Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Diethyl 2,8-diamino-4,10-bis(3-nitrophenyl)naphtho[1,2-*b*;6,5-*b*′]dipyran-3,9-dicarboxylate dimethylformamide disolvate

Yu-Cheng Wang,* Xiang-Shan Wang, Zhao-Sen Zeng and Da-Qing Shi

Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, People's Republic of China

Correspondence e-mail:
xswang1974@yahoo.com

Received 26 May 2005
Accepted 31 May 2005
Online 10 June 2005

The title compound, $C_{34}H_{28}N_4O_{10}\cdot 2C_3H_7NO$, was synthesized by the reaction of ethyl 2-cyano-3-(3-nitrophenyl)-1-acrylate and 1,5-naphthalenediol in the presence of KF–Al_2O_3 in refluxing ethanol. The structure is centrosymmetric and the fused pyran ring adopts a boat conformation.

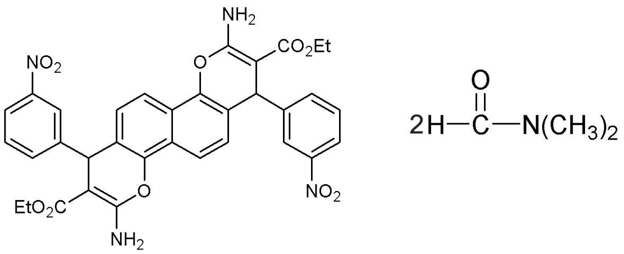
Key indicators

Single-crystal X-ray study
T = 289 K
Mean σ(C–C) = 0.004 Å
R factor = 0.071
wR factor = 0.242
Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

2-Aminochromenes are an important class of compounds found as the main components of many naturally occurring products employed as cosmetics and pigments and utilized as potential biodegradable agrochemicals (Morinaka & Takahashi, 1977; Witte *et al.*, 1986; Hafez *et al.*, 1987). The utility of fluoride salts as potential bases in a variety of synthetic reactions has been recognized in recent years. In particular, potassium fluoride coated with alumina (KF–alumina) has been a versatile base developed by Ando *et al.* (1982) for alkylation. Over the years, this reagent has found application in a large number of organic reactions (Clark, 1980). This background prompted us to synthesize compounds catalyzed by this solid-supported reagent. Here, we report the X-ray crystal structure analysis of the title compound, (I).



(I)

The structure of (I) is centrosymmetric. Each pyran ring is slightly distorted and adopts a boat conformation (Fig. 1). Atoms C3 and O1 deviate from the basal plane defined by atoms C1/C2/C4/C5 by 0.191 (2) Å and 0.084 (2) Å, respectively. A similar distortion was observed in methyl 2-amino-4-(4-methylphenyl)-5-oxo-5,6-dihydro-4*H*-pyrano[3,2-*c*]quinoline-3-carboxylate dimethylformamide solvate (Wang *et al.*, 2004) and 9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3,7-trimethyl-1,2,3,4-hexahydro-7*H*-xanthene (Li *et al.*, 2004). The basal plane of the pyran ring is nearly perpendicular to the C12–C17 benzene ring, forming a dihedral angle of 88.3 (2)°, and nearly parallel to the naphthalene ring system, forming a dihedral angle of 4.1 (2)°.

An intramolecular N1—H1*A*···O3 hydrogen bond (Table 2) is formed between the amino and carbonyl groups (Fig. 2).

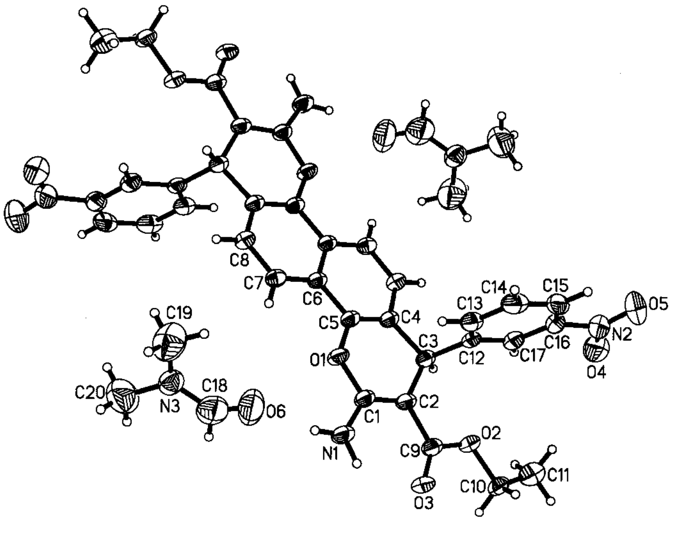


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry operator ($-x$, $1 - y$, $1 - z$).

The amino group also forms an N1—H1*B*···O6 hydrogen bond with the solvent dimethylformamide solvent molecule.

Experimental

Compound (I) was prepared by the reaction of ethyl 2-cyano-3-(3-nitrophenyl)-1-acrylate (0.98 g, 4 mmol) and 1,5-naphthalenediol (0.32 g, 2 mmol) in the presence of KF–Al_2O_3 (0.25 g) in EtOH (15 ml) at 363 K for 8 h (yield 84%, m.p. 559–561 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a dimethylformamide solution. Elemental analysis, calculated: C 60.14, H 5.30, N 10.52%; found: C 60.25, H 5.45, N 10.43%. ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 1.09 (*t*, J = 7.2 Hz, 6H, 2CH_3), 2.74 (*s*, 6H, 2CH_3), 2.90 (*s*, 6H, 2CH_3), 4.01 (*q*, J = 7.2 Hz, 4H, 2CH_2), 5.29 (*s*, 2H, 2CH), 7.46–7.58 (*m*, 4H, ArH), 7.64–7.74 (*m*, 2H, ArH), 7.85 (*s*, 4H, 2NH_2), 7.95 (*s*, 2H, 2CHO), 7.97–8.04 (*m*, 4H, ArH), 8.08–8.14 (*m*, 2H, ArH); IR (ν, cm^{-1}): 3435, 3302 (NH_2), 3032 (Ar—H), 2953 (C—H), 1687 (C═O), 1609, 1525, 1495 (phenyl ring).

