Refinement of the crystal structure of 3,4:9,10-perylene-bis(dicarboximide), $C_{24}H_{10}N_2O_4$, *at 263 K*

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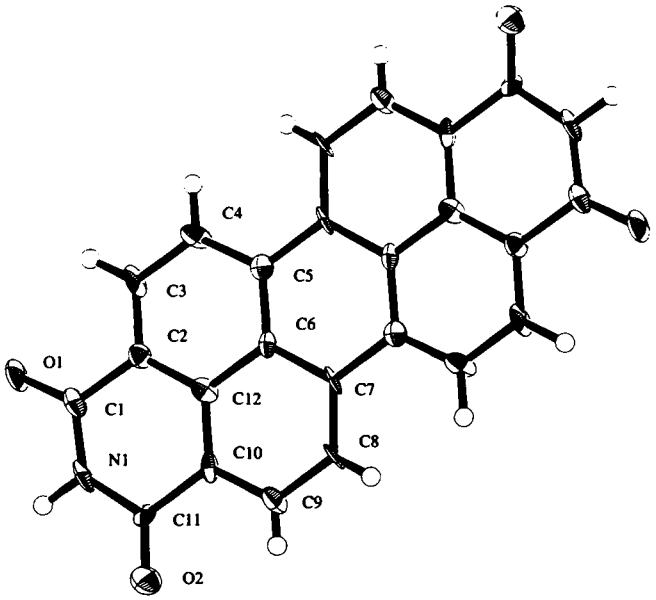

Abstract

$C_{24}H_{10}N_2O_4$, monoclinic, $P12_1/n1$ (No. 14), $a = 4.865(4)$ Å, $b = 14.660(7)$ Å, $c = 10.844(3)$ Å, $\beta = 91.33(4)°$, $V = 773.2$ Å^3, $Z = 2$, $R_{gt}(F) = 0.070$, $wR_{ref}(F^2) = 0.181$, $T = 263$ K.

Source of material

The title compound, pigment violet 29 (PV29), was obtained from BASF in Germany. The single crystals were grown from the vapor phase using a two-zone furnace [1]. To our surprise, the single crystals were also obtained by thermal decomposition of *N,N'*-bis(2-(4-pyridyl)ethyl)perylene-3,4:9,10-bis(dicarboximide) during its vapor growth.

Discussion

New data are presented for the title compound [2]. It is a commercial perylene pigment (PV29) as characterized by excellent weatherfastness [3]. Perylene derivatives 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. This evidently indicates that the difference in shade is ascribed to the molecular arrangement in the solid state. We have previously investigated the color generation mechanism of typical red, maroon and black perylene pigments from the standpoint of molecular and crystal structures as well as intermolecular interactions [4-6]. Our results concluded that the exciton coupling (that depends greatly on the molecular arrangement) plays the decisive role in the color determination and thus the color changes from red to black as the exciton coupling is increased.

The molecule is entirely planar. The molecules are closely-packed in a herringbone fashion as characterized by an extremely high density of 1.68 g·cm^{-3}. Another high-density perylene pigment is pigment red 179 (density: 1.60 g·cm^{-3}) [7] in which the =NH in dicaroximide of PV29 is replaced by =N–CH_3. This compound is also quite weatherfast. These facts indicate that the simple and small substituents at the NH group might lead to a closely-packed structure and thus strong intermolecular interactions, showing high weatherfastness.

Table 1. Data collection and handling.

Crystal:	red, prismatic, size 0.07 × 0.07 × 0.20 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	1.17 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7R, $\omega/2\theta$
$2\theta_{max}$:	55.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2066, 1938
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 528
$N(param)_{refined}$:	136
Programs:	SHELXS-86 [8], teXsan [9], ORTEPII [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.2962	0.3002	0.4510	0.0259
H(2)	4*e*	0.6143	0.2771	0.5946	0.0293
H(3)	4*e*	0.9585	0.4341	0.9282	0.0308
H(4)	4*e*	0.3513	0.6611	0.8387	0.0341
H(5)	4*e*	–0.0006	0.6849	0.6908	0.0308
H(1*)	4*e*	–0.2962	0.6998	0.5490	0.0259
H(5*)	4*e*	0.0006	0.3151	0.3092	0.0308
H(2*)	4*e*	–0.6143	0.7229	0.4054	0.0293
H(4*)	4*e*	–0.3513	0.3389	0.1613	0.0341
H(3*)	4*e*	–0.9585	0.5659	0.0718	0.0308

