Crystal structure of *N,N'*-bis(2-phenylpropyl)perylene-3,4:9,10-bis(dicarboximide), $C_{42}H_{30}N_2O_4$

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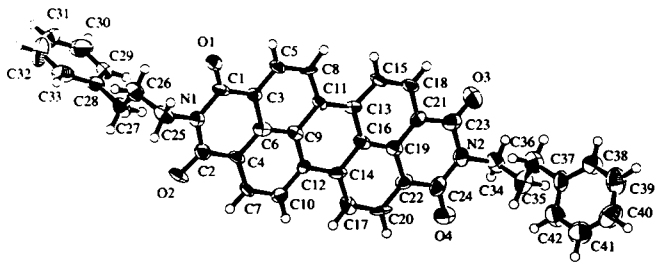

Abstract

$C_{42}H_{30}N_2O_4$, monoclinic, $P12_1/c1$ (No. 14), $a = 23.44(1)$ Å, $b = 16.751(5)$ Å, $c = 7.612(6)$ Å, $\beta = 97.92(8)°$, $V = 2959.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.061$, $wR_{obs}(F^2) = 0.284$, $T = 223$ K.

Source of material

The title compound was prepared by reaction of perylene-3,4:9,10-tetracarboxylic dianhydride with 3-phenylpropylamine at 403 K in water for 5 h. The single crystals were grown from the vapor phase at about 740 K using a two-zone furnace [1]. After 60 h of vapor growth, a number of red platelet crystals were obtained.

Discussion

Perylene pigments are widely known to exhibit a variety of colors in the solid state depending on the substituents, although there is no significant difference in their molecular spectra in solution [2]. This evidently indicates that the difference in shade is attributed 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 of intermolecular interactions [3,4]. Our results concluded that the exciton coupling (that greatly depends on the molecular arrangement) plays the decisive role in the determination of colors in the solid state and that the color changes from red to black as the exciton coupling is increased.

The title compound is based on the perylene-dicarboximide skeleton, to which the propylphenyl groups are attached at the imide nitrogen atom. This compound exbits a red color while the similar derivative with 2-phenylethyl groups is black [3,5,6] and the one with 2-(4-pyridyl)ethyl groups is again red [7]. The present structure analysis has been carried out as a part of the above investigation. The molecule is heavily deformed as characterized by C_1 symmetry. The perylene-dicarboximide skeleton is not entirely planar. The dihedral angles between the following six-membered rings are in the range between 176.7° and 177.3°: {N1C1C3C6C4C2}, {C3C5C8C11C9C6} and {C4C6C9C12C10C7}. On the other hand, the plane composed of the following six-membered rings is nearly planar within a deviation angle of about 0.5°: {N2C24C22C19C21C23}, {C13C15C18C21C19C16} and {C14C16C19C22C20C17}. The molecules are stacked along the *c*-axis with significant overlap of the perylene-dicarboximide skeleton.

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Table 1. Data collection and handling.

