Acta Cryst. (1989). C**45**, 1765–1767

Structure of 2,4,6-Trimethoxy-1,3,5-triazine

BY MAREK L. GŁÓWKA AND IWONA IWANICKA

Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90-924 *Łódź, Poland*

(*Received* 6 *February* 1989; *accepted* 23 *March* 1989)

Abstract. $C_6H_9N_3O_3$, $M_r = 171{\cdot}2$, orthorhombic, *Pnma*, $a = 8{\cdot}474$ (2), $b = 6{\cdot}719$ (1), $c = 14{\cdot}409$ (2) Å, $V = 820{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}39$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}11$ mm^{-1}, $F(000) = 360$. The structure was solved by direct methods and refined to $R = 0{\cdot}050$ for 577 unique X-ray diffractometer data. Delocalization of the *s*-triazine π electrons ranges over adjacent O atoms resulting in the formation of a planar 2,4,6-trimethoxy-1,3,5-triazine system with stacking of triazine rings lying in the mirror planes at $\frac{1}{4}$ and $\frac{3}{4}b$ levels.

Introduction. *s*-Triazines are easily prepared from 2,4,6-trichloro derivatives, which in turn are industrially synthesized by trimerization of cyanogen chloride (Smolin & Rapoport, 1959). The Cl atoms are very reactive and they may be substituted by desirable groups. The other convenient *s*-triazine substrate is the less reactive 2,4,6-trimethoxy-*s*-triazine. A characteristic feature of this compound is its rapid isomerization to 1,3,5-trimethyl-2,4,6-trioxohexahydro-*s*-triazine. Comparing methoxy-*s*-triazine derivatives with their benzene analogues, considerable differences in electron distribution and spatial orientation of substituents were noticed (Główka, Iwanicka & Kamiński, 1989) which may also explain differences in methoxy-group behaviour. This study was undertaken as part of a wider project on the crystallography of triazines and, in particular, on the structure of methoxy groups joined to the triazine system.

Experimental. A single crystal ($0{\cdot}40 \times 0{\cdot}32 \times 0{\cdot}28$ mm) was used for data collection and accurate cell determination on a CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell parameters were obtained from least squares refinement of 25 reflections in the θ range 8 to 16°. 780 independent intensities [577 considered observed with $I > 4\sigma(I)$] were measured with the $\omega/2\theta$ scan technique ($\theta_{max} = 25°$, $h_{max} = 10$, $k_{max} = 7$, $l_{max} = 17$). Three standard reflections monitored during data collection did not show significant variations in intensity. No correction for absorption was applied.

The structure was solved by direct methods (*SHELXS*86, Sheldrick, 1986) and refined by full-matrix least squares on F (*SHELX*76, Sheldrick, 1976) with anisotropic temperature factors for non-H and isotropic ones for H atoms. The largest Δ/σ in the final cycle was 0·04. Final $R = 0{\cdot}050$, $wR = 0{\cdot}055$, $S = 0{\cdot}33$. The weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}05F^2$ was used. The final difference Fourier map showed no peaks above 0·15 e Å^{-3}. All calculations were performed on an Amstrad 1512 microcomputer. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic coordinates and equivalent isotropic temperature factors are presented in Table 1,* while bond distances and angles are given in Table 2. The atom-numbering system and a general view of the molecule are shown in Fig. 1.

The N—C bond lengths in the triazine ring range from 1·311 to 1·344 Å and the average endocyclic angles at the N and C atoms are 113·3 and 126·8°, respectively. Such differentiation of bonds and angles in the triazine ring is characteristic of the *s*-triazine system and has been observed earlier (Graham, Akrigg & Sheldrick, 1977, 1978*a*,*b*; Reck & Jankowsky, 1981; Reck, Bannier, Just & Goldhahn, 1985).

