Data collection: *SMART* (Siemens, 1994). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SX1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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meso-(3,5-Di-*tert*-butylphenyl)-2,2′-dipyrromethane

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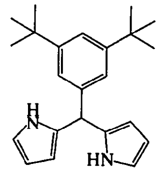
Abstract

In molecules of the title compound, *meso*-(3,5-di-*tert*-butylphenyl)methylenebis(2-pyrrole), $C_{23}H_{30}N_2$, the moieties surrounding the *meso*-C atoms form a tetrahedral geometry. There is no N—H···N hydrogen bonding present in the compound and molecules interact with each other through weak N—H···π interactions.

Comment

One-flask syntheses of *meso*-substituted β-unsubstituted dipyrromethanes have been reported recently (Hammel, Erk, Schuler, Heinze & Müllen, 1992; Lee & Lindsey, 1994). This easy access to *meso*-substituted dipyrromethanes provides a route to the direct synthesis of β-unsubstituted *trans*-substituted porphyrins. The structure of the title compound is equivalent to a $\frac{3}{8}$ segment of the tetraarylporphyrinogen, a cyclic intermediate in Lindsey's method of porphyrin synthesis (Lindsey, Schreiman, Hsu, Kearney & Marguerettaz, 1987). Based on the computational molecular modelling of *meso*-substituted dipyrromethanes, *i.e.* 5-mesityldipyrromethane, it was shown that the extent of the steric hindrance around the *meso*-C atom of the *meso*-substituted dipyrromethane affects the yields in synthesizing *ortho*-disubstituted tetraphenylporphyrin (Lindsey & Wagner, 1989). We present here the crystal structure of *meso*-(3,5-di-*tert*-butylphenyl)-2,2′-dipyrromethane, (I).



(I)

To our knowledge, this is the first structure report on a *meso*-substituted β-unsubstituted dipyrromethane. The crystal structure (Fig. 1) of (I) shows a slightly distorted tetrahedron around the *meso*-C atom, with an average

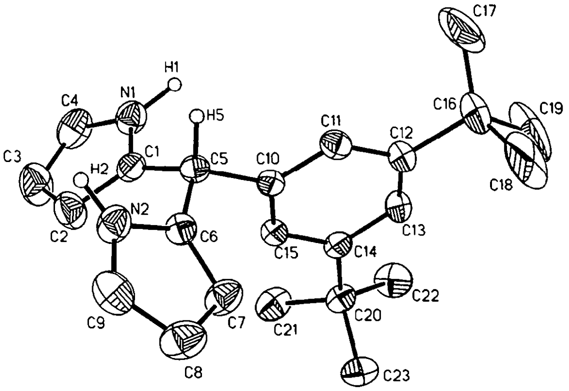


Fig. 1. The atomic labelling scheme for (I). H atoms have been omitted for clarity, except for H1, H2 and H5 on the pyrrole N and *meso*-C atoms, respectively. Displacement ellipsoids are drawn at the 30% probability level.

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C—C5—H angle of 107 (2)° and an average C—C5—C angle of 111.6 (9)°. The average C—C5—C angle is smaller than the corresponding angle (112.6°) found in triphenylmethane (Riche & Pascard-Billy, 1974) and can be attributed to the smaller ring size of pyrrole. No N—H···N hydrogen bonding was found in the crystal packing (Fig. 2). In fact, there are no close encounters (<3.75 Å) between molecules, only some weak hydrogen bonding due to N—H···π interactions (Jeffrey & Saenger, 1991). Each molecule interacts with two adjacent molecules through N—H···π interactions. It is the H1 atom bonded to N1 that interacts with the centroid of the C8—C9 bond in the neighbouring molecules. The H1···centroid distance is 2.518 (5) Å and the N1—H1···centroid angle is 163 (2)°.

