]perylene (DDTP), (I), is a new purple–violet light-stable insoluble pigment based on the diazaperylene skeleton. Kitahara, Nishi, Hasegawa & Maeda (1988) prepared it from diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate and 2-aminobenzophenone and claimed a patent with a keto structure. The colour of the pigment was reddish purple. Kitahara & Nishi (1988) later reported the synthesis and properties of diazaperylene derivatives. They proposed three possible structures, namely, an enol structure, (I), a keto structure and 5,15-diaza-5b,15b-dihydrotetrabenzo[*b*,*e*,*k*,*n*]perylene-6,16-dione. From these they selected the last structure, since they could not observe the NH and OH stretching bands in the IR spectra. Jaffe (1991) independently prepared the same substance by essentially the same synthetic route and claimed a patent with the aforementioned keto structure. The colour was, however, black–violet. In order to clarify the molecular structure and investigate the reason for the different colours, the present structure determination was undertaken.



(I)

The X-ray analysis supports the enol structure (Fig. 1) over the other two proposed structures. The molecule is overcrowded in the area between the two opposing phenyl rings. The condensed aromatic molecule is then forced into a non-planar configuration due to steric repulsion between two H atoms attached to opposing phenyl rings. The ring strain is spread over the ring system and is relieved by an out-of-plane bending of the phenyl rings. One of these is bent below the planar skeleton and the other ring is bent above it, so that each deviation angle when viewed from the side of the skeleton is about 30.4 (5)°. The distance between the two inner H atoms is 2.2 (1) Å.

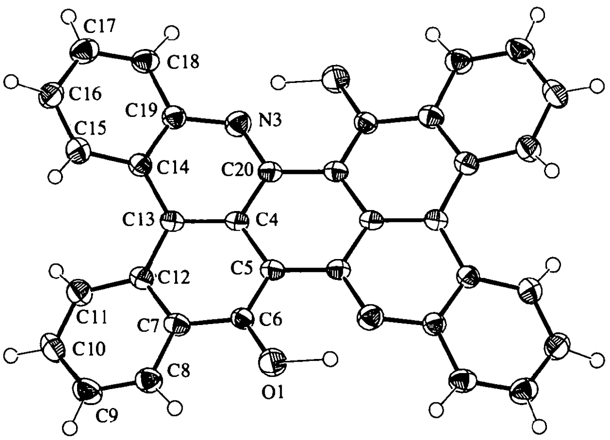


Fig. 1. *ORTEP* (Johnson, 1976) plot of DDTP showing the numbering of the non-H atoms. Displacement ellipsoids are scaled to the 40% probability level; for N3 and C6 these represent averages of the disordered atoms.

Due to the ring strain induced by bending, the C—C bonds in each of the aromatic rings are not equal, indicating that the electrons are not properly delocalized in the bent phenyl rings. The C—O bond length of 1.33 (1) Å is typical of phenol-type compounds having some double-bond character and characterized by an acidic hydroxy group (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). There are intramolecular hydrogen bonds between the OH group and the N atom which stabilize the molecule.

A stereodiagram of the crystal structure of DDTP is shown in Fig. 2. The molecules are stacked in a herringbone fashion along the *b* axis. The angle between the two differently tilted stacking molecules is about 20°. There are close interatomic contacts along the stacking *b* axis, with C16···C17 [3.349 (9) Å] being the shortest and C12···C13 [3.737 (8) Å] the longest. It should be noted that in the investigated crystal, roughly two thirds of the molecules are ordered as shown in Fig. 2, where all molecules are oriented in the same direction parallel to the *ac* plane. About one third of the molecules, however, are rotated by 180° around the C4—C4′ axis. The refinement was therefore carried out considering the two possible molecular orientations (see *Experimental* text).

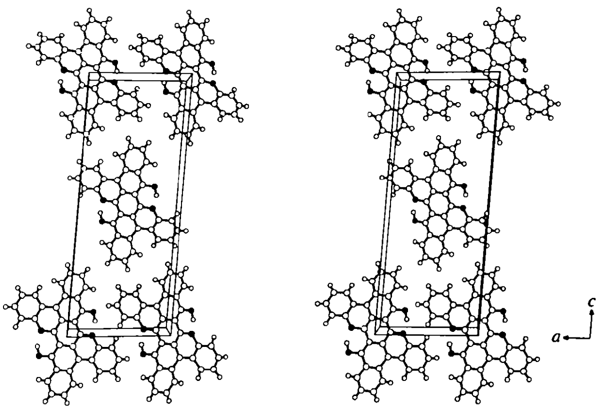


Fig. 2. Stereoview of the crystal structure of DDTP showing the out-of-plane bending of the phenyl rings. Only one molecular orientation is shown.

Details of the optical properties of DDTP, especially the two different colours, are now under investigation on the basis of the present structure analysis and will be reported elsewhere.

Experimental

DDTP was prepared according to the previously described method of Jaffe (1991). The black powder obtained was purified twice by vacuum sublimation using apparatus described by Mizuguchi (1981). Single crystals were grown from the vapour phase using the same sublimation equipment. DDTP was sublimed at about 635 K and the argon flow rate was controlled to 10 mm^3 s^{-1} using a mass flow meter (F-100/200, Bronkhorst BV). After 48 h of vapour growth, a number of lustrous acicular platelets were obtained. The density D_m was measured by flotation in chloroform/dichloromethane solution.

