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A triazine derivative with a triple-decker sandwich conformation

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In dimethyl 3,3′-[6-methoxy-1,3,5-triazine-2,4-diyl)bis(oxy)]-bis(4-benzyloxy-5-methoxybenzoate), $C_{36}H_{33}N_3O_{11}$, a new triazine derivative, the benzyloxy groups adopt an interesting conformation in which they are positioned above and below the triazine ring 'core' of the molecule to form an intramolecular triple-decker sandwich. The ester carbonyl O atoms of adjacent molecules in the crystal structure participate in non-conventional (alkyl)C—H···O hydrogen bonds [averaging 2.45 (1)Å] about an inversion centre to give a weakly hydrogen-bonded dimer.

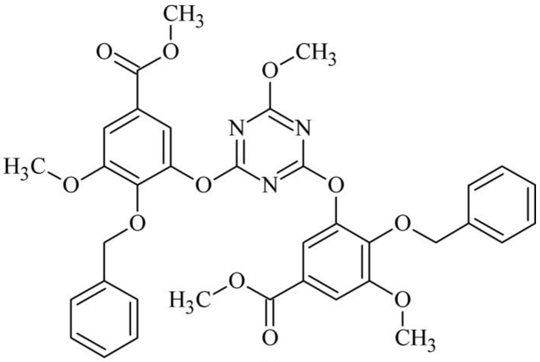
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.066
wR factor = 0.224
Data-to-parameter ratio = 16.1

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

Comment

A new triazine derivative (I) was isolated in crystalline form after work-up of the reaction of 2,4-dichloro-6-methoxy-1,3,5-triazine and methyl 4-benzyloxy-3-hydroxy-5-methoxybenzoate in the presence of *N*-methylmorpholine (NMM) using conditions described in the literature (Kunishima *et al.*, 1999). The structure of (I) is of general interest since phenoxytriazine derivatives have recently been shown to form intriguing supramolecular structures when a suitable hydrogen-bonding substituent is present on the phenoxy ring (Aakeröy *et al.*, 2005; Lebel *et al.*, 2006; Süss *et al.*, 2005).



(I)

The triazine ring core of (I) is sandwiched between the two phenyl rings of the benzyloxy groups (Figs. 1 and 2). The dihedral angles between the top (C11–C15) and bottom (C36–C33) phenyl rings and the triazine ring are 10.9 (2) and 12.9 (2)°, respectively. The distance between the centroid of the C11–C15 ring and the triazine ring is 3.58 (1) Å, while that between the C33–C36 ring is somewhat longer at 3.85 (1) Å. Although the intramolecular ring···ring separations in (I) exceed the graphite spacing (3.35 Å) and the rings are canted, the possibility that the triple-decker sandwich conformation of (I) is brought about by $\pi\cdots\pi$ interactions cannot be excluded,

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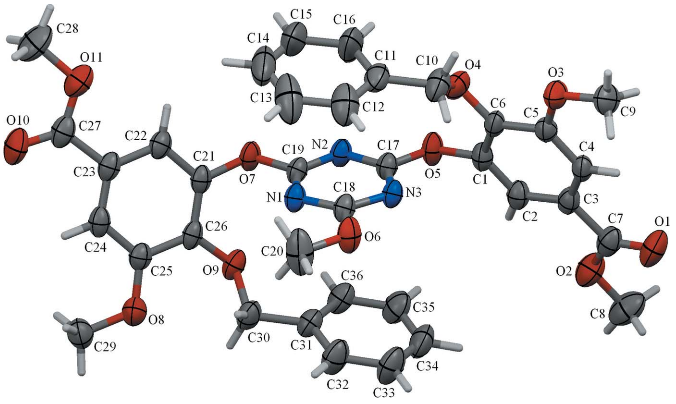

Figure 1
The molecular structure of (I) (45% probability displacement ellipsoids for all non-H atoms).

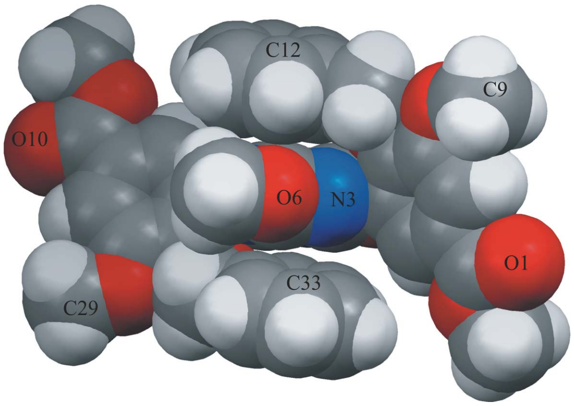

Figure 2
Space-filling plot (van der Waals radii) for (I), viewed approximately down the O6—C18 bond, illustrating the triple-decker sandwich arrangement of the phenyl and central triazine ring systems.

particularly since intramolecular interactions of this type and magnitude have been described previously (Hunter *et al.*, 2001; Munro *et al.*, 2003). Bond distances and angles are normal and warrant no further discussion.

The anisotropic displacement parameters for the C atoms of both benzylic phenyl rings reflect libration of these groups in the room-temperature X-ray structure. Collection of the X-ray data at 100 (2) K to remedy this situation, however, afforded a data set of poorer quality ($R_{\rm int}$ = 0.055) due to partial fracturing of the crystal below 200 K.

