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Key indicators

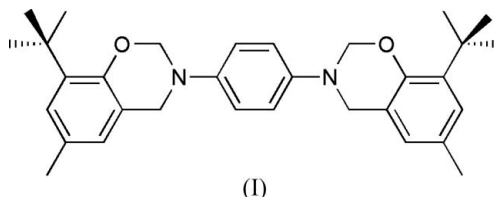
Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.062
 wR factor = 0.160
Data-to-parameter ratio = 15.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.1,4-Bis(8-*tert*-butyl-6-methyl-4*H*-1,3-
benzoxazin-3-yl)benzene

The solid-state structure of the title compound, $\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_2$, is characterized by benzoxazine units with a *cisoid* geometry, and with the N atoms displaced from the planes of the heterocycles. The two benzoxazine groups are nearly coplanar.

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Comment

Solid-state structures of benzoxazine derivatives are of interest partly due to their potential to inhibit the enzyme γ -aminobutyric acid transaminase (Andrews *et al.*, 1986). The benzoxazine system is also a critical component of a series of resorcinarene derivatives (Arnecke *et al.*, 1995, El Gihani *et al.*, 1995), which have been employed as macrocyclic receptors to encapsulate small molecules or ions selectively (Atwood & Szumna, 2002; Kröck *et al.*, 2004).



The reaction of 1,4-diaminobenzene with 2-*tert*-butyl-4-methylphenol and four equivalents of formaldehyde results in the formation of the title bis-benzoxazine derivative, (I). The bond lengths in the heterocyclic groups of (I) are comparable with those of related compounds (Andrews *et al.*, 1986), with average distances of 1.455 (3) Å for O–C(methylene) and 1.419 (3) Å for N–C(methylene), and an average N–C–O angle of 114.4 (2)°. Atoms N9 and N24 are displaced from the benzoxazine planes, defined by C10–C18/O7 and C25–C33/O22, by 0.522 (2) and 0.541 (2) Å, respectively. The methylene group located between O and N lies at distances of 0.203 (2) (C8) and 0.212 (3) Å (C23) for C8 and C23, respectively, from the benzoxazine plane. A *cisoid* arrangement of the *tert*-butyl groups on the two heterocyclic units is observed.

The solid-state structure of (I) is further characterized by the nearly perpendicular orientation of the benzoxazine planes with respect to the phenylenediamine unit. The angles between the phenylenediamine plane, defined by atoms C1–C6/N9/N24, and the heterocyclic planes containing O7 and O22 are 81.14 (8) and 83.39 (8)°, respectively. This results in a small angle of 2.61 (6)° between the two benzoxazine systems.

Molecules of (I) pack into columns parallel to the *a* axis, with C–H··· π contacts between H8A and H8B on the methylene atom C8, and the benzene rings of an adjacent molecule (see Table 2). A second set of C–H··· π interactions is observed between H23A and H23B on the methylene atom C23, and the benzene rings on another adjacent molecule.

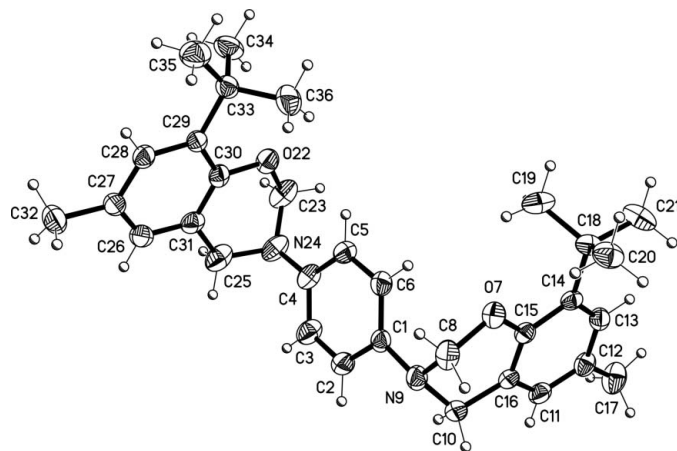


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

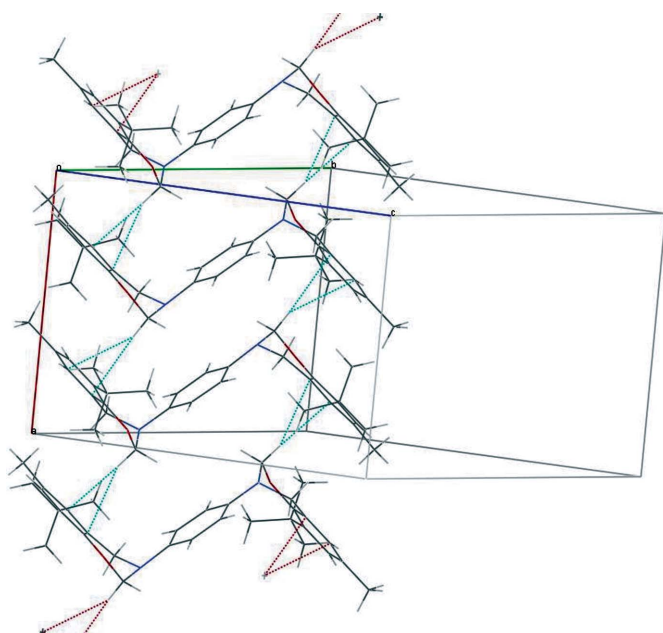


Figure 2
View of the crystal packing, showing the columns of (I) aligned parallel to the *a* axis. C—H... π interactions are shown as blue lines.

