Crystal structure of a second modification of *N*,*N*′-di-*n*-butylperylene-3,4:9,10-bis(dicarboximide), $C_{32}H_{26}N_2O_4$

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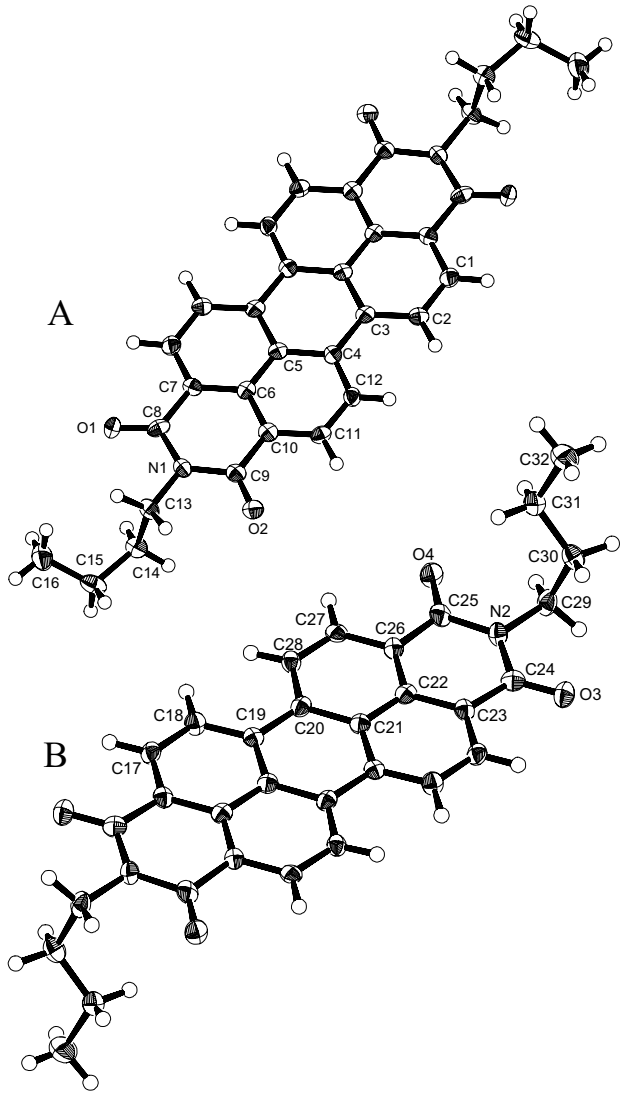

Abstract

$C_{32}H_{26}N_2O_4$, monoclinic, $P12_1/n1$ (No. 14), a = 18.41(1) Å, b = 4.630(3) Å, c = 27.61(2) Å, β = 105.74(5)°, V = 2265.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.046, T = 93 K.

Source of material

The title compound was synthesized by reaction of perylene tetracarboxylic dianhydride with *n*-butylamine in imidazol at 433 K for one hour in an autoclave. The product was purified by sublimation under argon at about 673 K, using a two-zone furnace [1]. The single crystals were then grown from the vapor phase in a closed system at about 680 K. After 48 hours, several black needle crystals were obtained.

