Derivatives of 2,4-dimethoxy-1,3,5-triazine

Natalya Fridman, Moshe Kapon and Menahem Kaftory*

Department of Chemistry, Technion–Israel Institute of Technology, Haifa 32000, Israel

Correspondence e-mail: kaftory@tx.technion.ac.il

The crystal structure of three derivatives of 2,4-dimethoxy-1,3,5-triazine are described. In 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)morpholine, $C_9H_{14}N_4O_3$, the morpholine moiety adopts a chair conformation, and the dimethoxytriazine molecule adopts a butterfly conformation with respect to the two methoxy groups. In 3-(4,6-dimethoxy-1,3,5-triazin-2-yloxy)-2-methylphenol, $C_{12}H_{13}N_3O_4$, the dimethoxytriazine moiety adopts a propeller conformation with respect to the methoxy groups, and the molecules form dimers held together by O—H···N hydrogen bonds. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl-oxy)phenyl phenyl ketone, $C_{18}H_{15}N_3O_4$, crystallizes with two crystallographically independent molecules in the asymmetric unit. The two molecules adopt different conformations with respect to the geometric relations between the phenyl ketone and triazine moieties.

Comment

The title compounds, *viz.* 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)morpholine, (I), 3-(4,6-dimethoxy-1,3,5-triazin-2-yloxy)-2-methylphenol, (II), and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl-oxy)phenyl phenyl ketone, (III), have been prepared and studied in order to examine their potential 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 structures of the three compounds, none of which undergo solid-state rearrangement.

(I)   (II)   (III)
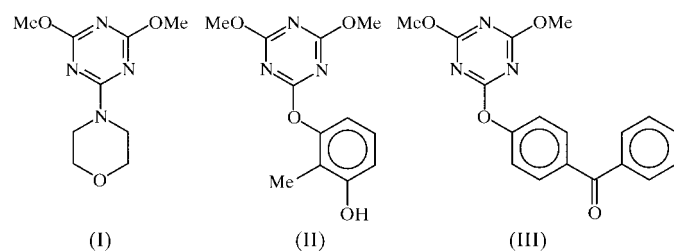
The 4,6-dimethoxy-1,3,5-triazine moiety is common to the three compounds. Comparison of the external-ring bond angles at the two methoxy groups (Table 1) shows that they

are strongly affected by the bulky methyl group, so that the bond angle at the same side as the methyl group is larger by 5–8° than the bond angle at the opposite side. A similar steric effect is also observed at the external-ring bond angle at atom C1 in each of the three structures, where the substituents are larger groups than methyl (Table 1). These two bond angles are practically equal when the substituent is morpholine [*i.e.* in (I)], because the molecule has a pseudo-mirror symmetry (Fig. 1), but the difference between the angles is ~7.7° in (III).

The molecules in (I) are packed in pairs that consist of two molecules related by an inversion center. Translation of pairs of molecules along the *a* axis forms columns, with each of the columns surrounded by four neighboring columns.

Molecules of (II) (Fig. 2) are packed as dimers formed *via* O—H···N hydrogen bonds [O4···N1 = 3.028 (2) Å and O4—H4O···N1 = 172°; Fig. 3]. The phenyl ring is almost perpendicular to the triazine moiety [C1—O3—C6—C11 = −98.1 (2)°]. The molecules of (II) are packed in such a way that the triazine planes of two neighboring molecules and the phenyl planes of two neighboring molecules are arranged face-to-face.

Compound (III) crystallizes with two crystallographically non-equivalent molecules that adopt completely different
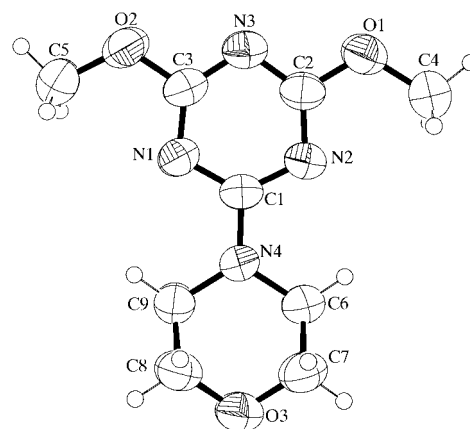

Figure 1
The molecular structure of (I). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.