The torsion angle *X*—C—O—C describes the orientation of the methoxy group in relation to the planar aromatic system (X = N in the case of *s*-triazines). The conjugation of the lone-pair electrons at the O atom with the ring π electrons causes the methoxy group to be coplanar with the adjacent aromatic ring. However, in methoxybenzenes the torsion angle is usually about 10° due to repulsion between the methyl group and an *ortho*-H atom. Introduction of bulky groups in two *ortho* positions forces the methoxy group to adopt a perpendicular orientation {for example, in 7,8-dimethoxybenzo[*j*]-fluoranthene these angles are 73 and 82° (Briant & Jones, 1987), and 83° in *exo*-2,3-dimethoxy-*N*-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52032 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/89/111765-03$03.00

Table 1. *Final positional and equivalent isotropic temperature parameters for non-*H *atoms with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}(a^{*2}B_{11} + \ldots + b^*c^*B_{23}\cos\alpha^*)$.

	x	y	z	B_{eq}(Å^2)
O(4)	0·6639 (3)	0·25	0·5373 (2)	5·82 (7)
N(1)	1·1217 (3)	0·25	0·4818 (1)	3·95 (6)
O(2)	1·1698 (3)	0·25	0·6342 (1)	4·90 (6)
O(6)	1·0566 (3)	0·25	0·3271 (2)	4·67 (6)
N(5)	0·8575 (3)	0·25	0·4278 (2)	3·97 (7)
N(3)	0·9115 (3)	0·25	0·5895 (2)	4·06 (6)
C(6)	1·0144 (3)	0·25	0·4159 (2)	3·53 (6)
C(4)	0·8154 (4)	0·25	0·5153 (2)	3·96 (7)
C(2)	1·0615 (4)	0·25	0·5671 (2)	3·65 (7)
C(60)	1·2225 (5)	0·25	0·3084 (2)	6·11 (12)
C(40)	0·5528 (5)	0·25	0·4606 (3)	7·89 (15)
C(20)	1·1124 (6)	0·25	0·7287 (2)	5·79 (11)

Table 2. *Bond lengths* (Å) *and angles* (°) *for non-*H *atoms*

O(4)—C(4)	1·322 (4)	C(4)—O(4)—C(40)	116·6 (3)
O(4)—C(40)	1·452 (5)	C(6)—N(1)—C(2)	113·7 (3)
N(1)—C(6)	1·315 (3)	C(2)—O(2)—C(20)	116·8 (3)
N(1)—C(2)	1·331 (3)	C(6)—O(6)—C(60)	116·5 (3)
O(2)—C(2)	1·333 (4)	C(6)—N(5)—C(4)	113·2 (3)
O(2)—C(20)	1·446 (4)	C(4)—N(3)—C(2)	113·1 (3)
O(6)—C(6)	1·329 (4)	O(6)—C(6)—N(5)	113·0 (3)
O(6)—C(60)	1·431 (5)	N(1)—C(6)—N(5)	126·4 (3)
N(5)—C(6)	1·341 (4)	N(1)—C(6)—O(6)	120·6 (2)
N(5)—C(4)	1·310 (4)	N(5)—C(4)—N(3)	126·9 (3)
N(3)—C(4)	1·344 (4)	O(4)—C(4)—N(3)	113·4 (3)
N(3)—C(2)	1·311 (4)	O(4)—C(4)—N(5)	119·7 (3)
		O(2)—C(2)—N(3)	119·3 (3)
		N(1)—C(2)—N(3)	126·8 (3)
		N(1)—C(2)—O(2)	114·0 (3)

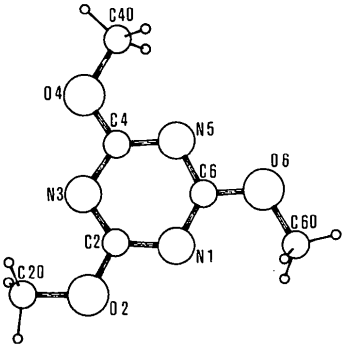

Fig. 1. General view of the molecule with numbering scheme.