The unit-cell contents of (I) comprise the expected pair of molecules situated about the inversion centre and located at general positions in the triclinic unit cell. More interesting is the observation that molecules of (I) associate by weak non-conventional hydrogen bonds (Table 1) to form a centrosymmetric hydrogen-bonded dimer (Fig. 3). The C–H donors in these nominally weak (Steiner, 2002) C—H$\cdots$O(carbonyl) interactions are not particularly acidic, yet the contact distances are shorter than the sum of the van der Waals radii of oxygen and hydrogen (2.72 Å) by more than 0.25 Å. This fact suggests that the interactions listed in Table 1 are more than simple non-bonded contacts in the case of (I).

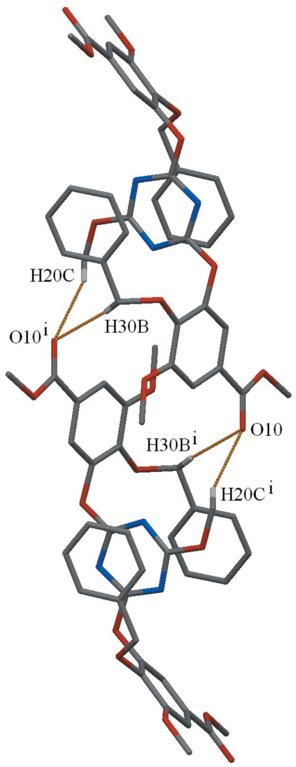

Figure 3
Hydrogen-bonded dimer with inversion symmetry. Atoms involved in the interaction have been labelled. Hydrogen bonds are shown as dashed lines. All other H atoms have been omitted for clarity. [Symmetry code: (i) $-x$, $2 - y$, $-z$.]

Experimental

A mixture of 100 ml of methanol, 13.5 ml of water and 16.5 g (0.2 mol) of sodium bicarbonate was cooled to 283–288 K. Cyanuric chloride (18.4 g, 0.1 mol) was added and the resulting mixture was warmed to 308 K then stirred at 308 K for 20 min and at room temperature for 30 min. Water was added to the reaction mixture and the precipitated product filtered under vacuum, washed with water and dried under vacuum to yield 2,4-dichloro-6-methoxy-1,3,5-triazine as a white solid (5.2 g, 28% yield). A solution of 2,4-dichloro-6-methoxy-1,3,5-triazine (72 mg, 0.40 mmol) and methyl 4-benzyloxy-3-hydroxy-5-methoxybenzoate (58 mg, 0.20 mmol) in THF (20 ml) was stirred under nitrogen. *N*-Methylmorpholine (24 mg, 0.24 mmol) was added and, after stirring for 4 h, the reaction mixture was poured into water and extracted with ethyl acetate. The organic phase was washed successively with a saturated $NaHCO_3$ solution, water, 1 *N* HCl, water and brine and dried over $MgSO_4$. The crude product was purified by column chromatography on SiO_2 (hexane–ethyl acetate = 7:3) to afford compound (I) as a cream–white solid (92 mg, 67%). Recrystallisation by slow evaporation of a methanol solution of (I) gave the compound as colourless crystals (m.p. 371–373 K). Atom numbering consistent with the crystallographic labelling scheme of Fig. 1 applies to the following characterization data where necessary. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.51 (2H, *d*, J = 1.9 Hz, H4/H24), 7.43 (2H, *d*, J = 1.9 Hz, H2/H22), 7.23–7.25 (10H, *m*, Ar-H), 5.06 (4H, *s*, –CH_2–), 3.92 (6H, *s*, COOMe), 3.90 (6H, *s*, C9-OMe/C29-OMe), 3.77 (3H, *s*, C206-OMe). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.6 (C17/C19), 173.0 (C18), 165.9 (C=O), 153.3 (C5/C25), 144.7 (C6/C26), 144.0 (C3/

C23) 136.9 (C11/C31), 128.2 (*m*-C, phenyl), 127.8 (*p*-C, phenyl), 127.6 (*o*-C, phenyl), 125.2 (C1/C21), 116.8 (C2/C22), 111.2 (C4/C24), 74.8 (C10/C30), 56.2 (C9/C29), 55.4 (C20), 52.2 (C8/C28).

Crystal data

$C_{36}H_{33}N_3O_{11}$
$M_r = 683.65$
Triclinic, $P\overline{1}$
$a = 8.5540$ (7) Å
$b = 11.1363$ (8) Å
$c = 17.9894$ (13) Å
$\alpha = 92.746$ (6)°
$\beta = 94.278$ (6)°
$\gamma = 96.246$ (6)°
$V = 1696.0$ (2) Å^3
$Z = 2$
$D_x = 1.339$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.1$ mm^{-1}
$T = 295$ (2) K
Rhomb, colourless
0.6 × 0.4 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur 2 CCD diffractometer
ω scans
Absorption correction: none
13313 measured reflections
7354 independent reflections
4422 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 27.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.224$
$S = 1.06$
7354 reflections
456 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1153P)^2 + 0.3795P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H20*C*···O10$^{\rm i}$	0.96	2.45	3.272 (6)	144
C30—H30*B*···O10$^{\rm i}$	0.97	2.46	3.381 (4)	157

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

Methyl H atoms were placed geometrically and refined as rigid rotating groups (torsion angles from the electron density), with C—H = 0.96Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. Methylene H atoms were placed geometrically and refined using a riding model, with C—H = 0.97Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Aromatic H atoms were placed geometrically and refined using a riding model, with C—H = 0.93Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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