Discussion

Hädicke and Graser reported previously the crystal structure of the title compound (phase I: $P2_1/c$, a = 4.734 Å, b = 28.233 Å, c = 9.396 Å, β = 110.86°) based on single crystals recrystallized from nitrobezene and the color was red-maroon [2]. On the other hand, we have found a new modification (phase II) when the single crystals were grown from the vapor phase, and the color was, however, black. Perylene compounds are industrially important organic pigments which exhibit a variety of shades in the range from red, via bordeaux to black [3]. It is of interest to note that that the molecular spectra in solution of all perylene pigments are nearly the same, quite irrespective of the substituents at the imide site. It follows that the color in the solid state can mostly be determined by intermolecular interactions based on the geometrical arrangement of the molecules with various substituents. Actually, the title compound gives two different colors (red-maroon and black), depending on the molecular conformation and arrangement. The present paper reports on the crystal structure of phase II. The title compound crystallizes with two molecules in the asymmetric unit. Both molecules lie on different centro-symmetric sites. Each conformation is, however, slightly different in the alkyl chains at the corner. In molecule A, the butyl chains extend in a zigzag fashion from the imide site along the long molecular axis, but the methyl group at the end is horizontally bent. On the other hand, the butyl chains stand, in a zigzag fashion, almost in perpendicular to the molecular plane. The latter conformation is quite similar to the one in phase I [2]. The molecules A and B are independently stacked with two different columns along the *b* axis. The molecules A form one column while the molecules B are stacked in the neighboring column.

Table 1. Data collection and handling.

Crystal:	black needle, size 0.04 × 0.05 × 0.70 mm
Wavelength:	Cu K_α radiation (1.5419 Å)
μ:	7.88 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, 72 frames, $\Delta\omega$ = 10°
$2\theta_{max}$:	135.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19567, 3797
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1246
$N(param)_{refined}$:	343
Programs:	SHELXS-86 [4], teXsan [5], ORTEP-III [6], ABSCOR [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.7261	–0.1160	0.3596	0.037
H(2)	4*e*	1.2429	1.3512	0.5162	0.033
H(3)	4*e*	1.1654	1.0061	0.4650	0.027
H(4)	4*e*	1.0977	0.7142	0.4228	0.033
H(5)	4*e*	1.0181	0.3844	0.3712	0.029
H(6)	4*e*	0.7840	–0.1576	0.3286	0.037
H(7)	4*e*	0.7337	0.2267	0.2766	0.042
H(8)	4*e*	0.6835	0.3150	0.3111	0.042
H(9)	4*e*	0.6619	–0.2094	0.2567	0.048
H(10)	4*e*	0.6121	0.0601	0.2382	0.048
H(11)	4*e*	0.6152	–0.2338	0.3304	0.068
H(12)	4*e*	0.5653	0.0356	0.3119	0.068
H(13)	4*e*	0.5473	–0.2538	0.2828	0.068
H(14)	4*e*	–0.0350	1.3121	–0.1656	0.034
H(15)	4*e*	0.0444	0.9530	–0.1129	0.034
H(16)	4*e*	0.1074	0.6789	–0.0671	0.033
H(17)	4*e*	0.1900	0.3573	–0.0112	0.036
H(18)	4*e*	0.2614	–0.1344	0.1494	0.046
H(19)	4*e*	0.2134	–0.0899	0.1872	0.046
H(20)	4*e*	0.3316	0.0420	0.2295	0.035
H(21)	4*e*	0.2876	0.3298	0.2162	0.035
H(22)	4*e*	0.3798	0.1061	0.1585	0.036
H(23)	4*e*	0.3396	0.4032	0.1488	0.036
H(24)	4*e*	0.4162	0.5745	0.2266	0.059
H(25)	4*e*	0.4564	0.2771	0.2365	0.059
H(26)	4*e*	0.4675	0.4736	0.1935	0.059

