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2-Chloro-4,6-dimethoxy-1,3,5-triazine

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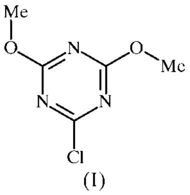
The molecules of 2-chloro-4,6-dimethoxy-1,3,5-triazine, $C_5H_6ClN_3O_2$, lie on a crystallographic mirror plane. There is a close contact of 3.180 (3) Å between one of the methyl C atoms and the N atom of a neighboring molecule. Differential scanning calorimetry measurements show that methyl rearrangement does not take place in the solid state, despite the close proximity of the methyl group to the N atom.

Comment

2-Chloro-4,6-dimethoxy-1,3,5-triazine, (I), has been studied in order to examine its ability to undergo methyl rearrangement in the solid or liquid state (Kaftory & Handelsman-Benory, 1994; Handelsman-Benory *et al.*, 2000; Greenberg *et al.*, 2001; Kaftory *et al.*, 2001; Kaftory, 2002). We investigate here the structure and thermal behavior of (I), which crystallizes in the orthorhombic crystal system, in space group *Pbcm* (Fig. 1). Based on their work on *s*-triazine derivatives, Głowka & Iwanicka (1989*a*,*b*) concluded that the endocyclic bond angles at all N atoms are less than 120°, while those at the C atoms are larger than 120°, irrespective of their hybridization. The molecular geometry of (I) has the same characteristics; the endocyclic bond angles at the N atoms lie in the range 126.9 (2)–128.7 (3)° and those at the C atoms lie in the range 111.9 (2)–112.8 (2)°. The steric effects are best observed by comparing the differences between the outer-ring bond angles at the C atoms. Those bond angles at the side of the methyl group [119.6 (2) and 120.0 (2)°] are larger than the other outer-ring bond angles [113.5 (2) and 112.7 (2)°]. Since the substituent on atom C1 is symmetric with respect to atoms N1 and N2, the outer bond angles at atom C1 are practically equal [115.4 (2) and 115.9 (2)°].



(I)

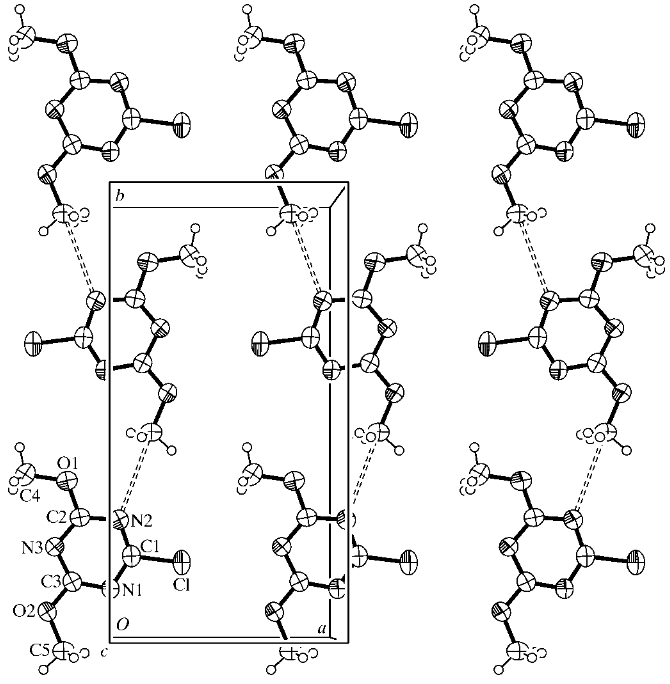


Figure 1
A layer of molecules of (I), showing the short distances between the methyl C atom and the N atoms of neighboring molecules (the two sets of disordered methyl H atoms are shown). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

