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4,6-Dimethoxy-3-methyl-1,3,5-triazin-2(3*H*)-one and 6-Methoxy-3,5-dimethyl-1,3,5-triazine-2,4(3*H*,5*H*)-dione

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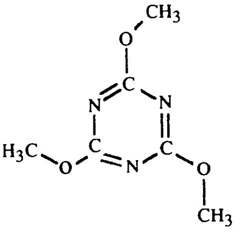
Abstract

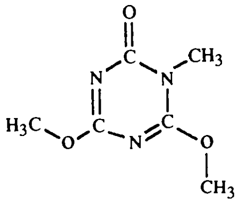
2,4,6-Trimethoxy-1,3,5-triazine, (I), undergoes methyl transfer in a few stages to 1,3,5-trimethyl-2,4,6-trioxohexahydro-*s*-triazine, (IV). The crystal structures of the two intermediates, 4,6-dimethoxy-3-methyl-1,3,5-triazin-2(3*H*)-one, (II) ($C_6H_9N_3O_3$), and 6-methoxy-3,5-dimethyl-1,3,5-triazine-2,4(3*H*,5*H*)-dione, (III) ($C_6H_9N_3O_3$), are described. Molecules of (II) form a layer structure made up of infinite ribbons. Molecules of (III) related by an inversion centre are arranged in pairs.

Comment

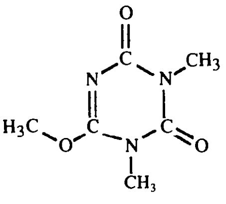
More than 120 years ago Hoffman & Olshausen (1870), and later Klason (1885), gathered evidence that alkyl derivatives of cyanuric acid and its thio analogues undergo alkyl migration. By the end of the 1960's the rearrangement of methyl groups in these systems had been investigated by Tosato and co-workers (Paolini, Tosato & Cignitti, 1968; Tosato, 1979, 1982, 1984). The lack of topochemical studies prompted us to study the crystal structures and the thermal behaviour of the four different compounds (I)–(IV) involved in the methyl rearrangement (Kaftory & Handelsman-Benory, 1994). The crystal structures of (I) (Glowka & Iwanicka, 1989) and (IV) (Belaj & Nachbaur, 1987) have been published; we describe here the crystal structures of (II) and (III).



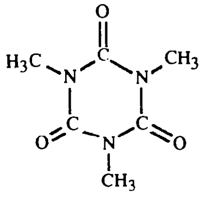
(I)



(II)



(III)



(IV)

In many aspects the crystal structure of (II) resembles the crystal structure of (I). However, the asymmetric unit of (II) consists of two independent molecules and there are pseudosymmetry elements such as an inversion centre and rotation/screw axis in the crystal structure. The possibility of a higher symmetric space group was eliminated after a careful check of the intensities. The relatively high *R* value (0.078) obtained for (III) is due to the instability of the crystal, for which the intensities decayed by 9.4% during the intensity measurements.

Both molecules (II) and (III) are planar and display bond lengths and angles comparable with those described for (I) and (IV). The most interesting structural feature of both compounds is their packing arrangement. The packing is strongly dependent on special intermolecular $H_3CO\cdots N$(lone-pair electrons) interactions. This type of interaction effects the packing in the same way as hydrogen bonds. Compound (II) forms a planar ribbon structure consisting of molecules arranged in infinite trimers made up by interactions between lone-pair electrons of one molecule and

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the H atoms of the methoxy group of a second molecule (see Fig. 1). The range of intermolecular short distances is 3.574–3.615 (5) Å, and the range of the N···C—O angles is 129.0–143.1 (3)°. It should also be noted that there are weak interactions between the methyl C atom of a methoxy group and either a carbonyl O atom or an O atom of another methoxy group of a second molecule. The range of the O—C···O═C and the O—C···O—C distances is 3.234–3.530 (5) Å.

Compound (III) has a single methoxy group and a single N-atom lone pair of electrons available for the intermolecular interaction. The resulting structure is very similar to that found in carboxylic acids, namely the formation of dimers. Fig. 2 shows a dimer formed by (III) and held by this type of weak hydrogen bond, with a short N···CH_3 distance [3.387 (6) Å] and short O—C···O═C distance of 3.364 (6) Å. Although the distances mentioned above do not indicate very strong hydrogen-bond interactions, they play an important role in determining the structure.