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*	0.7151(1)	0.3041(4)	0.41176(7)	0.025(1)	0.036(2)	0.031(1)	–0.003(1)	0.012(1)	0.001(1)
O(2)	4*e*	0.9005(1)	0.0793(4)	0.33771(7)	0.033(1)	0.030(2)	0.025(1)	0.001(1)	0.008(1)	–0.001(1)
O(3)	4*e*	0.1317(1)	0.3104(5)	0.19123(7)	0.038(1)	0.033(2)	0.023(1)	–0.003(1)	0.010(1)	0.000(1)
O(4)	4*e*	0.2458(1)	0.0954(4)	0.06868(7)	0.036(2)	0.031(2)	0.027(1)	0.009(1)	0.010(1)	–0.002(1)
N(1)	4*e*	0.8081(1)	0.1904(6)	0.37531(9)	0.024(2)	0.024(2)	0.024(2)	–0.002(2)	0.004(1)	–0.001(1)
N(2)	4*e*	0.1894(1)	0.2082(6)	0.13044(9)	0.032(2)	0.027(2)	0.018(1)	0.001(2)	0.005(1)	0.000(1)
C(1)	4*e*	1.1925(2)	1.3106(7)	0.5212(1)	0.027(2)	0.032(3)	0.023(2)	0.000(2)	0.006(2)	0.008(2)
C(2)	4*e*	1.1463(2)	1.1074(7)	0.4903(1)	0.028(2)	0.022(2)	0.020(2)	0.004(2)	0.003(2)	0.001(2)
C(3)	4*e*	1.0747(2)	1.0486(7)	0.4949(1)	0.027(2)	0.022(2)	0.018(2)	0.001(2)	0.005(2)	0.011(2)
C(4)	4*e*	1.0252(2)	0.8415(7)	0.4627(1)	0.025(2)	0.021(2)	0.022(2)	–0.002(2)	0.004(2)	0.005(2)
C(5)	4*e*	0.9515(2)	0.7960(7)	0.4685(1)	0.025(2)	0.020(2)	0.016(2)	0.004(2)	0.002(2)	0.009(2)
C(6)	4*e*	0.9042(2)	0.5938(7)	0.4374(1)	0.021(2)	0.018(2)	0.020(2)	0.006(2)	0.005(2)	0.011(2)
C(7)	4*e*	0.8313(2)	0.5448(7)	0.4428(1)	0.028(2)	0.018(2)	0.020(2)	–0.002(2)	0.002(2)	0.000(2)
C(8)	4*e*	0.7796(2)	0.3400(7)	0.4096(1)	0.032(2)	0.025(2)	0.021(2)	0.008(2)	0.008(2)	0.006(2)
C(9)	4*e*	0.8806(2)	0.2240(7)	0.3685(1)	0.027(2)	0.026(3)	0.021(2)	–0.001(2)	0.004(2)	0.006(2)
C(10)	4*e*	0.9286(2)	0.4383(7)	0.4010(1)	0.025(2)	0.019(2)	0.023(2)	0.002(2)	0.006(2)	0.007(2)
C(11)	4*e*	1.0000(2)	0.4875(6)	0.3963(1)	0.029(2)	0.025(2)	0.020(2)	0.007(2)	0.009(2)	0.003(2)
C(12)	4*e*	1.0472(2)	0.6841(7)	0.4265(1)	0.018(2)	0.029(2)	0.025(2)	0.000(2)	0.005(2)	0.004(2)
C(13)	4*e*	0.7562(2)	–0.0066(6)	0.3418(1)	0.030(2)	0.016(2)	0.032(2)	–0.006(2)	0.005(2)	–0.002(2)
C(14)	4*e*	0.7041(2)	0.1501(6)	0.2978(1)	0.033(2)	0.024(2)	0.031(2)	–0.001(2)	0.004(2)	0.001(2)
C(15)	4*e*	0.6395(2)	–0.0391(7)	0.2681(1)	0.035(2)	0.043(3)	0.029(2)	0.004(2)	–0.002(2)	–0.004(2)
C(16)	4*e*	0.5863(2)	–0.1294(7)	0.2992(1)	0.033(2)	0.063(3)	0.058(3)	–0.006(2)	0.012(2)	–0.013(2)
C(17)	4*e*	–0.0386(2)	1.2737(7)	–0.1313(1)	0.027(2)	0.027(2)	0.023(2)	–0.007(2)	0.006(2)	0.004(2)
C(18)	4*e*	0.0079(2)	1.0777(7)	–0.1002(1)	0.030(2)	0.026(2)	0.025(2)	0.003(2)	0.009(2)	0.000(2)
