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1,4:8,11:15,18:22,25-Tetraethano-29*H*,31*H*-tetrabenzo[*b*,*g*,*l*,*q*]porphine toluene trisolvate

Shinji Aramaki,[a] Yoshimasa Sakai,[a] Hiroyuki Yanagisawa[b] and Jin Mizuguchi[b]*

[a]Mitsubishi Chemical Group Science and Technology Research Centre, Kamoshida-cho 1000, Aoba-ku, Yokohama 227-8502, Japan, and [b]Department of Applied Physics, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

Correspondence e-mail: mizu-j@ynu.ac.jp

Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.073
wR factor = 0.197
Data-to-parameter ratio = 9.6

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

In the title compound, $C_{44}H_{38}N_4\cdot3C_7H_8$, the porphine (CP) is a soluble precursor of metal-free porphyrin which exhibits an excellent field-effect transistor characteristic. The CP molecule is not entirely flat in its crystal structure (*i.e.* not D_{2h}), but is slightly deformed, as characterized by crystallographic C_i symmetry. The geometric isomer of CP could not be identified due to orientational disorder.

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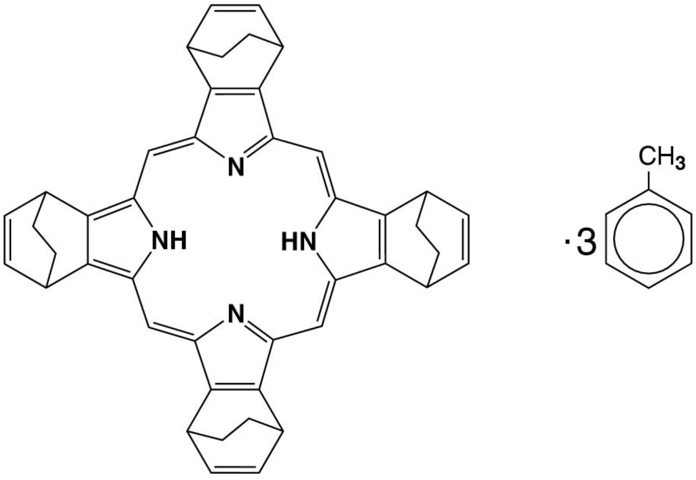
Comment

Organic field-effect transistors (FET) are advantageous due to lower fabrication costs and larger-area devices compared with inorganic FETs. We have recently reported that metal-free porphyrin, so-called benzoporphyrin (BP), exhibits an excellent FET characteristic (Aramaki *et al.*, 2004). Our FET system is characterized by the use of a soluble BP precursor, CP, and its thermal transformation into BP directly on the substrate at about 473 K. In order to improve the FET performance further, it is crucial to study the correlation between structure and solid-state properties. The structure of BP has previously been reported (Aramaki & Mizuguchi, 2003). The present paper deals with the structure of the title compound, (I), which is the toluene trisolvate of CP.



(I)

Fig. 1 shows the structure of the CP molecule of (I). The centrosymmetric molecule is not entirely planar. The angle between the plane of the four N atoms [N1/N1^i/N2/N2^i; symmetry code: (i) $1 - x$, $2 - y$, $1 - z$] and the C3/C4/C7/C8 plane is 2.9 (3)°, while the angle between the central plane and that composed of atoms C14/C15/C16/C19 is 7.1 (3)°. According to the scheme, there should be one single bond and one double bond in the bicyclic ring system at the periphery of

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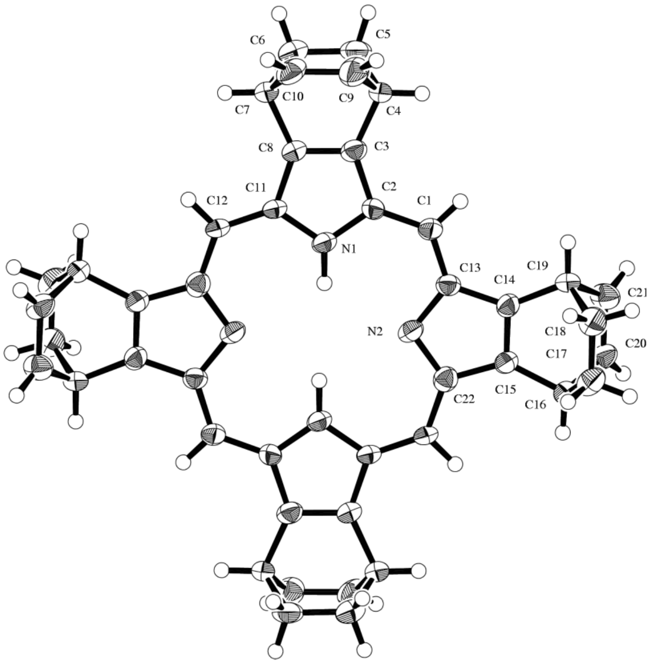

Figure 1
A view of the structure of the CP molecule of (I), showing 50% probability displacement ellipsoids. The toluene solvent molecules have been omitted for clarity. Unlabelled atoms are related to labelled atoms by $(1 - x, 2 - y, 1 - z)$.

the molecule. However, the C5—C6, C9—C10, C17—C18 and C20—C21 bond lengths are in the range 1.426 (9)–1.436 (8) Å. These are intermediate between single and double bonds. This presumably occurs because the molecule and its inverse are arranged randomly in the crystal structure, giving a crystallographically averaged bond length.

