Crystal structure of *N,N'*-bis(3,5-xylyl)perylene-3,4:9,10-bis(dicarboximide), $C_{40}H_{26}N_2O_4$

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Abstract

$C_{40}H_{26}N_2O_4$, monoclinic, $P12_1/c1$ (No. 14), $a = 17.0133(5)$ Å, $b = 4.869(3)$ Å, $c = 17.096(5)$ Å, $\beta = 93.40(2)^\circ$, $V = 1413.7$ Å³, $Z = 2$, $\rho_m = 1.399$ g·cm⁻³, $R_{gt}(F) = 0.050$, $wR_{obs}(F) = 0.077$, $T = 296$ K.

Source of material

The title compound was obtained from BASF. The sample was purified by sublimation at about 600 K, using the two-zone furnace [1]. After 60 h of vapor growth, a number of red prismatic crystals were obtained.

Discussion

The title compound is a commercial red pigment based on the perylene skeleton (Pigment Red 149 manufactured by BASF AG) [2]. Perylene pigments are widely known to exhibit a variety of colors in the solid state depending on the substituents, although their solution spectra are practically the same. The difference in shade has been attributed to a structurally controlled special arrangement of the pigment molecules within the crystal lattice [2]. We have previously clarified the color generation mechanism of the perylene black (Pigment Black 31) on the basis of the crystal structure and intermolecular interactions [3, 4].

The present structure analysis aims at extending our investigation on the electronic structure of perylene pigments. As shown in the figure, the xylyl rings are almost attached vertically to the planar perylene-skeleton with a torsion angle of about 95.7° (molecular symmetry: C_2). The vertical arrangement presumably occurs because of the steric hindrance between the hydrogen atom at the

ortho position of the xylyl group and the carbonyl oxygen atom of the perylene skeleton. Obviously, the present arrangement inhibits the conjugation between the xylyl ring and the perylene system. Therefore, the chromophore is effectively small and thus the absorption maximum occurs at a relatively shorter wavelength as compared with the one in ordinary perylene derivatives. This is in accord with experiment. All molecules are arranged in the same direction and stacked along the *b*-axis in a herringbone fashion. The stacked molecules in one column are almost arranged vertically to those in the neighboring column. The present molecular conformation and arrangement might play an important role in interactions between transition dipoles in the solid state, inducing a profound influence on the optical absorption. Details on the correlation between the crystal structure and optical properties will be reported elsewhere.

In the open literature, there is a similar compound to the title one (-bis(2,6-xylyl) instead of -bis(3,5-xylyl)) and its structure has already been reported [5]. The space group is the same and the molecular conformation is similar, but the lattice parameters as well as the molecular arrangement are quite different.

Table 1. Data collection and handling.

Crystal:	red prism, size 0.07 × 0.12 × 0.25 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ :	0.91 cm ⁻¹
Diffractometer, scan mode:	Rigaku AFC7R, $\omega/2\theta$
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4693, 4558
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 1.5 \sigma(I_{obs})$, 1525
$N(param)_{refined}$:	209
Programs:	SHELXS-86 [6], teXsan [7], ORTEPII [8]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1a)	4e	0.4577	-0.4442	0.1461	0.045
H(2a)	4e	0.5546	-0.3823	0.2465	0.045
H(6a)	4e	0.7277	0.5668	0.0434	0.061
H(7a)	4e	0.6321	0.4900	-0.0650	0.061
H(14a)	4e	0.8732	-0.1659	0.2505	0.061
H(16a)	4e	0.9654	0.2098	0.4616	0.061
H(18a)	4e	0.7330	0.4456	0.3714	0.061

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(19a)	4e	0.9962	-0.3176	0.3461	0.083
H(19b)	4e	1.0288	-0.0778	0.2978	0.083
H(19c)	4e	1.0432	-0.0819	0.3883	0.083
H(20a)	4e	0.8932	0.5378	0.5268	0.077
H(20b)	4e	0.8370	0.7247	0.4757	0.077
H(20c)	4e	0.8031	0.4859	0.5234	0.077