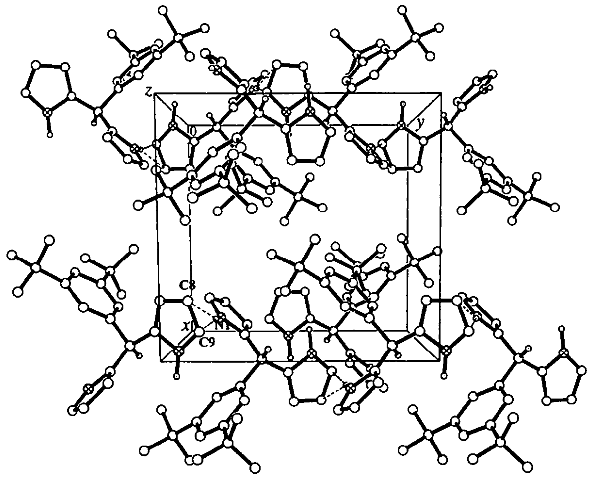

Fig. 2. Packing diagram for (I) showing the N—H···π interaction network (as dashed lines). H atoms have been omitted for clarity, except for those on the *meso*-C and pyrrole N atoms. All N atoms are indicated by crossed circles.

Experimental

The title compound was synthesized by reacting 3,5-di-*tert*-butylbenzaldehyde (Newman & Lee, 1972) with excess pyrrole according to the method of Lee & Lindsey (1994). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the solution obtained from column chromatography (cyclohexane/ethyl acetate/triethylamine 95/4/1).

Crystal data

$C_{23}H_{30}N_2$
$M_r = 334.49$
Monoclinic
$P2_1/c$
$a = 10.529 (2)$ Å
$b = 10.9805 (14)$ Å
$c = 18.362 (4)$ Å
$\beta = 99.72 (2)°$
$V = 2092.4 (6)$ Å^3
$Z = 4$
$D_x = 1.062$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.56–12.18°$
$\mu = 0.062$ mm^{-1}
$T = 293 (2)$ K
Chunk
0.52 × 0.36 × 0.32 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.95$, $T_{max} = 1.00$
2884 measured reflections
2710 independent reflections

1840 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.008$
$\theta_{max} = 22.5°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 2.0%

Refinement

Refinement on F^2
$R(F) = 0.0434$
$wR(F^2) = 0.1495$
$S = 0.921$
2710 reflections
284 parameters
$w = 1/[\sigma^2(F_o^2) + (0.115P)^2 + 0.7322P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.205$
$\Delta\rho_{max} = 0.177$ e Å^{-3}
$\Delta\rho_{min} = -0.211$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0025 (19)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	−0.1381 (2)	0.3073 (2)	0.18979 (14)	0.0600 (7)
N2	0.0213 (2)	−0.0477 (2)	0.14976 (13)	0.0583 (7)
C1	−0.0645 (2)	0.2172 (2)	0.16659 (14)	0.0482 (7)
C2	−0.0971 (3)	0.2115 (3)	0.0918 (2)	0.0707 (9)
C3	−0.1932 (3)	0.2996 (3)	0.0699 (2)	0.0883 (11)
C4	−0.2158 (3)	0.3570 (3)	0.1311 (2)	0.0772 (9)
C5	0.0327 (2)	0.1488 (2)	0.22057 (13)	0.0448 (6)
C6	0.0931 (2)	0.0470 (2)	0.18365 (13)	0.0448 (6)
C7	0.2171 (3)	0.0243 (2)	0.1774 (2)	0.0619 (8)
C8	0.2194 (3)	−0.0856 (3)	0.1378 (2)	0.0747 (9)
C9	0.0987 (3)	−0.1279 (3)	0.1216 (2)	0.0693 (8)
C10	0.1365 (2)	0.2315 (2)	0.26274 (12)	0.0421 (6)
C11	0.1807 (2)	0.2126 (2)	0.33735 (13)	0.0491 (7)
C12	0.2749 (2)	0.2866 (2)	0.37723 (13)	0.0512 (7)
C13	0.3239 (2)	0.3796 (2)	0.33879 (14)	0.0521 (7)
C14	0.2840 (2)	0.4013 (2)	0.26398 (13)	0.0448 (6)
C15	0.1885 (2)	0.3252 (2)	0.22699 (12)	0.0437 (6)
C16	0.3236 (3)	0.2650 (3)	0.46010 (15)	0.0689 (9)
C17†	0.2159 (8)	0.2568 (12)	0.5026 (4)	0.111 (3)
C18†	0.4003 (10)	0.1414 (9)	0.4693 (3)	0.112 (3)
C19†	0.4199 (12)	0.3626 (9)	0.4948 (4)	0.122 (3)
C20	0.3489 (2)	0.4991 (2)	0.22319 (14)	0.0513 (7)
C21	0.2569 (3)	0.5514 (3)	0.1575 (2)	0.0729 (9)
C22	0.4011 (3)	0.6039 (3)	0.2737 (2)	0.0813 (10)
C23	0.4615 (3)	0.4382 (3)	0.1944 (2)	0.0683 (9)
C17*A*‡	0.234 (3)	0.1692 (14)	0.4894 (7)	0.147 (9)
C18*A*‡	0.4623 (12)	0.2469 (19)	0.4701 (7)	0.127 (5)
C19*A*‡	0.2942 (14)	0.3877 (12)	0.4989 (4)	0.116 (4)