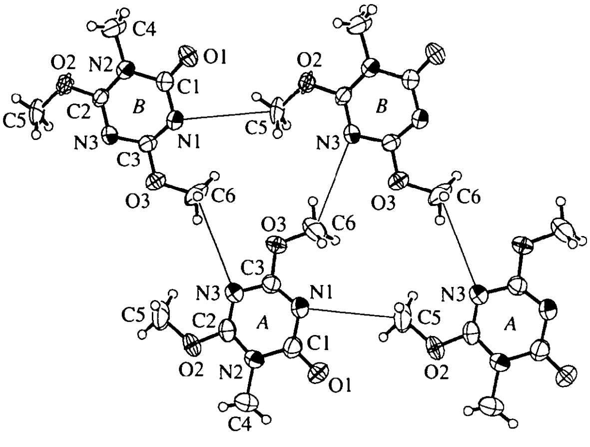

Fig. 1. Trimer arrangement in the crystal structure of (II). The displacement ellipsoids are drawn at the 50% probability level.

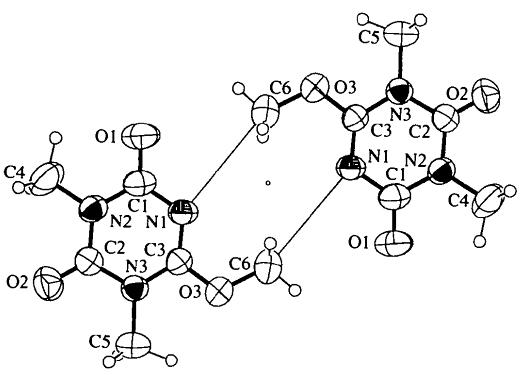

Fig. 2. Dimer arrangement in the crystal structure of (III). The displacement ellipsoids are drawn at the 50% probability level.

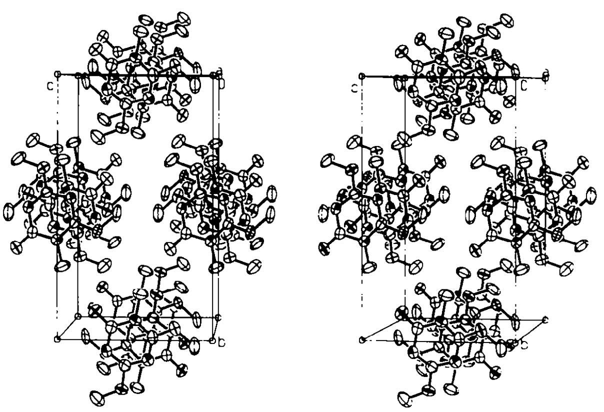

Fig. 3. Stereoscopic view of the packing of molecules of (II).

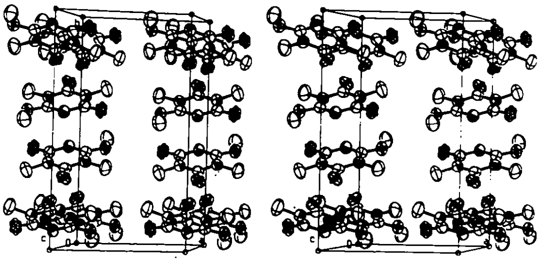

Fig. 4. Stereoscopic view of the packing of molecules of (III).

Experimental

The title compounds were synthesized according to Paolini, Tosato & Cignitti (1968)

Compound (II)