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	4e	0.6734(1)	-0.1777(5)	0.3196(1)	0.038(1)	0.056(2)	0.037(1)	0.000(1)	-0.0052(9)	0.006(1)
O(2)	4e	0.7935(1)	0.4675(6)	0.1758(1)	0.051(1)	0.075(2)	0.050(2)	-0.031(1)	-0.013(1)	0.009(1)
N(1)	4e	0.7375(1)	0.1290(6)	0.2455(1)	0.029(1)	0.047(2)	0.035(1)	-0.002(1)	-0.007(1)	0.000(1)
C(1)	4e	0.4981(2)	-0.3123(7)	0.1399(2)	0.035(2)	0.041(2)	0.034(2)	-0.004(1)	-0.001(1)	0.003(2)
C(2)	4e	0.5562(2)	-0.2761(7)	0.2000(2)	0.035(2)	0.042(2)	0.035(2)	0.000(1)	0.000(1)	0.005(1)
C(3)	4e	0.6155(2)	-0.0891(7)	0.1928(2)	0.029(1)	0.038(2)	0.033(1)	-0.001(1)	0.000(1)	-0.003(1)
C(4)	4e	0.6180(2)	0.0686(7)	0.1236(2)	0.028(1)	0.034(2)	0.033(1)	-0.002(1)	0.001(1)	-0.002(1)
C(5)	4e	0.6795(2)	0.2611(7)	0.1157(2)	0.032(1)	0.041(2)	0.033(2)	-0.006(1)	-0.002(1)	0.001(1)
C(6)	4e	0.6825(2)	0.4114(7)	0.0481(2)	0.037(2)	0.047(2)	0.041(2)	-0.013(1)	-0.001(1)	-0.001(2)
C(7)	4e	0.6251(2)	0.3791(7)	-0.0129(2)	0.037(2)	0.049(2)	0.035(2)	-0.013(1)	-0.001(1)	0.004(2)
C(8)	4e	0.5633(2)	0.1951(6)	-0.0076(2)	0.031(1)	0.031(2)	0.030(1)	-0.003(1)	0.002(1)	-0.004(1)
C(9)	4e	0.5591(2)	0.0362(7)	0.0622(2)	0.028(1)	0.036(2)	0.028(2)	-0.001(1)	0.000(1)	-0.003(1)
C(10)	4e	0.4979(2)	-0.1608(6)	0.0713(2)	0.030(1)	0.034(2)	0.031(2)	-0.004(1)	0.002(1)	-0.004(1)
C(11)	4e	0.6765(2)	-0.0537(7)	0.2575(2)	0.029(1)	0.041(2)	0.034(2)	0.005(1)	-0.001(1)	-0.003(1)
C(12)	4e	0.7415(2)	0.2980(8)	0.1793(2)	0.033(2)	0.052(2)	0.040(2)	-0.006(1)	0.000(1)	-0.001(2)
C(13)	4e	0.8008(2)	0.1509(7)	0.3067(2)	0.033(1)	0.045(2)	0.035(2)	-0.003(1)	-0.007(1)	0.002(1)
C(14)	4e	0.8689(2)	0.0022(8)	0.2979(2)	0.033(2)	0.054(2)	0.044(2)	0.001(2)	0.001(1)	-0.002(2)
C(15)	4e	0.9316(2)	0.0309(8)	0.3538(2)	0.032(1)	0.057(2)	0.048(2)	0.001(2)	-0.005(1)	0.007(2)
C(16)	4e	0.9221(2)	0.2035(8)	0.4166(2)	0.038(2)	0.055(2)	0.040(2)	-0.007(2)	-0.011(1)	0.005(2)
C(17)	4e	0.8535(2)	0.3525(7)	0.4255(2)	0.042(2)	0.045(2)	0.040(2)	-0.005(2)	-0.003(1)	0.001(2)
C(18)	4e	0.7919(2)	0.3246(8)	0.3689(2)	0.040(2)	0.045(2)	0.041(2)	0.000(2)	-0.003(1)	0.000(2)
C(19)	4e	1.0069(2)	-0.127(1)	0.3458(3)	0.040(2)	0.097(3)	0.069(3)	0.012(2)	-0.010(2)	-0.003(3)
C(20)	4e	0.8460(2)	0.543(1)	0.4942(2)	0.064(2)	0.070(3)	0.056(2)	-0.007(2)	-0.006(2)	-0.019(2)

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