Crystal structure of (2,5-dihydro-2,5-dimethyl-3,6-diphenylpyrrolo[3,4-*c*]-pyrrole-1,4-diylidene)biscyanamide, $C_{22}H_{16}N_6$

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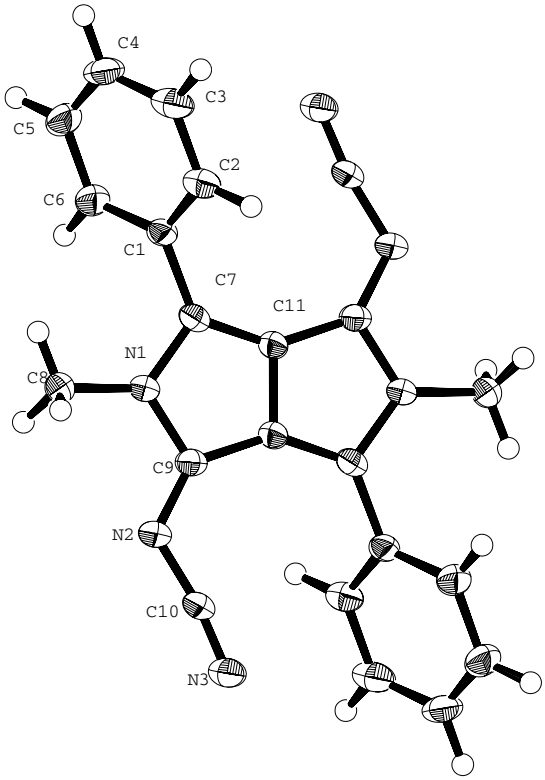
Received January 7, 2003, accepted and available on-line January 16, 2003; CCDC-No. 1267/1005



Abstract

$C_{22}H_{16}N_6$, monoclinic, $P12_1/c1$ (No. 14), a = 6.4349(8) Å, b = 6.4587(7) Å, c = 21.613(2) Å, β = 92.79(1)°, V = 897.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.054, $wR_{ref}(F^2)$ = 0.139, T = 93 K.

Source of material

The title compound was prepared by reacting 1,4-diketo-3,6-diphenylpyrrolo-[3,4-*c*]-pyrrole with bis(trimethylsilyl)carbodiimide in the presence of $TiCl_4$ [1]. The product was purified by sublimation under argon at about 575 K, using a two-zone furnace [2]. The single crystals were then grown from the vapor phase in the same sublimation tube at about 550 K. After 24 hours, several prismatic crystals were obtained.

Discussion

The title compound is an analogue of 3,6-diphenylpyrrolo-[3,4-c]pyrrole-1,4-dione (DPP [3]) known as a red pigment on the market. The present compound exhibits brilliant orange luminescence when recrystallized from methylene chloride. However, little luminescence is observed in crystals grown from the vapor phase. In order to clarify the luminescence mechanism, we have grown the single crystals not only from solution (platelet form) but also from the vapor phase (prismatic shape) and analyzed their structures. It turned out, however, that the both single crystals showed exactly the same structure. The present paper reports on the crystal structure based on the single crystals grown from the vapor phase.

The molecule possesses C_i symmetry as shown in the ORTEP plot. The phenyl rings are deviated, in the same direction, from the heterocyclic ring system by 50°. The angle ∠N2–C10–N3 is not exactly 180° because of the repulsion between N3 and C3 atoms. It is also of interest to note that in the present crystal structure the cyano group faces the phenyl ring (form I); whereas the structure with the outward cyano group (rotation around the C9–N2 bond by 180°, form II) can also exist and be more stable in the free space as revealed from the geometry optimization by MOPAC93 using the AM1 Hamiltonian (heat of formation 261.0 kcal/mole for form I and 251.3 kcal/mole for form II). All other bond parameters of the title compound agree well with those of DPP [3]. The molecules are arranged in a zigzag fashion along the *c*-axis with a tilt angle of about 60°. The overlap occurrs only at the cyano group. The mechanism that might explain the different luminescent properties of the two kinds of single crystals is under investigation.