Experimental

A mixture of 1,4-diaminobenzene (0.50 g, 4.62 mmol) and aqueous formaldehyde solution (37% wt, 1.52 g, 18.50 mmol) in ethanol (25 ml) was stirred for 16 h at room temperature. 2-*tert*-Butyl-4-methylphenol (1.52 g, 9.25 mmol) was added and the mixture was then refluxed for 48 h. The reaction mixture was allowed to cool to room temperature and the volatile materials were removed under vacuum. The aqueous mixture obtained was chilled before acidifying with 5 ml of 3*N* HCl, followed by extraction with diethyl ether (60 ml) and chloroform (40 ml). The combined organic phases were washed with an aqueous potassium carbonate solution (20 ml) and distilled water (20 ml), followed by drying with anhydrous MgSO₄. After evaporation of the solvents under reduced pressure, (I) was purified

by column chromatography on silica gel eluting with a 3:1 hexanes-dichloromethane mixture (yield: 0.90 g, 40%; m.p. 422–424 K).

Crystal data

C₃₂H₄₀N₂O₂
M_r = 484.66
 Monoclinic, *P*2₁/*c*
a = 10.267 (1) Å
b = 15.443 (2) Å
c = 17.913 (2) Å
 β = 92.098 (2)°
V = 2838.3 (6) Å³

Z = 4
D_x = 1.134 Mg m⁻³
 Mo *K* α radiation
 μ = 0.07 mm⁻¹
T = 294 (2) K
 Block, colourless
 0.25 × 0.23 × 0.12 mm

Data collection

Bruker SMART APEX CCD
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004)
T_{min} = 0.965, *T_{max}* = 0.996

21975 measured reflections
 5180 independent reflections
 3379 reflections with *I* > 2 σ (*I*)
R_{int} = 0.062
 θ_{max} = 25.4°

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.062
wR (*F*²) = 0.160
S = 1.03
 5180 reflections
 333 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 0.5199P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.18 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.16 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1—N9	1.424 (3)	N9—C10	1.464 (3)
C4—N24	1.427 (3)	O22—C30	1.374 (3)
O7—C15	1.373 (3)	O22—C23	1.457 (3)
O7—C8	1.452 (3)	C23—N24	1.417 (4)
C8—N9	1.419 (3)	N24—C25	1.460 (4)
C15—O7—C8	115.29 (18)	C30—O22—C23	115.3 (2)
N9—C8—O7	114.25 (19)	N24—C23—O22	114.5 (2)
C8—N9—C1	117.7 (2)	C23—N24—C4	117.3 (2)
C8—N9—C10	108.66 (19)	C23—N24—C25	108.8 (2)
C1—N9—C10	116.4 (2)	C4—N24—C25	116.0 (2)
N9—C10—C16	111.5 (2)	N24—C25—C31	111.4 (2)

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 represents the centroid of phenyl ring C1—C6, Cg2 that of ring C11—C16 and Cg3 that of ring C26—C31.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8—H8A...Cg3 ⁱ	0.97	2.66	3.608 (3)	166
C8—H8B...Cg1 ⁱ	0.97	2.75	3.592 (3)	145
C23—H23A...Cg2 ⁱⁱ	0.97	2.68	3.650 (3)	174
C23—H23B...Cg1 ⁱⁱⁱ	0.97	2.95	3.807 (3)	148

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 2, -y + 1, -z$.

H atoms were positioned geometrically and refined as riding, with $U_{iso}(\text{H}) = 1.2U_{eq}$ of the parent methylene and aromatic C atoms, and $U_{iso}(\text{H}) = 1.5U_{eq}$ of the parent methyl C atoms, with C—H distances in the range 0.93–0.97 Å.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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References

Andrews, P. R., Cody, V., Gulbis, J. M., Iskander, M. N., Jeffrey, A. I., Mackay, M. F., Di Paola, C. & Sadek, M. (1986). *Aust. J. Chem.* **39**, 1575–1585.
Arnecke, R., Böhmer, V., Paulus, E. F. & Vogt, W. (1995). *J. Am. Chem. Soc.* **117**, 3286–3287.

Atwood, J. L. & Szumna, A. (2002). *J. Am. Chem. Soc.* **124**, 10646–10647.
Bruker (1999). *SMART* (Version 5.625), *SAINT-Plus* (Version 6.23c) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
El Gihani, M. T., Heaney, H. & Slawin, A. M. Z. (1995). *Tetrahedron Lett.* **36**, 4905–4908.
Kröck, L., Shivanyuk, A., Goodin, D. B. & Rebek, J. Jr (2004). *Chem. Commun.* pp. 272–273.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2004). *SADABS*. Version 2004-1. University of Göttingen, Germany.