Figure 2
The molecular structure of (II). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.
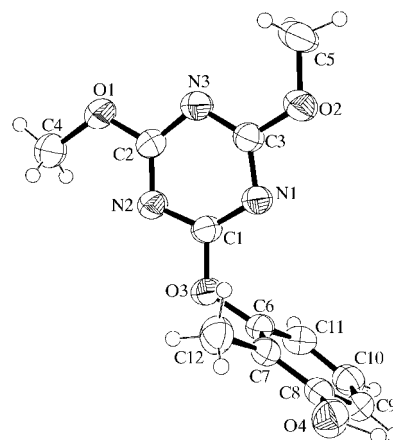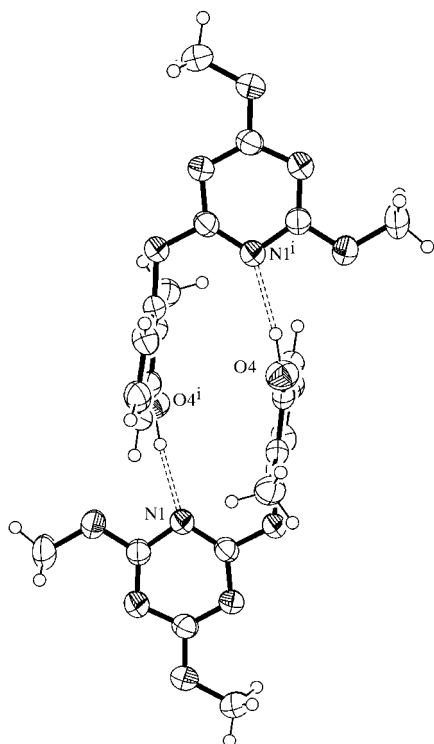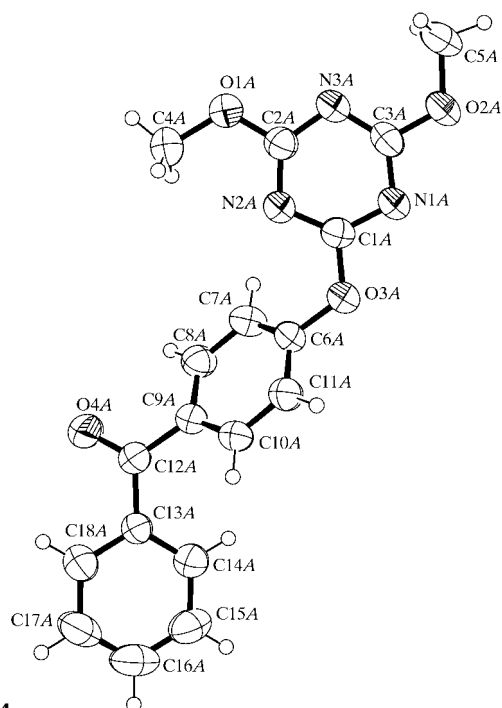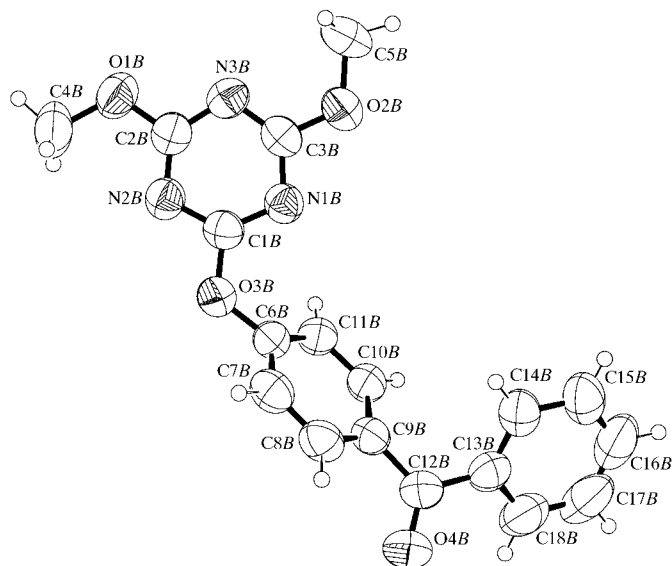
organic compounds

Figure 3
The structure of dimers of (II). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

Figure 4
The molecular structure of (III) (molecule *A*). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.

conformations (Figs. 4 and 5); molecule *A* is rod-shaped, while molecule *B* is folded. Relevant torsion angles are given in Table 2. The molecules are stacked along the *a* axis.