Crystal data

$C_{34}H_{28}N_4O_{10}\cdot 2C_3H_7NO$
M_r = 798.80
Triclinic, $P\bar{1}$
a = 8.355 (1) Å
b = 9.750 (1) Å
c = 12.202 (2) Å
α = 99.292 (3)°
β = 96.912 (3)°
γ = 97.103 (3)°
V = 963.4 (2) Å^3
Z = 1
D_x = 1.377 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 reflections
θ = 3.3–29.6°
μ = 0.10 mm^{-1}
T = 289 (2) K
Block, yellow
0.34 × 0.24 × 0.18 mm

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: none
5054 measured reflections
3340 independent reflections
2241 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022
$\theta_{\rm max}$ = 25.0°
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: 2.3%

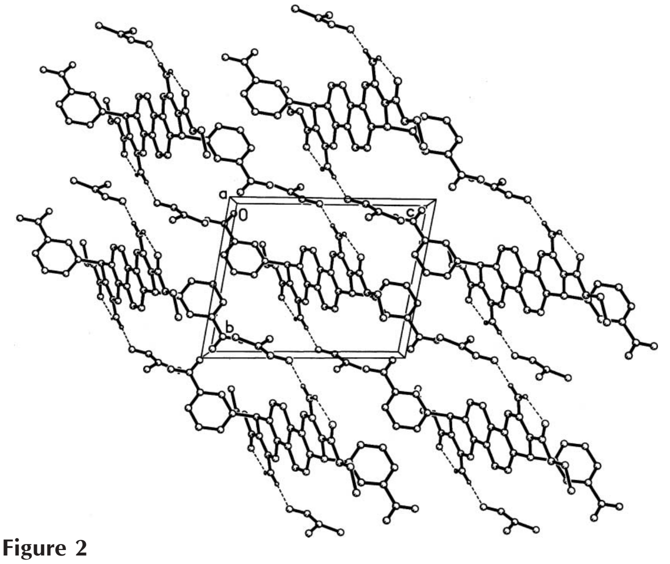


Figure 2
A molecular packing diagram for (I). Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.242
S = 1.02
3340 reflections
273 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.16P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.42 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.360 (3)	C2—C3	1.518 (4)
O1—C5	1.379 (3)	C3—C4	1.518 (3)
N1—C1	1.332 (4)	C4—C5	1.357 (4)
C1—C2	1.359 (4)	C6—C6$^{\rm i}$	1.417 (5)
C1—O1—C5	119.3 (2)	C2—C3—C4	110.4 (2)
C2—C1—O1	122.5 (2)	C5—C4—C3	120.7 (2)
C1—C2—C3	121.7 (2)	C4—C5—O1	123.1 (2)
C5—O1—C1—C2	9.4 (4)	C2—C3—C4—C5	15.8 (3)
O1—C1—C2—C3	2.1 (4)	C3—C4—C5—O1	−6.3 (4)
C1—C2—C3—C4	−13.9 (4)	C1—O1—C5—C4	−7.2 (4)

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3	0.86 (1)	2.11 (3)	2.713 (3)	127 (3)
N1—H1*B*···O6	0.86 (1)	2.02 (1)	2.866 (5)	170 (4)

Atoms H1*A* and H1*B* were refined isotropically, with the N—H bond lengths restrained to 0.86 Å. All other H atoms were positioned geometrically and refined as riding, with C—H distances in the range 0.93–0.98 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine

o2028 Wang *et al.* • $C_{34}H_{28}N_4O_{10}\cdot 2C_3H_7NO$ *Acta Cryst.* (2005). E**61**, o2027–o2029

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank the Natural Science Foundation of the Education Committee of Jiangsu Province for financial support (grant No. 04KJB150139).

References

Ando, T., Yamawaki, J., Kawate, T., Sumi, S. & Hanafusa, T. (1982). *Bull. Chem. Soc. Jpn*, **55**, 2504–2507.

Clark, J. H. (1980). *Chem. Rev.* **80**, 429–452.

Hafez, E. A., Elnagdi, M. H., Elagamey, A. A. & El-Taweel, F. A. (1987). *Heterocycles*, **26**, 903-907.

Li, Y. L., Wang, X. S., Shi, D. Q., Tu, S. J. & Zhang, Y. (2004). *Acta Cryst.* E**60**, o1439–o1441.

Morinaka, Y. & Takahashi, K. (1977). Jpn. Patent JP 52 017 498.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS*. Version 2.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wang, X. S., Zeng, Z. S., Shi, D. Q., Wei, X. Y. & Zong, Z. M. (2004). *Acta Cryst.* E**60**, o1606–o1608.

Witte, E. C., Neuert, P. & Roesch, A. (1986). Ger. Offen. DE 3 427 985.

Acta Cryst. (2005). E**61**, o2027–o2029 Wang *et al.* • $C_{34}H_{28}N_4O_{10}\cdot 2C_3H_7NO$ **o2029**