(9-phenylmethyl-9-azobicyclo[3.3.1]non-3-yl)benzamide (Collin, Evrard & Durant, 1987)}. The result is a lengthening of the C(sp^2)—O bond (from about 1·65 to 1·78 Å) as the conjugation effect is diminished. The situation is different in methoxy-*s*-triazines owing to the presence of an N atom with a lone pair instead of a C atom with at least one H atom in the *ortho* position and therefore the N—C—O—C torsion angles are 2·5° in 2,4-bis-(isopropylamino)-6-methoxy-*s*-triazine (Graham, Akrigg & Sheldrick, 1977), 1·0° in 2,4-bis(ethyl-

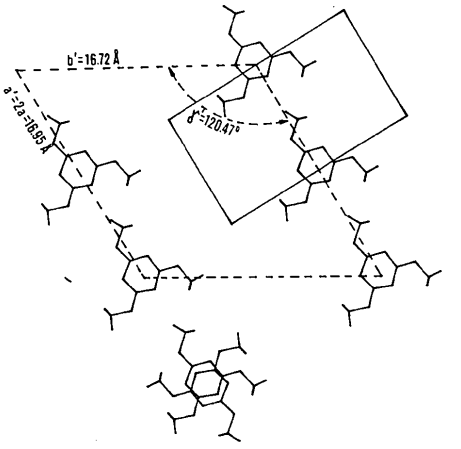

Fig. 2. Pseudotrigonal arrangement of molecules in the orthorhombic unit cell ($\frac{1}{4}$ level shown only). The stacking is shown for the bottom left molecule.

amino)-6-methoxy-*s*-triazine (Graham, Akrigg & Sheldrick, 1978*a*,*b*), 0·7 and 1·8° in 2-(2,2-dimethylpropanoyloxy)-4,6-dimethoxy-1,3,5-triazine (Główka, Iwanicka & Kamiński, 1989), and 2·1 and 2·6° in 2-cyclohexylamino-4,6-dimethoxy-1,3,5-triazine (Główka & Iwanicka, 1989). In this structure the angle is 0° owing to a special position of the molecule.

The flat molecules of 2,4,6-trimethoxy-1,3,5-triazine form in the crystal molecular layers at $\frac{1}{4}$ and $\frac{3}{4}b$ levels (*i.e.* the molecules lie in the mirror planes) each being $b/2 = 3{\cdot}36$ Å from the others. There is almost perfect stacking of molecules from successive layers related by a centre of symmetry (Fig. 2). All three methoxy groups are turned in the same direction so that the molecule has 3/*m* molecular symmetry. Also, the unit cell may be transformed into an approximate trigonal space group, but there is a significant difference between a' and b' dimensions of the pseudotrigonal cell and the γ angle differs from 120° (Fig. 2). X-ray photographs confirm the orthorhombic space group.

We thank the Ministry of National Education for financial support under project RP.II.10 and Dr Z. J. Kamiński from the Institute of Organic Chemistry, Technical University of Łódź, for providing us with the crystals.

References

Briant, C. E. & Jones, D. W. (1987). *Acta Cryst.* C**43**, 775–778.
Collin, S., Evrard, G. & Durant, F. (1987). *Acta Cryst.* C**43**, 697–699.
Główka, M. L. & Iwanicka, I. (1989). *Acta Cryst.* C**45**, 1762–1764.
Główka, M. L., Iwanicka, I. & Kamiński, Z. J. (1989). *Acta Cryst.* Submitted.
Graham, A. J., Akrigg, D. & Sheldrick, B. (1977). *Cryst. Struct. Commun.* **6**, 281–286.

GRAHAM, A. J., AKRIGG, D. & SHELDRICK, B. (1978*a*). *Cryst. Struct. Commun.* **7**, 227–232.
GRAHAM, A. J., AKRIGG, D. & SHELDRICK, B. (1978*b*). *Cryst. Struct. Commun.* **7**, 473–479.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
RECK, G., BANNIER, G., JUST, M. & GOLDHAHN, F. (1985). *Cryst. Res. Technol.* **20**, 1341–1344.
RECK, G. & JANKOWSKY, W. (1981). *Cryst. Struct. Commun.* **10**, 111–115.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELXS*86. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.
SMOLIN, E. M. & RAPOPORT, L. (1959). *s-Triazines and Derivatives*. New York: Interscience.