The morpholine moiety in (I) adopts a chair conformation, and the triazine moiety adopts a butterfly conformation with

Figure 5
The molecular structure of (III) (molecule *B*). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.

respect to the two methoxy groups, as was found in 2-(4′-nitroanilino)-4,6-dimethoxy-1,3,5-triazine (Taycher *et al.*, 2001). The same moiety in (II) and (III) adopts a propeller conformation. The torsion angles are given in Table 2.

Experimental

Compound (I) was prepared according to the procedure described by Kunishima and co-workers (Kunishima, Kaeachi, Iwasaki *et al.*, 1999; Kunishima, Kaeachi, Morita *et al.*, 1999). Crystals suitable for X-ray diffraction were grown from a methanol solution. For the preparation of compound (II), a solution (10 mmol) of sodium hydroxide (0.2 g, 5 mmol) in methanol was heated to 313 K. A solution of 2,2′-(2-methyl-1,3-phenylenedioxy)bis(4,6-dichloro-1,3,5-triazine) (0.84 g, 2 mmol) in tetrahydrofuran (10 ml) was added and the resulting mixture was refluxed at 353 K for 1.5 h. The mixture was diluted with water (20 ml), and the solution was treated with ether (15 ml) in order to extract the product. The solution was dried over $MgSO_4$ and the resulting mixture was allowed to stand for 2 h. The ether extract was filtered and concentrated to dryness *in vacuo*, and the product was obtained in 96% yield. Crystals suitable for X-ray diffraction were grown from a solution (1:1) of ethyl acetate and methanol. Compound (III) was prepared according to the procedure described by Yonehara *et al.* (1994). Crystals suitable for X-ray diffraction were grown from a mixture (1:1) of methanol and methylene chloride.

Compound (I)

Crystal data

$C_9H_{14}N_4O_3$	$D_x = 1.391$ Mg m^{-3}
$M_r = 226.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2944
$a = 10.244$ (2) Å	reflections
$b = 9.208$ (3) Å	$\theta = 2.5$–25.0°
$c = 11.615$ (3) Å	$\mu = 0.11$ mm^{-1}
$\beta = 99.70$ (3)°	$T = 293$ (2) K
$V = 1079.9$ (5) Å^3	Needle, colorless
$Z = 4$	$0.33 \times 0.15 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.060$
φ scans	$\theta_{max} = 25.0°$
2944 measured reflections	$h = -12 \rightarrow 11$
1799 independent reflections	$k = -9 \rightarrow 10$
883 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2]$
$wR(F^2) = 0.159$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{max} = 0.001$
1799 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
147 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}

Compound (II)

Crystal data

$C_{12}H_{13}N_3O_4$	$Z = 2$
$M_r = 263.25$	$D_x = 1.409$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.386$ (2) Å	Cell parameters from 2195
$b = 9.718$ (2) Å	reflections
$c = 9.868$ (2) Å	$\theta = 2.2–25.1°$
$\alpha = 108.73$ (2)°	$\mu = 0.11$ mm^{-1}
$\beta = 93.36$ (2)°	$T = 293$ (2) K
$\gamma = 109.67$ (2)°	Plate, colorless
$V = 620.5$ (3) Å^3	$0.45 \times 0.30 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer	$\theta_{max} = 25.1°$
φ scans	$h = 0 \rightarrow 8$
2195 measured reflections	$k = -11 \rightarrow 10$
2195 independent reflections	$l = -11 \rightarrow 11$
1496 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.129$	$(\Delta/\sigma)_{max} = 0.033$
$S = 1.03$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
2195 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}
180 parameters	Extinction correction: *SHELXL*97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.147 (19)