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	0.732(1)	0.5793(5)	0.9548(6)	0.030(4)	0.042(4)	0.020(4)	0.001(4)	–0.013(3)	–0.005(3)
O(2)	4*e*	0.933(1)	0.3071(5)	0.7844(6)	0.042(5)	0.033(4)	0.030(4)	0.008(4)	–0.009(3)	0.001(3)
N(1)	4*e*	0.822(2)	0.4431(6)	0.8651(7)	0.017(5)	0.035(6)	0.017(4)	–0.004(4)	–0.014(3)	0.010(4)
C(1)	4*e*	0.685(2)	0.5219(7)	0.8726(9)	0.022(6)	0.036(6)	0.018(5)	–0.001(5)	–0.010(4)	0.005(5)
C(2)	4*e*	0.462(2)	0.5370(7)	0.7799(8)	0.020(5)	0.022(5)	0.016(5)	0.000(5)	–0.003(4)	0.000(4)
C(3)	4*e*	0.313(2)	0.6153(8)	0.7780(8)	0.029(6)	0.051(7)	0.011(5)	0.002(6)	–0.013(4)	–0.001(5)
C(4)	4*e*	0.104(2)	0.6300(7)	0.6879(8)	0.026(6)	0.039(7)	0.016(5)	0.014(6)	0.003(4)	–0.002(5)
C(5)	4*e*	0.050(2)	0.5669(7)	0.5954(8)	0.017(5)	0.021(5)	0.019(5)	–0.002(5)	0.003(4)	0.002(4)
C(6)	4*e*	0.204(2)	0.4852(6)	0.5955(8)	0.017(5)	0.022(5)	0.011(4)	–0.005(5)	–0.004(4)	–0.002(4)
C(7)	4*e*	0.159(2)	0.4167(7)	0.5008(7)	0.010(5)	0.026(6)	0.014(5)	–0.005(5)	–0.007(4)	0.011(4)
C(8)	4*e*	0.320(2)	0.3392(7)	0.5043(8)	0.012(5)	0.038(7)	0.019(5)	0.006(5)	–0.010(4)	–0.004(4)
C(9)	4*e*	0.524(2)	0.3246(6)	0.5951(7)	0.023(5)	0.034(6)	0.020(5)	0.004(5)	–0.006(4)	–0.001(5)
C(10)	4*e*	0.574(2)	0.3899(6)	0.6849(7)	0.020(5)	0.028(6)	0.007(4)	–0.006(5)	–0.002(4)	–0.005(4)
C(11)	4*e*	0.797(2)	0.3744(6)	0.7791(8)	0.029(6)	0.005(5)	0.021(5)	–0.002(5)	–0.006(5)	0.006(4)
C(12)	4*e*	0.417(2)	0.4701(7)	0.6885(8)	0.018(6)	0.028(6)	0.013(5)	0.000(5)	0.001(4)	0.004(4)
C(7*)	4*e*	–0.159(2)	0.5833(7)	0.4992(7)	0.010(5)	0.026(6)	0.014(5)	–0.005(5)	–0.007(4)	0.011(4)
C(5*)	4*e*	–0.050(2)	0.4331(7)	0.4046(8)	0.017(5)	0.021(5)	0.019(5)	–0.002(5)	0.003(4)	0.002(4)
C(6*)	4*e*	–0.204(2)	0.5148(6)	0.4045(8)	0.017(5)	0.022(5)	0.011(4)	–0.005(5)	–0.004(4)	–0.002(4)
C(8*)	4*e*	–0.320(2)	0.6608(7)	0.4957(8)	0.012(5)	0.038(7)	0.019(5)	0.006(5)	–0.010(4)	–0.004(4)
C(4*)	4*e*	–0.104(2)	0.3700(7)	0.3121(8)	0.026(6)	0.039(7)	0.016(5)	0.014(6)	0.003(4)	–0.002(5)
C(12*)	4*e*	–0.417(2)	0.5299(7)	0.3115(8)	0.018(6)	0.028(6)	0.013(5)	0.000(5)	0.001(4)	0.004(4)
C(9*)	4*e*	–0.524(2)	0.6754(6)	0.4049(7)	0.023(5)	0.034(6)	0.020(5)	0.004(5)	–0.006(4)	–0.001(5)
C(3*)	4*e*	–0.313(2)	0.3847(8)	0.2220(8)	0.029(6)	0.051(7)	0.011(5)	0.002(6)	–0.013(4)	–0.001(5)
C(2*)	4*e*	–0.462(2)	0.4630(7)	0.2201(8)	0.020(5)	0.022(5)	0.016(5)	0.000(5)	–0.003(4)	0.000(4)
C(10*)	4*e*	–0.574(2)	0.6101(6)	0.3151(7)	0.020(5)	0.028(6)	0.007(4)	–0.006(5)	–0.002(4)	–0.005(4)
C(1*)	4*e*	–0.685(2)	0.4781(7)	0.1274(9)	0.022(6)	0.036(6)	0.018(5)	–0.001(5)	–0.010(4)	0.005(5)
C(11*)	4*e*	–0.797(2)	0.6256(6)	0.2209(8)	0.029(6)	0.005(5)	0.021(5)	–0.002(5)	–0.006(5)	0.006(4)
O(1*)	4*e*	–0.732(1)	0.4207(5)	0.0452(6)	0.030(4)	0.042(4)	0.020(4)	0.001(4)	–0.013(3)	–0.005(3)
N(1*)	4*e*	–0.822(2)	0.5569(6)	0.1349(7)	0.017(5)	0.035(6)	0.017(4)	–0.004(4)	–0.014(3)	0.010(4)
O(2*)	4*e*	–0.933(1)	0.6929(5)	0.2156(6)	0.042(5)	0.033(4)	0.030(4)	0.008(4)	–0.009(3)	0.001(3)

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