Acta Cryst. (1989). C**45**, 1767–1770

The Stereochemistry of the Phosphorus–Selenium Bond. VII.* Structure of 5,5-Dimethyl-2-(*o*-nitrophenyl)amino-1,3,2-dioxaphosphorinane 2-Selenide

BY WOJCIECH M. WOLF† AND TADEUSZ J. BARTCZAK

Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90-924 *Łódź, Poland*

(*Received* 19 *January* 1989; *accepted* 22 *February* 1989)

Abstract. $C_{11}H_{15}N_2O_4PSe$, $M_r = 349{\cdot}2$, monoclinic, $P2_1/c$, $a = 10{\cdot}204$ (3), $b = 19{\cdot}891$ (3), $c = 6{\cdot}823$ (3) Å, $\beta = 94{\cdot}41$ (3)°, $U = 1380{\cdot}8$ Å^3, $Z = 4$, $D_m = 1{\cdot}66$, $D_x = 1{\cdot}68$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}05$ mm^{-1}, $F(000) = 704$, room temperature, $R = 0{\cdot}026$ for 1755 observed reflections [$I > 3\sigma(I)$]. The dioxaphosphorinane ring adopts a flattened chair conformation with P=Se and P—N bonds in equatorial and axial positions respectively. The properties of the molecule are mainly governed by anomeric interactions between endocyclic oxygen lone pairs and antibonding orbitals of the axial P—N bond.

Introduction. Numerous organothiophosphorus compounds are powerful inhibitors of cholinoesterase. Certain organothiophosphorus compounds are effective and relatively safe pesticides produced industrially.

However, very little is known about toxicity and biological activity of the corresponding seleno compounds. Some organoselenophosphorus compounds as described by Åkerfeldt & Fagerlind (1967) are among the most toxic phosphorus compounds, with LD_{50} values ranging from 0·02 to 0·06 mg kg^{-1} when injected subcutaneously into mice. They are more toxic than corresponding sulfur analogs. Their toxicity is due to the ability to inhibit cholinoesterase, as has been shown in tests with human erythrocyte enzyme (Michalski & Markowska, 1973, and references cited therein). The different biological activities of selenophosphorus and thiophosphorus analogues are presumably caused by very subtle differences between the characters of phosphorus–selenium and phosphorus–sulfur bonds. As has been shown by McFarlane & Rycroft (1972), Grim & Walton (1980) and confirmed recently by Allen & Taylor (1986) these bonds may be described by a resonance hybrid of two canonical forms: —P=*X* and —P$^+$—*X*$^-$ (where *X* = Se or S). The real structure depends on the ability of the substituents at phosphorus to be involved in p_π–d_π interactions with phosphorus orbitals. In 2-amino-1,3,2-dioxaphosphorinanes these interactions are in equilibrium with stereoelectronic effects which outweigh the usual steric interactions and are responsible for the main conformational properties of the molecule (Wolf, 1988). Therefore careful analyses of the whole pattern of conformational deformations in a large group of 2-seleno-2-amino-1,3,2-dioxaphosphorinanes as well as in their thio analogues may give valuable indications to the real nature of the phosphorus–selenium bonds in these compounds. For this reason, the title compound (1) was synthesized and its structure determined. Structural features of this compound are discussed in comparison with those reported for *cis*-2-*tert*-butylamino-4-methyl-1,3,2-dioxaphosphorinane 2-selenide (2) (Bartczak, Christensen, Kinas & Stec, 1975), 5,5-dimethyl-2-ethylamino-1,3,2-dioxaphosphorinane 2-selenide (3) (Bartczak, Gałdecki, Wolf, Lesiak & Stec, 1986), *trans*-2-*tert*-butylamino-4-methyl-1,3,2-dioxaphosphorinane 2-selenide (4) (Bartczak, Christensen, Kinas & Stec, 1976), 2-(3,5-dichloroanilino)-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-selenide (5) (Bartczak & Wolf, 1983) and 2-anilino-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-selenide (6) (Bartczak, Gałdecki, Trzeźwińska & Wolf, 1983). In all the

* Part VI: Bartczak, Wolf, Swepston & Zerong (1987).
† Author to whom all correspondence should be addressed.

0108-2701/89/111767-04$03.00