Compound (III)

Crystal data

$C_{18}H_{15}N_3O_4$	$D_x = 1.351$ Mg m^{-3}
$M_r = 337.33$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 11 206
$a = 32.610$ (6) Å	reflections
$b = 13.757$ (3) Å	$\theta = 1.3–25.1°$
$c = 15.904$ (3) Å	$\mu = 0.10$ mm^{-1}
$\beta = 111.56$ (2)°	$T = 293$ (2) K
$V = 6636$ (2) Å^3	Prism, colorless
$Z = 16$	$0.60 \times 0.30 \times 0.27$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.028$
φ scans	$\theta_{max} = 25.1°$
11 206 measured reflections	$h = -38 \rightarrow 38$
5860 independent reflections	$k = -16 \rightarrow 15$
3022 reflections with $I > 2\sigma(I)$	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.85$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
5860 reflections	$\Delta\rho_{min} = -0.14$ e Å^{-3}
456 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0043 (3)

H atoms were located from difference Fourier maps. The position of the hydroxy H atom in (II) was refined freely. All other H atoms were constrained to ride on their parent atoms.

For all compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997).

Table 1
Comparison of selected bond angles (°).

	(I)	(II)	(III*A*)	(III*B*)
O1—C2—N3	113.3 (3)	113.8 (2)	113.7 (2)	113.0 (2)
O2—C3—N3	113.7 (3)	119.7 (2)	119.4 (2)	120.1 (2)
O1—C2—N2	118.7 (3)	119.1 (2)	119.1 (2)	119.5 (2)
O2—C3—N1	118.1 (3)	112.8 (2)	113.0 (2)	112.3 (2)
N2—C1—C4	117.6 (3)	111.8 (2)	118.8 (2)	112.0 (2)
N1—C1—C4	117.8 (3)	120.5 (2)	–	–
N2—C1—O3	–	–	118.8 (2)	112.0 (2)
N1—C1—O3	–	–	112.6 (2)	119.7 (2)

Table 2
Comparison of selected torsion angles (°).

	(I)	(II)	(III*A*)	(III*B*)
N2—C2—O1—C4	−2.3 (4)	175.7 (2)	3.8 (2)	−4.7 (2)
N1—C3—O2—C5	−2.7 (5)	1.0 (2)	−176.5 (2)	178.5 (2)
N1—C1—N4—C9	0.3 (5)	–	–	–
(N1—C1—O3—C6)	–	3.5 (2)	169.6 (2)	−0.9 (3)
C1—O3—C6—C11	–	−98.1 (2)	140.5 (2)	59.4 (3)

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Greenberg, M., Shteiman, V. & Kaftory, M. (2001). *Acta Cryst.* B**57**, 428–434.

Handelsman-Benory, E., Botoshansky, M., Greenberg, M., Shteiman, V. & Kaftory, M. (2000). *Tetrahedron*, **56**, 6887–6897.

Kaftory, M. (2002). *Organic Solid State Reaction*, edited by F. Toda, pp. 47–67. Dordrecht: Kluwer Academic Publishers.

Kaftory, M., Botoshansky, M., Kapon, M. & Shteiman, V. (2001). *Acta Cryst.* B**57**, 791–799.

Kaftory, M. & Handelsman-Benory, E. (1994). *Mol. Cryst. Liq. Cryst.* **240**, 241–249.

Kunishima, M., Kaeachi, C., Iwasaki, F., Terao, K. & Tani, S. (1999). *Tetrahedron Lett.* **40**, 5327–5330.

Kunishima, M., Kaeachi, C., Morita, J., Terao, K., Iwasaki, F. & Tani, S. (1999). *Tetrahedron*, **55**, 13159–13170.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Taycher, H., Botoshanski, M., Shteiman, V. & Kaftory, M. (2001). *Supramol. Chem.* **13**, 181–192.

Yonehara, H., Kang, W.-B., Kawara, T. & Pac, C. (1994). *J. Mater. Chem.* **4**, 1571–1577.