It is also to be noted that we have successfully isolated two geometric isomers by column chromatography and confirmed that their NMR spectra are different. However, the crystals of the two isomers showed the same cell constants and similar disorder of the bicyclic ring system by X-ray analyses.

Fig. 2 shows the packing arrangement of CP with the toluene molecules. The solvent molecules are sandwiched between two CP molecules.

Experimental

CP was synthesized according to the method previously reported by Ito *et al.* (1998). The product was purified by column chromatography and recrystallization. Single crystals of (I) were then grown from a toluene solution. Since the crystal was found to include solvent molecules, X-ray intensity data were collected at 93 K.

Crystal data

$C_{44}H_{38}N_4 \cdot 3C_7H_8$
$M_r = 899.18$
Triclinic, $P\bar{1}$
$a = 9.986$ (3) Å
$b = 11.682$ (3) Å
$c = 12.222$ (4) Å
$\alpha = 117.17$ (2)°
$\beta = 103.69$ (2)°
$\gamma = 92.56$ (2)°
$V = 1213.0$ (7) Å^3
$Z = 1$
$D_x = 1.231$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 8380 reflections
$\theta = 4.2$–56.9°
$\mu = 0.54$ mm^{-1}
$T = 93.2$ K
Block, dark red
0.40 × 0.40 × 0.20 mm

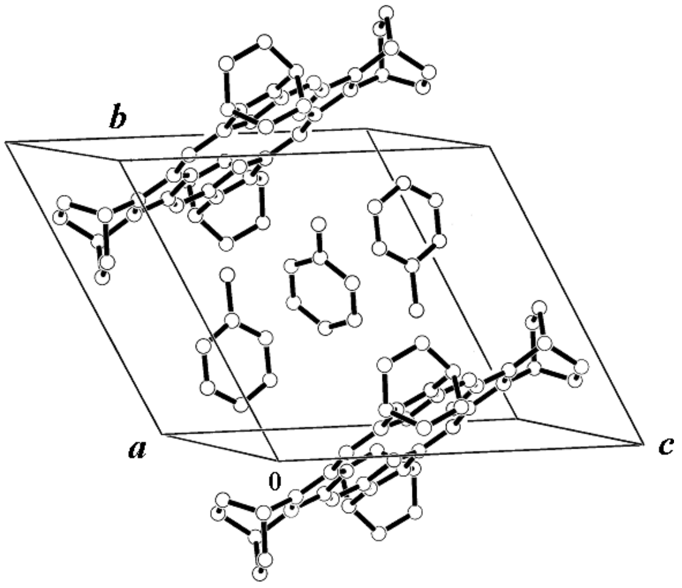

Figure 2
The crystal structure of (I). H atoms and one of two possible positions of the methyl C33 atom of toluene have been omitted for clarity.

Data collection

Rigaku R-AXIS RAPID imaging plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.471$, $T_{\max} = 0.897$
8409 measured reflections
3020 independent reflections
1754 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 56.9°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.197$
$S = 1.26$
3020 reflections
316 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + \{0.05[\max(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.376 (7)	C8—C11	1.433 (7)
N1—C11	1.382 (7)	C9—C10	1.435 (10)
N2—C13	1.392 (7)	C11—C12	1.382 (8)
N2—C22	1.381 (7)	C12—C22$^{\rm i}$	1.397 (8)
C1—C2	1.391 (8)	C13—C14	1.446 (8)
C1—C13	1.382 (8)	C14—C15	1.343 (8)
C2—C3	1.441 (8)	C15—C22	1.452 (8)
C3—C8	1.361 (8)	C17—C18	1.426 (9)
C5—C6	1.433 (9)	C20—C21	1.436 (8)
C2—N1—C11	110.0 (4)	C8—C11—C12	127.6 (5)
C13—N2—C22	106.5 (4)	C11—C12—C22$^{\rm i}$	128.3 (5)
C2—C1—C13	127.5 (5)	N2—C13—C1	124.4 (5)
N1—C2—C1	124.7 (5)	N2—C13—C14	109.3 (5)
N1—C2—C3	107.0 (5)	C1—C13—C14	126.3 (5)
C1—C2—C3	128.2 (5)	C13—C14—C15	107.2 (5)
C2—C3—C8	107.6 (5)	C14—C15—C22	108.1 (5)
C3—C8—C11	108.9 (5)	N2—C22—C12$^{\rm i}$	125.8 (5)
N1—C11—C8	106.5 (5)	N2—C22—C15	108.8 (5)
N1—C11—C12	125.9 (5)	C12$^{\rm i}$—C22—C15	125.3 (5)

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

All the H atoms were positioned geometrically and included in a riding-model approximation, with C—H and N—H distances of 0.95 Å and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,*N*). A positive peak was found near atom N1 in the difference density map. However, it deviated slightly from the plane composed of the four N atoms. Therefore, the H atom bonded to N1 was calculated by assuming sp^2 hybridation. Six H atoms attached to the bicyclic ring system at the periphery of the CP molecule were positioned in the following way. As described in the *Comment*, one of the two C—C bonds is a single bond, whereas the other one is double. At one corner, since the C5—C6 bond is just slightly shorter than the C9—C10 one, two –CH were tentatively attached to the former, and two –CH_2 to the latter. Similarly, at another corner, two –CH were attached to the C17—C18 bond, and two –CH_2 to the C20—C21 bond. There are one and a half independent toluene molecules in the asymmetric unit. The benzene ring of one of the three toluene molecules in the unit cell has a crystallographic centre of symmetry, and the methyl group (C33) is disordered over two sites of 50% occupancy each.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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