Crystal data

$C_6H_9N_3O_3$
$M_r = 171.16$
Monoclinic
$P2_1/n$
$a = 13.529\,(8)$ Å
$b = 14.323\,(8)$ Å
$c = 8.447\,(4)$ Å
$\beta = 91.93\,(2)°$
$V = 1635.9\,(4)$ Å^3
$Z = 8$
$D_x = 1.390$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.8$–$14.6°$
$\mu = 0.113$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.4 × 0.1 × 0.1 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3061 measured reflections
2863 independent reflections
1698 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.02$
$\theta_{\rm max} = 25.0°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.160$
$S = 1.064$
2863 reflections
289 parameters
H-atom parameters refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.1732P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.095$
$\Delta\rho_{\max} = 0.231$ e Å^{-3}
$\Delta\rho_{\min} = -0.176$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Molecule *A*				
O1*A*	0.1202 (3)	0.9025 (2)	0.7724 (3)	0.082 (1)
O2*A*	0.1223 (2)	0.9655 (2)	0.2505 (3)	0.066 (1)
O3*A*	0.1561 (2)	1.2031 (2)	0.6014 (3)	0.062 (1)
N1*A*	0.1364 (2)	1.0560 (2)	0.7004 (3)	0.051 (1)
N2*A*	0.1178 (2)	0.9339 (2)	0.5093 (3)	0.048 (1)
N3*A*	0.1406 (2)	1.0886 (2)	0.4240 (3)	0.050 (1)
C1*A*	0.1247 (3)	0.9618 (3)	0.6691 (4)	0.053 (1)
C2*A*	0.1275 (2)	1.0000 (3)	0.3963 (4)	0.046 (1)
C3*A*	0.1436 (3)	1.1111 (2)	0.5793 (4)	0.045 (1)
C4*A*	0.1055 (4)	0.8335 (3)	0.4731 (7)	0.070 (1)
C5*A*	0.1298 (5)	1.0340 (5)	0.1214 (5)	0.081 (2)
C6*A*	0.1582 (5)	1.2388 (4)	0.7633 (6)	0.081 (2)
Molecule *B*				
O1*B*	0.1011 (3)	0.6561 (2)	1.2802 (3)	0.090 (1)
O2*B*	0.1125 (2)	0.5914 (2)	0.7594 (3)	0.058 (1)
O3*B*	0.1445 (2)	0.3554 (2)	1.1123 (3)	0.061 (1)
N1*B*	0.1234 (2)	0.5031 (2)	1.2091 (3)	0.050 (1)
N2*B*	0.1078 (2)	0.6243 (2)	1.0172 (3)	0.046 (1)
N3*B*	0.1284 (2)	0.4684 (2)	0.9328 (3)	0.046 (1)
C1*B*	0.1102 (3)	0.5964 (3)	1.1780 (4)	0.052 (1)
C2*B*	0.1166 (2)	0.5585 (2)	0.9051 (4)	0.043 (1)
C3*B*	0.1315 (2)	0.4474 (2)	1.0889 (4)	0.042 (1)
C4*B*	0.0963 (5)	0.7253 (3)	0.9803 (7)	0.066 (1)
C5*B*	0.1219 (4)	0.5239 (4)	0.6306 (5)	0.072 (1)
C6*B*	0.1495 (5)	0.3227 (4)	1.2768 (6)	0.072 (1)

Table 2. *Selected geometric parameters* (Å, °) *for* (II)

	Molecule *A*	Molecule *B*
O1—C1	1.221 (4)	1.225 (4)
O2—C2	1.327 (4)	1.317 (4)
O2—C5	1.473 (6)	1.464 (5)
O3—C3	1.340 (4)	1.343 (4)
O3—C6	1.460 (5)	1.465 (5)
N1—C3	1.299 (4)	1.299 (4)
N1—C1	1.383 (5)	1.372 (4)
N2—C2	1.354 (4)	1.344 (4)
N2—C1	1.408 (5)	1.415 (4)
N2—C4	1.479 (5)	1.487 (5)
N3—C2	1.301 (4)	1.319 (4)
N3—C3	1.350 (4)	1.353 (4)
C2—O2—C5	115.8 (4)	117.2 (3)
C3—O3—C6	118.3 (3)	117.1 (3)
C3—N1—C1	117.0 (3)	117.5 (3)
C2—N2—C1	118.2 (3)	118.6 (3)
C2—N2—C4	123.2 (4)	123.1 (3)
C1—N2—C4	118.5 (4)	118.3 (3)
C2—N3—C3	114.0 (3)	113.0 (3)
O1—C1—N1	123.4 (4)	124.1 (3)
O1—C1—N2	119.0 (3)	118.7 (3)
N1—C1—N2	117.6 (3)	117.2 (3)
N3—C2—O2	122.2 (3)	121.1 (3)
N3—C2—N2	124.8 (3)	113.9 (3)
O2—C2—N2	113.0 (3)	125.0 (3)
N1—C3—O3	120.0 (3)	120.1 (3)
N1—C3—N3	128.3 (3)	128.7 (3)
O3—C3—N3	111.7 (3)	111.2 (3)

Compound (III)