Crystal:	red platelet, size 0.02 × 0.08 × 0.47 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	0.90 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7R, $\omega/2\theta$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7549, 5204
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 0\ \sigma(I_{obs})$, 5187
$N(param)_{refined}$:	433
Programs:	SHELXS-97 [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*	0.4778	–0.8728	0.7841	0.044
H(2)	4*e*	0.4063	–0.5057	0.6185	0.042
H(3)	4*e*	0.3956	–0.9149	0.6094	0.040
H(4)	4*e*	0.3175	–0.5448	0.4775	0.049
H(5)	4*e*	0.3162	–0.9535	0.4615	0.053
H(6)	4*e*	0.2421	–0.5801	0.3433	0.048
H(7)	4*e*	0.2305	–0.9891	0.2896	0.051
H(8)	4*e*	0.1560	–0.6203	0.1712	0.053
H(9)	4*e*	0.5783	–0.5683	1.0156	0.053
H(10)	4*e*	0.5845	–0.6538	1.0941	0.053
H(11)	4*e*	0.6381	–0.6922	0.8689	0.067
H(12)	4*e*	0.6686	–0.6218	0.9758	0.067
H(13)	4*e*	0.6031	–0.6043	0.6501	0.062
H(14)	4*e*	0.6377	–0.5366	0.7554	0.062
H(15)	4*e*	0.6430	–0.6558	0.4120	0.056
H(16)	4*e*	0.7220	–0.6904	0.2734	0.084
H(17)	4*e*	0.8146	–0.6586	0.4049	0.098
H(18)	4*e*	0.8294	–0.6022	0.6857	0.093
H(19)	4*e*	0.7511	–0.5727	0.8267	0.069
H(20)	4*e*	0.0537	–0.9256	–0.0743	0.058
H(21)	4*e*	0.0435	–0.8386	–0.1412	0.058
H(22)	4*e*	–0.0010	–0.8090	0.1038	0.065
H(23)	4*e*	–0.0331	–0.8783	–0.0027	0.065
H(24)	4*e*	0.0096	–0.9674	0.1987	0.069
H(25)	4*e*	0.0422	–0.8984	0.3048	0.069
H(26)	4*e*	–0.0611	–1.0211	0.3597	0.062
H(27)	4*e*	–0.1281	–1.0094	0.5493	0.091
H(28)	4*e*	–0.1590	–0.8831	0.6305	0.092
H(29)	4*e*	–0.1106	–0.7714	0.5442	0.098
H(30)	4*e*	–0.0388	–0.7842	0.3586	0.090

