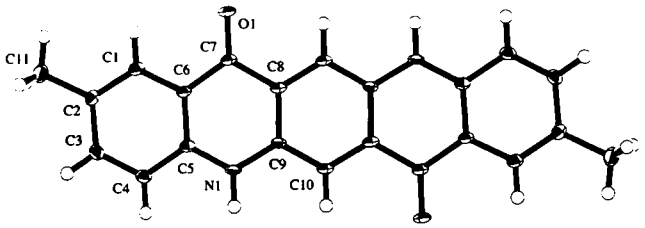
Crystal structure of 5,12-dihydro-2,9-dimethylquino[2,3-*b*]acridine-7,14-dione, $C_{22}H_{16}N_2O_2$, *at 123 K*

J. Mizuguchi*,[I], T. Senju[I] and M. Sakai[II]

[I] Yokohama National University, Graduate School of Engineering, Department of Applied Physics, 79-5 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan

[II] Yokohama National University, Faculty of Engineering, Department of Applied Physics, 79-5 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan

Received July 13, 2002, accepted and available on-line September 24, 2002; CCDC-No. 1267/904



Abstract

$C_{22}H_{16}N_2O_2$, triclinic, $P\bar{1}$ (No. 2), $a = 3.865(3)$ Å, $b = 6.372(3)$ Å, $c = 15.78(2)$ Å, $\alpha = 93.94(6)°$, $\beta = 91.51(8)°$, $\gamma = 100.00(6)°$, $V = 381.5$ Å^3, $Z = 1$, $R_{gt}(F) = 0.056$, $wR_{ref}(F^2) = 0.167$, $T = 123$ K.

Source of material

The title compound was obtained from CIBA Specialty Chemicals. The sample was purified by sublimation at about 703 K, using a two-zone furnace [1]. The single crystals were then grown from the vapor phase in a closed system for 17 h.

Discussion

The title compound is an industrially important bluish-red pigment on the market (Pigment Red 122) [2]. Although there are some X-ray powder diffraction studies on the present compound [3,4], no full structure analysis has been reported based on single crystals. Therefore, an attempt was made to grow the single crystals and analyze the structure in order to study the correlation between crystal and electronic structures.

The molecule is entirely planar and belongs to the point group of C_i. There are intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one, forming a two-dimensional hydrogen bond network as found in the β phase of unsubstituted quinacridone [5] and also in all pyrrolopyrrole pigments [6-15]. Each molecule is hydrogen-bonded to two molecules. However, the molecules are not entirely on the molecular plane, but there are steps (in other words, very flat stairs) of about 0.87 Å between hydrogen-bonded molecules which are arranged in parallel. The angle of the N–H···O and the distances between O···H, N–H and N···O are as follows: ∠N–H···O = 150.2°, d(O···H) = 1.988 Å, d(N—H) = 0.948 Å, d(N···O) = 2.850(3) Å. The present H-bond network is strikingly different from that of the γ phase of unsubstituted quinacridone [16,17], dithioquinacridone [18] and also indigos [19,20], in which one molecule is bonded to four different neighboring molecules as characterized by a three-dimensional H-bond network.

Table 1. Data collection and handling.

Crystal:	red platelet, size 0.07 × 0.12 × 0.23 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	0.96 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7R, $\omega/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1884, 1731
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 985
$N(param)_{refined}$:	118
Programs:	SHELXS-97 [21], teXsan [22], ORTEP-III [23]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.5144	0.8387	0.6416	0.018
H(2)	2*i*	0.2816	0.1111	0.7869	0.019
H(3)	2*i*	0.8764	0.6508	0.8963	0.021
H(4)	2*i*	0.7789	0.8345	0.7790	0.019
H(5)	2*i*	0.5994	0.3117	0.9797	0.026
H(6)	2*i*	0.9155	0.2395	0.9346	0.026
H(7)	2*i*	0.5453	0.0982	0.9235	0.026
H(8)	2*i*	0.2680	0.8614	0.5022	0.016

* Correspondence author (e-mail: mizu-j@ynu.ac.jp)

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)	2*i*	–0.0585(5)	0.0638(3)	0.6441(1)	0.022(1)	0.0087(7)	0.025(1)	–0.0027(6)	–0.0006(7)	0.0038(7)
N(1)	2*i*	0.4089(6)	0.6928(3)	0.6413(1)	0.016(1)	0.0071(8)	0.021(1)	–0.0021(7)	–0.0015(8)	0.0010(7)
C(1)	2*i*	0.3834(6)	0.2570(4)	0.7852(2)	0.014(1)	0.014(1)	0.021(1)	0.0001(8)	0.0015(9)	0.0046(9)
C(2)	2*i*	0.5917(7)	0.3576(4)	0.8531(2)	0.015(1)	0.017(1)	0.017(1)	0.0029(9)	0.0014(9)	0.005(1)
C(3)	2*i*	0.7355(7)	0.5773(4)	0.8494(2)	0.014(1)	0.018(1)	0.019(1)	–0.0009(9)	–0.002(1)	–0.000(1)
C(4)	2*i*	0.6770(7)	0.6879(4)	0.7800(2)	0.015(1)	0.014(1)	0.020(1)	–0.0015(8)	0.000(1)	0.0014(9)
C(5)	2*i*	0.4643(6)	0.5826(4)	0.7102(2)	0.011(1)	0.011(1)	0.018(1)	0.0007(8)	0.0022(9)	0.0017(9)
C(6)	2*i*	0.3141(6)	0.3653(4)	0.7132(2)	0.014(1)	0.010(1)	0.018(1)	–0.0006(8)	0.0011(9)	0.0032(9)
C(7)	2*i*	0.0875(6)	0.2543(4)	0.6428(2)	0.012(1)	0.009(1)	0.021(1)	0.0001(8)	0.0011(9)	0.0031(9)
C(8)	2*i*	0.0414(6)	0.3800(3)	0.5696(2)	0.012(1)	0.008(1)	0.019(1)	0.0001(8)	0.0026(9)	0.0025(9)
C(9)	2*i*	0.2055(6)	0.5981(3)	0.5713(2)	0.014(1)	0.0077(9)	0.017(1)	–0.0001(8)	–0.0001(9)	0.0003(8)
C(10)	2*i*	0.1586(6)	0.7152(3)	0.5016(2)	0.013(1)	0.0081(9)	0.020(1)	–0.0006(8)	0.0014(9)	0.0020(8)
C(11)	2*i*	0.6705(7)	0.2409(4)	0.9297(2)	0.022(1)	0.026(1)	0.019(1)	0.003(1)	–0.002(1)	0.007(1)

