Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A large delocalized π-electron system: diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine chloroform solvate

Miao Du,[a] Xian-He Bu[a]* and Kumar Biradha[b]

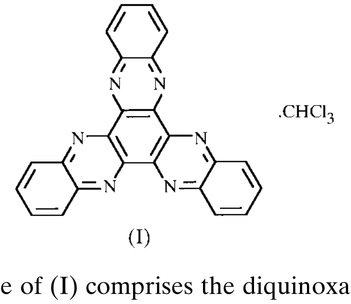
[a]Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China, and [b]Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan
Correspondence e-mail: buxh@nankai.edu.cn

Received 25 July 2000
Accepted 14 November 2000

The title compound, $C_{24}H_{12}N_6{\cdot}CHCl_3$, crystallizes in the monoclinic system in space group $P2_1/c$. The structure consists of one molecule of diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine (Dqpz), which is a large delocalized π-electron system, and a chloroform solvent molecule. There exist weak intermolecular C—H···N and π–π interactions between adjacent Dqpz molecules.

Comment

Bridging ligands providing three bidentate metal-binding sites, such as 1,4,5,8,9,12-hexaazatriphenylene (Hat; Moucheron & Mesmaeker, 1996; Baxter *et al.*, 1997), are particularly promising as building blocks for the construction of multi-dimensional structures because they provide robust networks with good electronic communication between the metal centres. Much pioneering work in this field has been performed by Robson and co-workers (Batten & Robson, 1998; Abrahams *et al.*, 1999). In our efforts to construct novel extended multi-dimensional networks, the title compound, (I), attracts our attention. This compound has a very similar backbone and coordination sites to Hat. But it has a bigger delocalized π-electron system than Hat which may provide more facile electronic communication between attached metal centres. The crystal structure of the title compound is the focus of our present report.



(I)

The structure of (I) comprises the diquinoxalino[2,3-*a*:2′,3′-*c*]phenazine and a chloroform molecule in the crystal lattice. A perspective view of (I) including the atomic numbering scheme is shown in Fig. 1. In the central C_6 ring, the maximum deviation of any atoms from the best-fit plane is 0.0106 (1) Å, while the average deviation is 0.0068 (2) Å. Furthermore, all non-H atoms lie roughly in a plane; the mean deviation of any non-H atoms in Dqpz from the best-fit plane describing them is 0.1282 (4) Å, forming a dihedral angle of 2.30 (2)° with the central C_6 ring. The distortions from planarity should have a noticeable effect on the electronic communication provided by this bridging ligand. The main molecule has a C_3 symmetry and the bond distances and angles are quite similar in three different directions. The C—N bond distances lie in the range 1.323 (3)–1.363 (3) Å, which are remarkably shorter than a normal C—N single bond (1.47 Å; Sasada, 1984) and longer than the value of a C═N double-bond distance (1.28 Å; Wang *et al.*, 1998) due to the π-electron repulsion of the bulky system. The C—C bond distances are in the range 1.351 (4)–1.483 (3) Å and all the bond angles are about 120°, falling within normal limits. All the features mentioned above indicate that the Dqpz molecule has a very large delocalized π-electron system which may provide facile electronic communication.

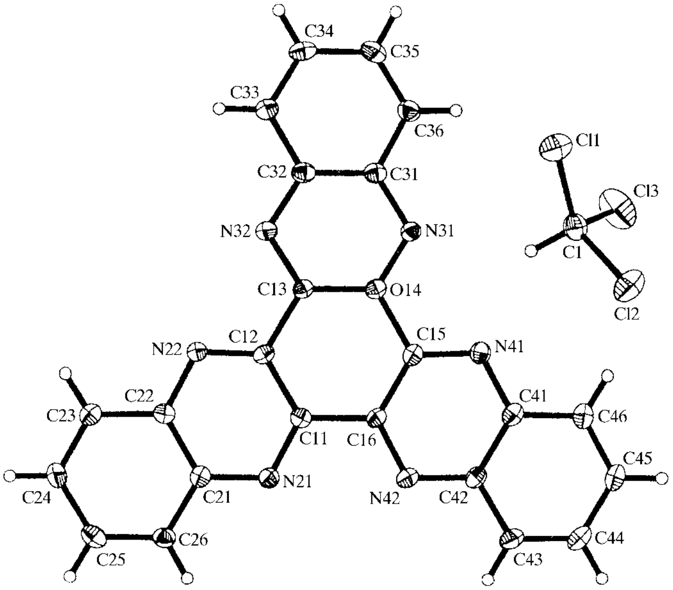


Figure 1
*ORTEP*II (Johnson, 1976) view of the title compound with 30% probability displacement ellipsoids.