C(19)	4*e*	0.0048(2)	1.0399(7)	–0.0511(1)	0.022(2)	0.017(2)	0.022(2)	–0.006(2)	0.003(2)	–0.002(2)
C(20)	4*e*	0.0539(2)	0.8318(7)	–0.0175(1)	0.022(2)	0.025(2)	0.023(2)	–0.007(2)	0.009(2)	–0.005(2)
C(21)	4*e*	0.0472(2)	0.8027(7)	0.0328(1)	0.022(2)	0.023(2)	0.022(2)	–0.004(2)	0.006(2)	0.000(2)
C(22)	4*e*	0.0945(2)	0.6009(7)	0.0650(1)	0.021(2)	0.024(2)	0.024(2)	–0.007(2)	0.009(2)	–0.005(2)
C(23)	4*e*	0.0896(2)	0.5680(7)	0.1148(1)	0.023(2)	0.024(2)	0.021(2)	–0.004(2)	0.003(2)	–0.001(2)
C(24)	4*e*	0.1365(2)	0.3557(7)	0.1489(1)	0.024(2)	0.022(3)	0.030(2)	–0.004(2)	0.008(2)	–0.002(2)
C(25)	4*e*	0.1986(2)	0.2353(7)	0.0816(1)	0.027(2)	0.025(3)	0.024(2)	–0.007(2)	0.000(2)	–0.008(2)
C(26)	4*e*	0.1467(2)	0.4387(7)	0.0482(1)	0.026(2)	0.016(2)	0.019(2)	–0.006(2)	0.002(2)	0.000(2)
C(27)	4*e*	0.1521(2)	0.4677(7)	–0.0004(1)	0.019(2)	0.027(2)	0.026(2)	–0.006(2)	0.003(2)	–0.004(2)
C(28)	4*e*	0.1060(2)	0.6641(7)	–0.0323(1)	0.026(2)	0.022(2)	0.019(2)	–0.004(2)	0.003(2)	–0.001(2)
C(29)	4*e*	0.2396(2)	0.0090(6)	0.1657(1)	0.041(2)	0.027(2)	0.029(2)	0.006(2)	0.010(2)	0.010(2)
C(30)	4*e*	0.3054(2)	0.1661(6)	0.2009(1)	0.033(2)	0.030(2)	0.027(2)	0.001(2)	0.004(2)	0.000(2)
C(31)	4*e*	0.3641(2)	0.2733(7)	0.1752(1)	0.032(2)	0.033(3)	0.029(2)	0.001(2)	0.006(2)	0.005(2)
C(32)	4*e*	0.4320(2)	0.4085(7)	0.2125(1)	0.036(2)	0.061(3)	0.039(2)	–0.005(2)	0.002(2)	–0.006(2)

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References

1. Mizuguchi, J.: An improved method for purification of β-copperphthalocyanine. Cryst. Res. Technol. **16** (1981) 695-700.
2. Hädicke, E.; Graser, F.: Structures of eleven perylene-3,4:9,10-bis(dicarboximide) pigments. Acta Crystallogr. C**42** (1986) 189-195.
3. Herbst, W.; Hunger, K.: Industrial Organic Pigments, 2nd Ed. VCH, Weinheim 1997.
4. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct methods for Larger Structure. Acta Crystallogr. A**46** (1990) 467-473.
5. teXsan. Single Crystal Structure Analysis Software. Version 1.11, Rev. 1. Molecular Structure Corporation, The Woodlands, TX , USA, and Rigaku Corporation, Tokyo, Japan 2001.
6. Burnett, M. N.; Johnson, C. K.: ORTEP-III. Oak ridge thermal ellipsoid plot program for crystal structure illustrations. Oak Ridge National Laboratory Report ORNL-6895, USA 1996.
7. Higashi, T.: ABSCOR. Program for absorption correction. Rigaku Corporation, Tokyo, Japan 1995.