References

1. Mizuguchi, J.: An improved method for purification of β-copperphthalocyanine. Cryst. Res. Technol. **16** (1981) 695-700.
2. Herbst, W.; Hunger, K.: Industrial Organic Pigments, 2nd Ed. VCH, Weinheim 1997.
3. Lincke, G.: Studies of the crystal structure of 2,9-dimethylquinacridone. Chem. Ztg. **109** (1985) 89-96.
4. Lincke, G.; Moebes, J.: Quantative studies of the crystal structure of 2,9-dimethylquinacridone with an interpretation of the pigment finish process. Chem. Ztg. **111** (1987) 49-55.
5. Lincke, G.: On quinacridones and their supramolecular mesomerism within the crystal lattice. Dyes and Pigments **52** (2002) 169-181.
6. Mizuguchi, J.; Grubenmann, A.; Wooden, G.; Rihs, G.: Structure of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione and 2,5-dimethyl-3,6- diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione. Acta Crystallogr. **B48** (1992) 696-700.
7. Mizuguchi, J.; Grubenmann, A.; Rihs, G.: Structure of 3,6-bis(3-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione and 3,6-bis(4-chlorophenyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione. Acta Crystallogr. **B49** (1993) 1056-1060.
8. Mizuguchi, J.; Matsumoto, S.: Crystal structure of 3,6-bis(3-cyanophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione, $C_{20}H_{10}N_4O_2$. Z. Kristallogr. NCS **215** (2000) 195-196.
9. Mizuguchi, J.: 3,6-bis(4-*tert*-butylphenyl)-1,2,4,5-tetrahydropyrrolo-[3,4-*c*]pyrrlole-1,4-dione. Acta Crystallogr. **C54** (1998) 1482-1484.
10. Mizuguchi, J.; Miyazaki, T.: Crystal structure of 3,6-bis(4-biphenyl-yl)pyrrolo[3,4-*c*]pyrrole-1,4-dione, $C_{30}H_{20}N_2O_2$. Z. Kristallogr. NCS **217** (2002) 43-44.
11. Mizuguchi, J.: Structure of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1-on-4-thione. Z. Kristallogr. **214** (1999) 677-680.
12. Mizuguchi, J.; Rochat, A. C.; Rihs, G.: Structure of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dithione. Acta Crystallogr. **C46** (1990) 1899-1903.
13. Mizuguchi, J.; Arita, M.; Rihs, G.: A new crystal structure of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dithione. Acta Crystallogr. **C47** (1991) 1952-1956.
14. Mizuguchi, J.; Shikamori, H.: Crystal structure of 3-[4-(1,1-dimethylethyl)phenyl]-2,5-dihydro-6-phenylpyrrolo[3,4-c]pyrrole-1,4-dione, $C_{22}H_{20}N_2O_2$, *at 93K*. Z. Kristallogr. NCS **217** (2002) 515-516.
15. Mizuguchi, J.; Takahashi, H.; Yamakami, H.: Crystal structure of 3,6-bis(4'-pyridyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione, $C_{16}H_{10}N_4O_2$, *at 93 K*. Z. Kristallogr. NCS **217** (2002) 519-520.
16. Potts, G. D.; Jones, W.; Bullock, J. F.; Andrews, S. J.; Maginn, S. J.: The crystal structure of quinacridone: an archetypal pigment. J. Chem. Soc., Chem. Commun. (1994) 2565-2566.
17. Mizuguchi, J.; Sasaki, T.; Tojo, K.: Refinement of the crystal structure of 5,7,12,14-tetrahydro[2,3-*b*]quinolinoacridine (γ-form), $C_{20}H_{12}N_2O_2$, *at 223 K*. Z. Kristallogr. NCS **217** (2002) 247-248.
18. Mizuguchi, J.; Rihs, G.: Structure of 5,7,12,14-tetrahydroquinolino[2,3-*b*]-acridine-7,14-dithione. Acta Crystallogr. **C48** (1992) 1553-1555.
19. Süsse, P.; Manfred, S.; Vladimir, K.: Indigo: crystal structure refinement based on synchrotron data. Z. Kristallogr. **184** (1988) 269-273.
20 Süsse, P.; Wolf, A.: A new crystalline phase of indigo. Naturwissenschaften **67** (1980) 453.
21 Sheldrick, G. M.: SHELXS-97. A program for the solution of crystal structures. University of Göttingen, Germany 1997.
22 teXsan. Single crystal structure analysis software. Version 1.11, Rev. 1. Molecular Structure Corporation, The Woodlands, TX, USA, and Rigaku Corporation, Tokyo, Japan 2001.
23 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.