The molecules lie on a crystallographic mirror plane. Successive layers along the *c* axis are shifted by 1.720 (3) Å relative to one another, parallel to the *b* axis. As a result, the overlap between two molecules (shown in Fig. 2) is such that parallel columns of Cl atoms are formed, the interatomic distance between the Cl atoms of two neighboring columns being 3.972 (3) Å. The molecules within a layer are arranged in rows along the *b* axis (Fig. 1), so that a methyl group of one molecule is close [3.180 (3) Å] to an N atom of the second molecule in the same row. This short contact and the O—C···N angle of 177.5 (2)° are the ideal geometry that is expected if methyl rearrangement is to take place in the solid state, as described in the references mentioned above. Similar geometry was found in 2-(*p*-trideuteromethoxyphenyl)-5-trideuteromethoxy-1,3,4-oxadiazole, which undergoes methyl rearrangement in the solid state (Dessolin *et al.*, 1992), where the distance between the methyl C atom and the N atom is

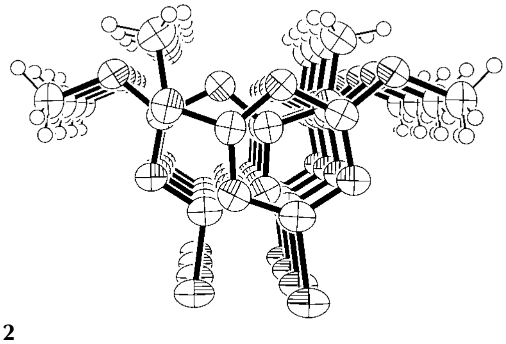


Figure 2
An overlap diagram, viewed along the *c* axis. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

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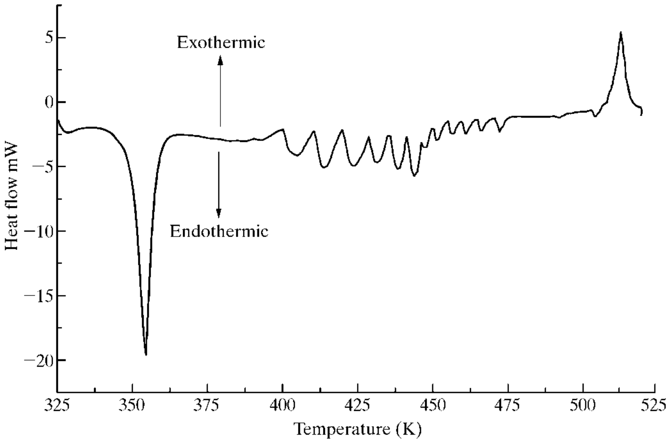

Figure 3
A DSC thermogram of a 5.8 mg sample of (I), measured at a heating rate of 10 K min^{-1}.

2.992 Å and the O—C···N bond angle is 164.9°. However, the DSC (differential scanning calorimetry) thermograph of (I) (Fig. 3) indicates that in this compound methyl rearrangement does not take place in the solid state. The first endothermic peak (at 354 K, with $\Delta H = 17.5$ kJ mol^{-1}) is attributed to the melting of the compound. The ripples at higher temperature are the result of spillage of the melt, and the exothermic peak at 512 K is assigned to methyl rearrangement in the liquid state. The melting temperature of (I) (354 K) is lower than the temperature expected (373 K) for topochemically assisted methyl rearrangement in the solid state of closely related compounds, as shown by Kaftory & Handelsman-Benory (1994), Handelsman-Benory *et al.* (2000) and Kaftory (2002); therefore, we conclude that methyl rearrangement does not take place in the solid state of (I).

Experimental

Compound (I) was prepared according to the procedure described by Cronin *et al.* (1996) and was crystallized from a 1:1 mixture of chloroform and *n*-heptane.

Crystal data

$C_5H_6ClN_3O_2$
$M_r = 175.58$
Orthorhomic, *Pbcm*
$a = 7.743$ (1) Å
$b = 14.940$ (3) Å
$c = 6.523$ (1) Å
$V = 754.6$ (2) Å^3
$Z = 4$
$D_x = 1.546$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1249 reflections
$\theta = 2.6$–25.0°
$\mu = 0.46$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.32 × 0.20 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
1249 measured reflections
726 independent reflections
493 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.075$
$S = 0.89$
726 reflections
70 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.016 (4)

During refinement, H atoms were constrained to ride on their parent atoms. The methyl H atoms are disordered over two sites with equal occupancies.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1154). Services for accessing these data are described at the back of the journal.

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