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*	0.5492(3)	–0.7765(4)	0.9491(8)	0.041(4)	0.031(4)	0.058(5)	–0.002(3)	0.003(3)	0.013(4)
O(2)	4*e*	0.5084(3)	–0.5187(4)	0.7965(9)	0.064(5)	0.016(4)	0.076(5)	–0.001(3)	0.006(4)	0.009(4)
O(3)	4*e*	0.1365(3)	–0.9749(4)	0.102(1)	0.067(5)	0.053(5)	0.070(5)	–0.014(4)	0.004(4)	–0.004(5)
O(4)	4*e*	0.0838(3)	–0.7150(4)	0.018(1)	0.059(5)	0.052(5)	0.073(6)	0.011(4)	0.003(4)	0.004(4)
N(1)	4*e*	0.5283(3)	–0.6480(5)	0.872(1)	0.036(5)	0.033(5)	0.041(5)	0.001(4)	0.003(4)	0.001(4)
N(2)	4*e*	0.1067(3)	–0.8467(5)	0.067(1)	0.040(6)	0.048(6)	0.044(5)	–0.007(5)	0.014(4)	0.003(5)
C(1)	4*e*	0.5162(4)	–0.7306(6)	0.863(1)	0.053(7)	0.019(6)	0.057(7)	0.007(5)	0.036(5)	0.006(5)
C(2)	4*e*	0.4928(4)	–0.5898(6)	0.789(1)	0.045(7)	0.033(6)	0.058(7)	–0.004(5)	0.024(5)	0.001(6)
C(3)	4*e*	0.4636(4)	–0.7554(5)	0.754(1)	0.036(6)	0.024(6)	0.028(5)	0.003(5)	0.009(4)	0.008(4)
C(4)	4*e*	0.4383(4)	–0.6145(5)	0.692(1)	0.041(6)	0.016(5)	0.037(6)	0.001(5)	0.015(5)	0.008(4)
C(5)	4*e*	0.4514(4)	–0.8341(5)	0.729(1)	0.044(6)	0.019(6)	0.052(7)	–0.001(5)	0.022(5)	0.008(5)
C(6)	4*e*	0.4238(4)	–0.6963(6)	0.671(1)	0.049(7)	0.033(6)	0.008(5)	0.007(5)	0.013(4)	0.005(4)
C(7)	4*e*	0.3975(4)	–0.5611(5)	0.612(1)	0.041(6)	0.017(5)	0.053(6)	–0.007(5)	0.023(5)	–0.002(5)
C(8)	4*e*	0.4016(4)	–0.8592(5)	0.627(1)	0.033(6)	0.020(6)	0.048(6)	0.018(5)	0.006(5)	0.005(5)
C(9)	4*e*	0.3718(4)	–0.7228(6)	0.574(1)	0.044(6)	0.025(6)	0.019(5)	–0.001(5)	0.014(4)	0.002(5)
C(10)	4*e*	0.3449(4)	–0.5841(6)	0.523(1)	0.036(6)	0.037(7)	0.052(7)	0.006(5)	0.012(5)	0.006(6)
C(11)	4*e*	0.3593(4)	–0.8066(5)	0.547(1)	0.042(6)	0.019(5)	0.029(5)	–0.005(5)	0.020(4)	–0.008(4)
C(12)	4*e*	0.3317(4)	–0.6650(6)	0.499(1)	0.027(6)	0.028(6)	0.051(6)	0.002(5)	0.026(5)	0.004(5)
C(13)	4*e*	0.3070(4)	–0.8323(6)	0.449(1)	0.038(6)	0.029(6)	0.030(5)	0.012(5)	0.004(5)	–0.001(5)
C(14)	4*e*	0.2764(4)	–0.6884(6)	0.396(1)	0.042(6)	0.029(6)	0.048(7)	0.014(5)	0.023(5)	0.015(5)
C(15)	4*e*	0.2907(4)	–0.9125(6)	0.413(1)	0.052(7)	0.014(5)	0.071(8)	–0.001(5)	0.025(6)	–0.001(5)
C(16)	4*e*	0.2653(4)	–0.7737(6)	0.374(1)	0.048(7)	0.024(6)	0.032(6)	0.000(5)	0.019(5)	0.002(5)
C(17)	4*e*	0.2352(4)	–0.6355(6)	0.324(1)	0.054(7)	0.039(6)	0.031(5)	–0.010(5)	0.025(5)	0.015(5)
C(18)	4*e*	0.2392(4)	–0.9343(5)	0.311(1)	0.049(7)	0.021(6)	0.063(7)	0.003(5)	0.028(5)	–0.009(5)
C(19)	4*e*	0.2129(4)	–0.7951(6)	0.271(1)	0.043(7)	0.032(6)	0.035(6)	0.002(5)	0.017(5)	0.000(5)
C(20)	4*e*	0.1830(4)	–0.6591(6)	0.222(1)	0.052(7)	0.032(6)	0.049(7)	0.031(6)	0.011(6)	0.011(5)
C(21)	4*e*	0.2008(4)	–0.8766(6)	0.241(1)	0.031(6)	0.043(7)	0.047(7)	0.004(5)	0.018(5)	–0.006(5)
C(22)	4*e*	0.1717(4)	–0.7398(6)	0.198(1)	0.036(7)	0.040(7)	0.042(6)	0.009(5)	0.005(5)	0.011(5)
C(23)	4*e*	0.1480(4)	–0.9056(7)	0.136(1)	0.049(7)	0.046(7)	0.046(7)	0.010(6)	0.024(5)	0.008(6)
C(24)	4*e*	0.1175(4)	–0.7652(7)	0.089(1)	0.036(7)	0.064(9)	0.048(7)	0.001(6)	0.018(5)	0.012(7)
C(25)	4*e*	0.5810(4)	–0.6234(6)	0.988(1)	0.069(8)	0.031(6)	0.030(6)	–0.005(6)	0.000(6)	0.002(5)
C(26)	4*e*	0.6358(5)	–0.6370(6)	0.895(1)	0.064(8)	0.042(7)	0.063(8)	–0.005(6)	0.015(6)	0.017(6)
C(27)	4*e*	0.6371(4)	–0.5920(6)	0.729(1)	0.066(7)	0.042(6)	0.051(7)	–0.014(6)	0.021(6)	–0.011(6)
C(28)	4*e*	0.6887(4)	–0.6107(6)	0.635(1)	0.048(7)	0.030(6)	0.049(7)	0.005(5)	–0.002(5)	–0.005(5)
C(29)	4*e*	0.6808(4)	–0.6453(5)	0.469(1)	0.047(7)	0.028(6)	0.063(7)	–0.008(5)	0.006(5)	–0.007(5)
C(30)	4*e*	0.7277(5)	–0.6648(7)	0.386(2)	0.075(9)	0.051(8)	0.086(9)	0.014(7)	0.018(7)	0.002(7)
C(31)	4*e*	0.7827(5)	–0.6472(8)	0.465(2)	0.054(8)	0.11(1)	0.09(1)	0.028(8)	0.037(7)	0.032(9)
C(32)	4*e*	0.7915(5)	–0.6134(8)	0.630(2)	0.050(8)	0.12(1)	0.065(8)	–0.024(8)	0.015(6)	0.005(8)
C(33)	4*e*	0.7449(5)	–0.5959(6)	0.712(1)	0.076(8)	0.046(7)	0.049(7)	0.014(7)	0.005(6)	0.003(6)
C(34)	4*e*	0.0509(5)	–0.8715(6)	–0.039(1)	0.063(8)	0.045(7)	0.039(6)	–0.013(6)	0.018(5)	–0.008(5)
C(35)	4*e*	0.0015(4)	–0.8633(7)	0.070(1)	0.046(7)	0.079(9)	0.038(6)	–0.007(6)	0.006(5)	0.003(6)
C(36)	4*e*	0.0075(4)	–0.9130(7)	0.233(1)	0.064(8)	0.058(7)	0.049(7)	–0.007(6)	0.004(6)	0.009(6)
C(37)	4*e*	–0.0409(4)	–0.9043(7)	0.340(1)	0.038(6)	0.058(7)	0.065(8)	–0.012(6)	0.014(6)	0.007(7)
C(38)	4*e*	–0.0702(4)	–0.9692(6)	0.398(1)	0.065(7)	0.050(7)	0.045(6)	0.003(6)	0.025(5)	0.001(6)
C(39)	4*e*	–0.1113(5)	–0.9625(8)	0.508(2)	0.073(8)	0.09(1)	0.068(8)	–0.024(8)	0.027(7)	–0.012(8)
C(40)	4*e*	–0.1287(5)	–0.8884(9)	0.560(2)	0.063(8)	0.10(1)	0.070(9)	0.011(8)	0.026(7)	–0.012(8)
C(41)	4*e*	–0.1006(5)	–0.8230(8)	0.506(2)	0.079(9)	0.07(1)	0.10(1)	–0.003(7)	0.030(8)	–0.029(8)
C(42)	4*e*	–0.0571(5)	–0.8308(7)	0.395(2)	0.076(9)	0.059(8)	0.10(1)	–0.017(7)	0.046(7)	–0.034(7)