Table 1. Data collection and handling.

Crystal:	red prism, size 0.10 × 0.20 × 0.20 mm
Wavelength:	Cu K_α radiation (1.5419 Å)
μ:	6.75 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, 48 frames, $\Delta\omega$ = 15°
$2\theta_{max}$:	136.32°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7950, 1614
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1207
$N(param)_{refined}$:	127
Programs:	SHELXS-86 [4], teXsan [5], ORTEP-III [6], ABSCOR [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	1.0675	0.5883	0.3377	0.038
H(2)	4*e*	1.2068	0.5142	0.2408	0.044
H(3)	4*e*	1.3435	0.1825	0.2223	0.047
H(4)	4*e*	1.3361	–0.0752	0.2987	0.047
H(5)	4*e*	1.1893	–0.0026	0.3943	0.038
H(6)	4*e*	0.6104	0.1370	0.4041	0.045
H(7)	4*e*	0.8178	0.0394	0.3848	0.045
H(8)	4*e*	0.7174	–0.0338	0.4449	0.045

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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}
N(1)	4*e*	0.8572(2)	0.2419(2)	0.45450(7)	0.0239(8)	0.0266(8)	0.0280(8)	–0.0038(6)	0.0086(7)	–0.0019(7)
N(2)	4*e*	0.6086(2)	0.2627(3)	0.52855(8)	0.0266(8)	0.0317(9)	0.0290(8)	–0.0046(7)	0.0103(7)	–0.0015(7)
N(3)	4*e*	0.4171(3)	0.4224(3)	0.61328(8)	0.0294(8)	0.040(1)	0.0292(8)	–0.0031(8)	0.0079(7)	0.0020(8)
C(1)	4*e*	1.1171(3)	0.2992(3)	0.37432(9)	0.0179(8)	0.030(1)	0.0273(9)	–0.0043(8)	0.0045(7)	–0.0039(8)
C(2)	4*e*	1.1219(3)	0.4509(3)	0.3288(1)	0.026(1)	0.039(1)	0.032(1)	–0.0027(9)	0.0071(8)	0.0025(9)
C(3)	4*e*	1.2045(3)	0.4075(4)	0.2723(1)	0.031(1)	0.055(1)	0.030(1)	–0.007(1)	0.0069(9)	0.004(1)
C(4)	4*e*	1.2848(3)	0.2131(4)	0.2613(1)	0.028(1)	0.060(1)	0.030(1)	–0.009(1)	0.0114(8)	–0.015(1)
C(5)	4*e*	1.2806(3)	0.0603(4)	0.3063(1)	0.030(1)	0.042(1)	0.046(1)	–0.001(1)	0.0122(9)	–0.015(1)
C(6)	4*e*	1.1958(3)	0.1032(3)	0.3627(1)	0.027(1)	0.034(1)	0.036(1)	0.0002(9)	0.0073(8)	–0.0046(9)
C(7)	4*e*	1.0267(3)	0.3497(3)	0.43403(9)	0.0211(9)	0.0242(9)	0.0272(9)	–0.0014(7)	0.0043(7)	0.0047(8)
C(8)	4*e*	0.7417(3)	0.0835(3)	0.4191(1)	0.030(1)	0.037(1)	0.042(1)	–0.0139(9)	0.0126(9)	–0.015(1)
C(9)	4*e*	0.7820(3)	0.3331(3)	0.50766(9)	0.0234(9)	0.027(1)	0.0240(9)	0.0000(8)	0.0056(7)	0.0012(8)
C(10)	4*e*	0.5184(3)	0.3571(3)	0.57513(9)	0.0238(9)	0.029(1)	0.029(1)	–0.0052(8)	0.0067(8)	0.0027(8)
C(11)	4*e*	1.0738(3)	0.5037(3)	0.47638(9)	0.0207(8)	0.0234(9)	0.0274(9)	–0.0013(7)	0.0050(7)	–0.0003(8)

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