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Diphenyl 3,6-bis(4-chlorophenyl)-1,2-dihydro-1,2,4,5-tetrazine-1,2-dicarboxylate

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Key indicators

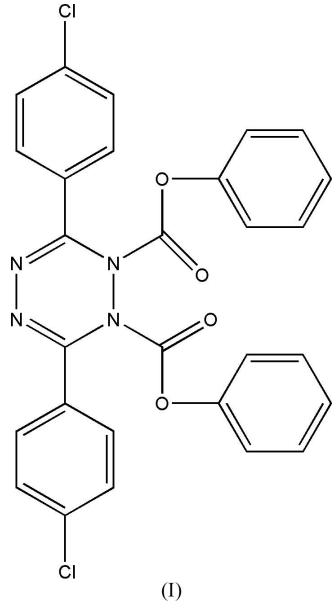
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.107
Data-to-parameter ratio = 13.4

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

The title compound, $C_{28}H_{18}Cl_2N_4O_4$, was prepared by the reaction of phenyl chloroformate and 3,6-bis(4-chlorophenyl)-1,4-dihydro-1,2,4,5-tetrazine. The structural identity, confirmed by crystal structure determination, revealed a re-arrangement, resulting in formation of the 1,2-dihydro-tetrazine derivative from the starting materials. The central tetrazine ring adopts a twist conformation.

Comment

s-Tetrazine derivatives have a high potential for biological activity, possessing a wide range of antiviral and antitumour properties (Neunhoeffer, 1984). These derivatives have been widely used as pesticides and herbicides (Sauer, 1996). In a continuation of our work on the structure–activity relationships of *s*-tetrazine derivatives (Hu *et al.*, 2002, 2004), we have obtained a colourless crystalline compound as the product of the reaction of phenyl chloroformate and 3,6-bis(4-chlorophenyl)-1,4-dihydro-1,2,4,5-tetrazine. The structural identity of our product, (I), was resolved using single-crystal X-ray diffraction.



(I)

The molecular structure of (I) is illustrated in Fig. 1. Selected bond lengths and angles are listed in Table 1. In (I), two phenyloxycarbonyl groups are attached to the atoms N1 and N2 of the tetrazine ring, so (I) is a 1,2-dihydrotetrazine derivative, revealing a re-arrangement during the synthesis. Atoms N1 and N2 deviate from the mean plane N3/C7/N4/C8 by −0.343 (4) and 0.308 (4) Å, respectively, showing the twist conformation of the central tetrazine ring.

Experimental

The title compound was obtained by adding dropwise phenyl chloroformate (10 mmol) to 3,6-bis(4-chlorophenyl)-1,4-dihydro-1,2,4,5-tetrazine (5 mmol), using dichloromethane (40 ml) as solvent at 298 K. The precipitate was filtered off. A solution of the compound in ethanol was concentrated gradually at room temperature to afford colourless crystals (m.p. 491–493 K) suitable for X-ray diffraction.

Crystal data

$C_{28}H_{18}Cl_2N_4O_4$
M_r = 545.36
Triclinic, $P\overline{1}$
a = 9.357 (4) Å
b = 12.439 (2) Å
c = 13.103 (3) Å
α = 116.800 (17)°
β = 108.38 (2)°
γ = 80.91 (2)°
V = 1291.6 (7) Å^3
Z = 2
D_x = 1.402 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 9.9–13.4°
μ = 0.29 mm^{-1}
T = 295 (2) K
Prism, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.917, T_{max} = 0.958
5540 measured reflections
4615 independent reflections
2615 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 25.2°
$h = -1 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.107
S = 1.02
4615 reflections
344 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.1993P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0057 (12)

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.395 (2)	N3—C8	1.287 (3)
N1—C7	1.418 (3)	N3—N4	1.394 (3)
N2—C8	1.419 (3)	N4—C7	1.283 (3)
N2—N1—C7	111.48 (16)	C7—N4—N3	118.41 (19)
N1—N2—C8	111.39 (16)	N4—C7—N1	118.6 (2)
C8—N3—N4	118.33 (18)	N3—C8—N2	118.6 (2)
C7—N1—N2—C8	−51.1 (2)	N2—N1—C7—N4	32.6 (3)
C8—N3—N4—C7	−31.3 (3)	N4—N3—C8—N2	10.0 (3)
N3—N4—C7—N1	8.4 (3)	N1—N2—C8—N3	30.9 (3)

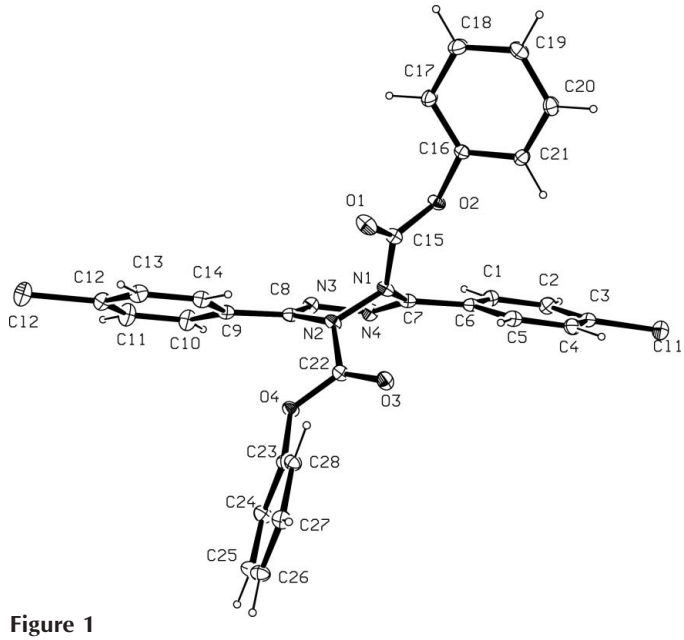


Figure 1
View of (I), shown with 30% probability displacement ellipsoids.

H atoms were placed at calculated positions and refined using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(parent atom).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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: *SHELXL97*.

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