† Site occupancy = 0.60. ‡ Site occupancy = 0.40.

Table 2. *Selected geometric parameters (Å, °)*

N1—C4	1.352 (4)	C2—C3	1.408 (4)
N1—C1	1.368 (3)	C3—C4	1.345 (5)
N1—H1	0.94 (3)	C5—C6	1.503 (4)
N2—C9	1.360 (4)	C5—C10	1.528 (3)
N2—C6	1.372 (3)	C6—C7	1.353 (4)
N2—H2	0.88 (3)	C7—C8	1.412 (4)
C1—C2	1.359 (4)	C8—C9	1.338 (4)
C1—C5	1.501 (3)		
C4—N1—C1	110.0 (3)	C1—C5—C10	112.8 (2)
C9—N2—C6	110.1 (2)	C6—C5—H5	108.4 (14)
C2—C1—N1	106.8 (2)	C1—C5—H5	105.3 (13)
C2—C1—C5	132.2 (2)	C10—C5—H5	108.1 (13)
N1—C1—C5	121.0 (2)	C7—C6—N2	106.8 (2)
C1—C2—C3	107.7 (3)	C7—C6—C5	131.5 (2)
C4—C3—C2	107.6 (3)	N2—C6—C5	121.7 (2)
C3—C4—N1	108.0 (3)	C6—C7—C8	107.5 (2)
C6—C5—C1	111.6 (2)	C9—C8—C7	108.2 (3)
C6—C5—C10	110.5 (2)	C8—C9—N2	107.4 (3)

Atoms C17, C18 and C19 were found to be disordered over two positions (C17/C17*A*, C18/C18*A* and C19/C19*A*). Their occupancies were initially refined and then later fixed at 0.6 (C17, C18 and C19) and 0.4 (C17*A*, C18*A* and C19*A*). The non-H atoms were refined anisotropically. The H atoms of the *meso*-C and N atoms were located on difference Fourier maps and were refined isotropically, while other H atoms were placed in idealized positions. The H atoms attached to C17, C18 and C19 have occupancies of 0.6 and those on C17*A*, C18*A* and C19*A* have occupancies of 0.4.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α,α-Diacetoxy-2,4-dichloro-5-nitrobenzaldehyde

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Abstract

The title compound, (2,4-dichloro-5-nitrophenyl)methylene diacetate, $C_{11}H_9Cl_2NO_6$, was obtained as an unexpected product from the reaction of 2,4-dichloro-5-nitrobenzaldehyde with 2-methylbenzothiazole in refluxing acetic anhydride. The single-crystal X-ray analysis showed the phenyl ring to be slightly disorientated with respect to the idealized C_s symmetry which the molecule would otherwise possess. Thus, the dihedral angle between C(1)—C(7)—H(3) and the phenyl ring is 29.8 (4)°.

Comment

As part of our continued interest in the synthesis of benzothiazolo[3,2-*a*]quinolinium salts (Cox *et al.*, 1982; Alegría, *et al.*, 1993) *via* the photochemically induced cyclization of 2-styrylbenzothiazoles, we investigated the reaction of 2,4-dichloro-5-nitrobenzaldehyde with 2-methylbenzothiazole in refluxing acetic anhydride. In addition to the expected 2-(2′,4′-dichloro-5′-nitrostyryl)-benzothiazole, an unknown product was also formed in the reaction. The ^{1}H and ^{13}C NMR studies showed that the latter is α,α-diacetoxy-2,4-dichloro-5-nitrobenzaldehyde, a product of the nucleophilic attack of 2,4-dichloro-5-nitrobenzaldehyde on the solvent. In order to