Weak intermolecular interaction exists between C44—H44···N22 with a C···N non-bonded separation of 3.355 (4) Å and a C—H···N angle of 141.0 (3)°. The chloroform molecule also donates C—H···N hydrogen bonds to Dqpz (C1—H1···N31 and C1—H1···N41), with C···N separations of 3.256 (3) and 3.330 (4) Å, and bond angles of 145.4 (2) and 143.6 (14)°. In addition, there are π–π stacks of parallel molecules along the *b* axis, with an interplanar spacing of 3.481 (2) Å, which stabilize the crystal (Fig. 2).

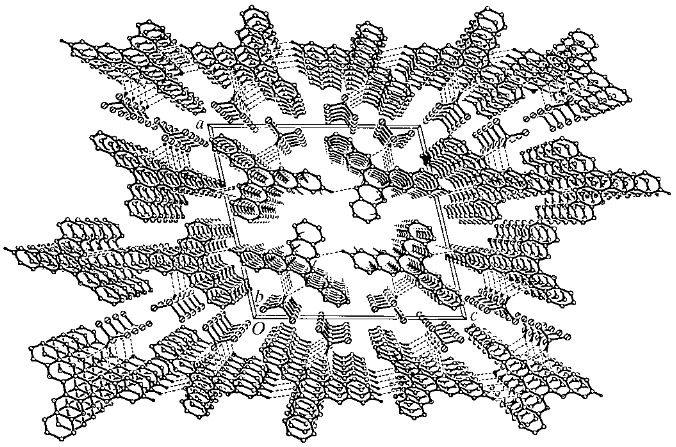


Figure 2
The molecular packing diagram of the unit cell in the title compound.

Experimental

The title compound was synthesized by stirring hexaketocyclohexane octahydrate (0.50 g, 1.6 mmol) and 1,2-phenylenediamine (0.52 g, 4.8 mmol) in the presence of several drops of acetic acid in ethanol solution (50 ml) at room temperature for 2 h. The solvent was concentrated *in vacuo* to afford a colourless solid which was purified by recrystallization from CH_2Cl_2/CH_3OH to obtain the single crystals suitable for X-ray diffraction. The product was characterized by NMR and mass spectrometry, giving results consistent with those in the literature (Skujins & Webb, 1969).

Crystal data

$C_{24}H_{12}N_6\cdot CHCl_3$
$M_r = 503.76$
Monoclinic, $P2_1/c$
$a = 19.5061$ (19) Å
$b = 5.3820$ (5) Å
$c = 20.976$ (2) Å
$\beta = 103.897$ (2)°
$V = 2137.7$ (4) Å^3
$Z = 4$
$D_x = 1.565$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 967 reflections
$\theta = 2.00$–27.90°
$\mu = 0.458$ mm^{-1}
$T = 193$ (2) K
Prism, colourless
0.15 × 0.15 × 0.15 mm

Data collection

Siemens CCD X-ray diffractometer
ω scans
Absorption correction: by integration (North *et al.*, 1968)
$T_{\min} = 0.736$, $T_{\max} = 0.935$
11 035 measured reflections
4988 independent reflections
1991 reflections with $I > 2.0\sigma(I)$
$R_{\text{int}} = 0.062$
$\theta_{\max} = 27.90°$
$h = -25 \rightarrow 14$
$k = -6 \rightarrow 7$
$l = -26 \rightarrow 27$
Intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.047$
$wR(F^2) = 0.093$
$S = 0.814$
4988 reflections
307 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.016$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

H atoms were allowed for as riding atoms with aromatic C—H = 0.95 Å and chloroform C—H = 1.00 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1997).

We gratefully acknowledge financial support from the National Natural Science Foundation of China (Nos. 29771022 and 29971019), Tianjin Natural Science Foundation and the Trans-Century Talents Training Program Foundation of the State Education Ministry of China to XHB. We gratefully acknowledge the kind support of Professor Mitsuhiko Shionoya and Dr Kentaro Tanaka.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1159). Services for accessing these data are described at the back of the journal.

References

Abrahams, B. F., Batten, S. R., Grannas, M. J., Hamit, H., Hoskins, B. F. & Robson, R. (1999). *Angew. Chem. Int. Ed. Engl.* **38**, 1475–1477.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed. Engl.* **37**, 1460–1462.
Baxter, P., DeCian, J.-M. A. & Fischer, J. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 1840–1842.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Moucheron, C. & Mesmaeker, A. K. D. (1996). *J. Am. Chem. Soc.* **118**, 12834–12835.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sasada, Y. (1984). *Molecular and Crystal Structures*. In *Chemistry Handbook*, 3rd ed. Maruzen, Tokyo: The Chemical Society of Japan.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Skujins, S. & Webb, G. A. (1969). *Tetrahedron*, **25**, 3935–3942.
Wang, Z.-X., Jian, F.-F., Duan, C.-Y., Bai, Z.-P. & You, X.-Z. (1998). *Acta Cryst.* C**54**, 1927–1929.