Crystal data

$C_6H_9N_3O_3$
$M_r = 171.16$
Monoclinic
$P2_1/c$
$a = 8.362$ (4) Å
$b = 14.356$ (8) Å
$c = 7.168$ (4) Å
$\beta = 114.41$ (2)°
$V = 783.5$ (4) Å^3
$Z = 4$
$D_x = 1.450$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 2.6$–10.6°
$\mu = 0.118$ mm^{-1}
$T = 293$ (2) K
Pseudo-cube
0.2 × 0.2 × 0.2 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1304 measured reflections
1191 independent reflections
752 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.03$
$\theta_{\max} = 22.0°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 15$
$l \Rightarrow 0 \rightarrow 6$
3 standard reflections
frequency: 120 min
intensity decay: 9.4% (corrected)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.078$
$wR(F^2) = 0.167$
$S = 1.130$
1191 reflections
145 parameters
H-atom parameters refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.1116P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.445$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (III)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
O1	−0.3178 (3)	0.0850 (2)	−0.3214 (5)	0.089 (1)
O2	0.0501 (4)	0.2046 (2)	0.2909 (4)	0.077 (1)
O3	0.2725 (3)	0.0742 (2)	−0.1199 (4)	0.068 (1)
N1	−0.0250 (3)	0.0735 (2)	−0.2313 (4)	0.058 (1)
N2	−0.1388 (3)	0.1439 (2)	−0.0138 (5)	0.057 (1)
N3	0.1641 (3)	0.1351 (2)	0.0898 (4)	0.052 (1)
C1	−0.1678 (4)	0.0991 (2)	−0.1973 (6)	0.061 (1)
C2	0.0252 (4)	0.1646 (2)	0.1322 (6)	0.054 (1)

C3	0.1283 (4)	0.0934 (2)	−0.0941 (5)	0.051 (1)
C4	−0.2889 (7)	0.1775 (4)	0.0221 (11)	0.089 (1)
C5	0.3413 (5)	0.1576 (4)	0.2350 (8)	0.077 (1)
C6	0.2480 (7)	0.0376 (4)	−0.3189 (8)	0.080 (1)

Table 4. *Selected geometric parameters* (Å, °) *for* (III)

O1—C1	1.218 (4)	N2—C2	1.370 (4)
O2—C2	1.213 (4)	N2—C1	1.392 (5)
O3—C3	1.323 (4)	N2—C4	1.464 (5)
O3—C6	1.453 (5)	N3—C3	1.364 (5)
N1—C3	1.284 (4)	N3—C2	1.382 (4)
N1—C1	1.365 (5)	N3—C5	1.452 (5)
C3—O3—C6	116.5 (3)	O1—C1—N2	119.5 (3)
C3—N1—C1	118.2 (3)	N1—C1—N2	118.0 (3)
C2—N2—C1	123.4 (3)	O2—C2—N2	123.3 (3)
C2—N2—C4	117.0 (4)	O2—C2—N3	121.1 (3)
C1—N2—C4	119.4 (4)	N2—C2—N3	115.6 (3)
C3—N3—C2	118.6 (3)	N1—C3—O3	121.7 (3)
C3—N3—C5	122.8 (3)	N1—C3—N3	126.1 (3)
C2—N3—C5	118.4 (3)	O3—C3—N3	112.2 (3)
O1—C1—N1	122.5 (4)		

For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993).

This research was partially supported by Technion V. P. R. Fund – E. and M. Mendelson Research Fund, and by the Fund for the Promotion of Research at the Technion.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 2424–2426

5,5-Dimethyl-1,3-dioxacyclohexane-2-spiro(2′,γ-dimethyl-3′-oxo-2′-cyclohexaneacrylic Acid)

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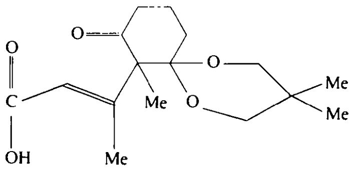
(*Received* 19 *December* 1994; *accepted* 24 *April* 1995)

Abstract

The cyclohexanone ring in the title compound, $C_{16}H_{24}O_5$, adopts a chair conformation with the methyl and acrylic acid groups in axial and equatorial positions, respectively. The dihedral angle between the planes of the two rings is 73 (1)°. The bond angles around the spiro C atom are all nearly tetrahedral [104.8 (2)–113.0 (2)°].

Comment

With the aim of elucidating the influence of the spiro C atom on ring-skeleton conformation, we have examined the conformation of several cyclohexanone-2-methylacrylic acid derivatives; the results of the X-ray analysis of one of these derivatives, (I), is reported here.



(I)

The two mean ring planes form a dihedral angle of 73°; the least-squares planes calculation indicates that the two rings are not individually planar. Following the Cremer & Pople (1975) notation, the ring-puckering parameters for the cyclohexanone ring are Q_2