References

1. Mizuguchi, J.: An improved method for purification of β-copper-phthalocyanine. Cryst. Res. Tech. **16** (1981) 695-700.
2. Herbst, M.; Hunger, K.: Industrial Organic Pigments. VCH (1993) 467-475.
3. Mizuguchi, J.: Electronic characterization of *N,N'*-bis(2-phenylethyl)-perylene-3,4:9,10-bis(dicarboximide) and its application to optical disks. J. Appl. Phys. **84** (1998) 4479-4486.
4. Mizuguchi, J.; Tojo, K.: Electronic structure of perylene pigments as viewed from the crystal structure and excitonic interactions. J. Phys. Chem. **106** (2002) 767-772.
5. Hädicke, E.; Graser, F.: Structures of eleven perylene-3,4:9,10-bis(dicarboximide) pigments. Acta Crystallogr. C**42** (1986) 189-195.
6. Mizuguchi, J.: Structure of *N,N'*-bis(2-phenylethyl)perylene-3,4:9,10-bis(dicarboximide). Acta Crystallogr. C**54** (1998) 1479-1481.
7. Mizuguchi, J.; Tojo, K.: Crystal structure of *N,N'*-bis(2-(4-pyridyl)ethyl)-perylene-3,4:9,10-bis(dicarboximide), $C_{38}H_{24}N_4O_4$. Z. Kristallogr. NCS **217** (2002) 247-248.
8. Sheldrick, G. M.: SHELXS-97. Program for the solution of crystal structures. University of Göttingen, Germany 1997.
9. teXsan; Single Crystal Structure Analysis Software. Version 1.7; Molecular Structure Corporation; 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1995.
10. Johnson, C. K.: ORTEPII, Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA 1976.