Crystal data

$C_{34}H_{18}N_2O_2$
$M_r = 486.53$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/n$
$a = 10.599\ (1)$ Å
$b = 3.775\ (1)$ Å
$c = 26.517\ (3)$ Å
$\beta = 95.17\ (1)°$
$V = 1056.7\ (3)$ Å^3
$Z = 2$
$D_x = 1.529$ Mg m^{-3}
$D_m = 1.520$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 11.6–22.1°$
$\mu = 0.096$ mm^{-1}
$T = 293$ K
Acicular platelet
$0.63 \times 0.36 \times 0.18$ mm
Black

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3162 measured reflections
3102 independent reflections
1822 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 30°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 37$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.065$
$S = 1.212$
1822 reflections
205 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = 0.028$

$\Delta\rho_{\rm max} = 0.211$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.184$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

All coordinates, except those of O1 and O2, are for composites of atoms related by the disorder noted in the text. $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
O1	−0.2433 (6)	0.065 (2)	0.0704 (3)	0.038 (4)
O2†	0.318 (2)	0.864 (5)	−0.0184 (6)	0.022 (7)
N3	0.2521 (5)	0.706 (2)	0.0171 (2)	0.033 (3)
C4	0.0661 (5)	0.454 (2)	0.0502 (2)	0.024 (3)
C5	−0.0639 (5)	0.348 (2)	0.0401 (2)	0.025 (3)
C6	−0.1275 (5)	0.201 (2)	0.0784 (2)	0.025 (3)
C7	−0.0702 (6)	0.211 (2)	0.1292 (2)	0.028 (3)
C8	−0.1443 (6)	0.119 (2)	0.1686 (3)	0.033 (3)
C9	−0.0976 (7)	0.160 (2)	0.2181 (3)	0.037 (4)
C10	0.0226 (7)	0.305 (2)	0.2298 (2)	0.035 (4)
C11	0.0973 (6)	0.389 (2)	0.1916 (2)	0.033 (3)
C12	0.0560 (5)	0.333 (2)	0.1402 (2)	0.026 (3)
C13	0.1304 (5)	0.416 (2)	0.0984 (2)	0.025 (3)
C14	0.2671 (5)	0.462 (2)	0.1032 (2)	0.026 (3)
C15	0.3493 (6)	0.337 (2)	0.1444 (2)	0.030 (3)
C16	0.4785 (6)	0.386 (2)	0.1461 (3)	0.033 (3)
C17	0.5321 (6)	0.561 (2)	0.1067 (3)	0.034 (4)
C18	0.4571 (6)	0.675 (2)	0.0648 (3)	0.031 (3)
C19	0.3252 (5)	0.618 (2)	0.0623 (2)	0.027 (3)
C20	0.1285 (5)	0.606 (2)	0.0092 (2)	0.025 (3)

† Disordered O1.

Table 2. *Selected geometric parameters (Å, °)*

O1—C6	1.330 (9)	N3—C19	1.409 (8)
N3—C20	1.362 (7)	C4—C5	1.437 (7)
C4—C13	1.401 (8)	C4—C20	1.440 (8)
C5—C6	1.385 (8)	C5—C20$^{\rm i}$	1.431 (8)
C6—C7	1.427 (8)	C7—C8	1.406 (8)
C7—C12	1.420 (8)	C8—C9	1.37 (1)
C9—C10	1.39 (1)	C10—C11	1.378 (9)
C11—C12	1.411 (9)	C12—C13	1.452 (8)
C13—C14	1.453 (8)	C14—C15	1.417 (9)
C14—C19	1.421 (8)	C15—C16	1.378 (9)
C16—C17	1.40 (1)	C17—C18	1.376 (9)
C18—C19	1.410 (8)		
N3—O2—O1$^{\rm i}$	116.0 (12)	C20—N3—C19	120.8 (5)
C13—C4—C5	121.5 (5)	C20—C4—C5	117.9 (5)
C20—C4—C13	120.7 (5)	C6—C5—C4	119.8 (5)
C20$^{\rm i}$—C5—C4	120.5 (5)	C20$^{\rm i}$—C5—C6	119.7 (5)
C5—C6—O1	122.7 (6)	C7—C6—O1	118.0 (6)
C7—C6—C5	119.2 (5)	C8—C7—C6	118.4 (6)
C12—C7—C6	121.0 (5)	C12—C7—C8	120.4 (6)
C9—C8—C7	120.4 (6)	C10—C9—C8	120.2 (6)
C11—C10—C9	120.0 (6)	C12—C11—C10	121.8 (6)
C11—C12—C7	116.9 (5)	C13—C12—C7	118.7 (5)
C13—C12—C11	124.2 (6)	C12—C13—C4	117.7 (5)
C14—C13—C4	117.8 (5)	C14—C13—C12	124.4 (5)
C15—C14—C13	124.5 (6)	C19—C14—C13	118.7 (5)
C19—C14—C15	116.5 (5)	C16—C15—C14	121.4 (6)
C17—C16—C15	120.5 (6)	C18—C17—C16	120.5 (6)
C19—C18—C17	119.2 (6)	C14—C19—N3	120.3 (5)
C18—C19—N3	118.0 (6)	C18—C19—C14	121.6 (6)
C4—C20—N3	119.7 (5)	C5$^{\rm i}$—C20—N3	118.6 (5)
C5$^{\rm i}$—C20—C4	121.6 (5)		

Symmetry code: (i) $-x, 1 - y, -z$.

The positional parameters of the eight phenyl H atoms were refined. The position of the hydroxy H atom was positioned by calculation and kept fixed during refinement. Refinement was by full-matrix least-squares methods. A considerable electron density which corresponds to the O atom of the inverted molecule appeared on the difference Fourier map after the anisotropic refinement. Further refinement was then carried out considering the complete molecules in the two possible orientations on the basis of the assumed coordinates (rotation by 180° around the C4—C4′ axis) and site occupancy factor [final value 0.649 (4)].

Program(s) used to solve structure: *SDP* in *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP* in *MULTAN*11/82. Molecular graphics: *ORTEP*II (Johnson, 1976), *SCHAKAL*92 (Keller, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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