

Fig. 2. Relationships between Cl-triazine bond length and endocyclic N—C—N angle. The points shown refer to: 1 CCMT; 2 CMPT; 3 2-chloro-4-dimethylamino-6-triphenylphosphoranylideneamino-1,3,5-triazine (Cameron, Mannan, Biddlestone & Shaw, 1975); 4 and 5 2-(*N'*-acetylhydrazino)-4,6-dichloro-1,3,5-triazine (Reck & Jankowsky, 1981). Bars represent e.s.d.'s.

Coulson, 1975). The sensitivity of N—C—N ring angles in chloro-*s*-triazines to electronic effects is revealed in Fig. 2 which suggests that the N—C—N angle is positively correlated with the length of the bond from the central C atom to its chlorine substituent.

The average C—Cl bond distance in *s*-triazines and benzene derivatives is the same (about 1.74 Å) but the reactivity of chloro-*s*-triazines exceeds manyfold that of chlorobenzene due to substitution of

C(*sp*²) by more electronegative N(*sp*²) atoms at *ortho* and *para* positions in the *s*-triazine ring.

The *s*-triazine rings of the two chlorotriazine derivatives show partial stacking in the solid: the distances between the rings are 3.84 and 3.28 Å for CCMT and CMPT, respectively. Due to the conjugation between lone-pair electrons at the N atom of the piperidine moiety and the *s*-triazine system in CMPT, flattening of the piperidine ring at the N atom is observed and the sum of the three C—N(7)—C angles is 359.1° (Table 2).

The authors wish to thank Dr Zbigniew J. Kamiński of the Institute of Organic Chemistry, Technical University of Łódź for the compounds and the Ministry of National Education for financial support under project RP.II.10.

References

- CAMERON, T. S., MANNAN, KH., BIDDLESTONE, M. & SHAW, R. A. (1975). *Z. Naturforsch. Teil B*, **30**, 973–974.
 DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234.
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KAMIŃSKI, Z. J. (1985). *Tetrahedron Lett.* **26**, 2901–2904.
 KAMIŃSKI, Z. J. (1987). *Synthesis*, 917–920.
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
 RECK, G. & JANKOWSKY, W. (1981). *Cryst. Struct. Commun.* **10**, 111–115.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRICK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Germany.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1991). **C47**, 618–620

Structure of the 4-Oxo-2-butenic Acid Alkyl Ester Moiety. II. Structure of Dimethyl 4,4'-(Methylhydrazo)bis(4-oxo-2-butenate)

BY MAREK L. GŁÓWKA AND IWONA IWANICKA

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

AND LILIANA NAJMAN

Department of Pharmaceutical Chemistry and Analysis of Drugs, Medical Academy, 90-145 Łódź, Poland

(Received 29 January 1990; accepted 31 July 1990)

Abstract. Dimethyl *N*-methyl-4,4'-dioxo-4,4'-hydrazo-2-butenate, C₁₁H₁₄N₂O₆, *M_r* = 270.24, triclinic, *P* $\bar{1}$, *a* = 4.604 (1), *b* = 8.543 (1), *c* = 16.940 (1) Å, α = 85.60 (1), β = 89.21 (1), γ = 85.97 (1)°, *V* = 662.7 Å³, *Z* = 2, *D_x* = 1.354 Mg m⁻³,

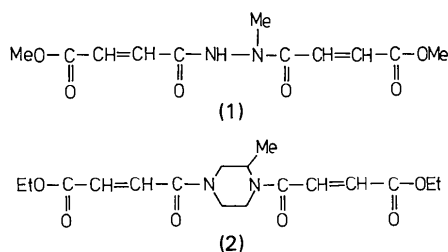
$\lambda(\text{Cu } K\alpha) = 1.54178 \text{ \AA}$, $\mu = 0.91 \text{ mm}^{-1}$, *F*(000) = 284, *R* = 0.060 for 2276 reflections. The molecules in the crystal form chains by means of N—H⋯O hydrogen bonds [N⋯O distance 2.794 (2) Å] running in the [100] direction. The configurations at the C=C

0108-2701/91/030618-03\$03.00

© 1991 International Union of Crystallography

double bonds are *trans* and adjacent carbonyl groups are *syn* oriented towards the double bond. The molecule is twisted by $-83.3(2)^\circ$ at the central hydrazine link.

Introduction. Diethyl 4,4'-(2-methyl-1,4-piperazinediyl)bis(4-oxo-2-butenoate) (2) shows cytostatic activity against leukemias L1210 and P388 and sarcoma Sa180 (Graczyk, Pakulska, Groszkowski & Najman, 1980; Groszkowski & Najman, 1983). This has led to the synthesis of a series of piperazides, methylpiperazides and oxopiperazides of α,β -unsaturated carboxylic acids and their esters (Groszkowski, Najman & Sienkiewicz, 1972; Groszkowski & Najman, 1979; Groszkowski & Najman, 1986). The crystal structures of two 1,4-piperazinediyl and 2,5-dioxo-1,4-piperazinediyl derivatives have been determined (Głowska & Iwanicka, 1990). We now present the crystal structure of the new compound (1) comprising two 4-oxo-2-butenoic acid alkyl esters joined by a hydrazine link instead of the piperazine ring of (2).



Experimental. Transparent plate-like crystals of (1) were grown from warm water solution. A crystal of dimensions $0.30 \times 0.23 \times 0.08$ mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer. 25 reflections used for measuring lattice parameters in the range $17 \leq \theta \leq 33^\circ$. The intensities of 2715 unique reflections were collected to a maximum $\theta = 75^\circ$ using $\omega/2\theta$ scans and a maximum measurement time of 200 s. $-5 \leq h \leq 5$, $-10 \leq k \leq 10$, $0 \leq l$

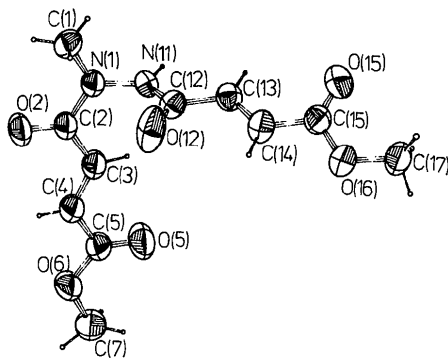


Fig. 1. A view of the molecule with the atomic labeling scheme (Johnson, 1976).

Table 1. Final positional and equivalent isotropic temperature factors for non-H atoms

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
N(1)	0.3283 (4)	0.0247 (2)	0.2335 (1)	3.82 (4)
C(1)	0.4786 (7)	-0.1316 (3)	0.2396 (2)	5.06 (7)
C(2)	0.3820 (5)	0.1295 (3)	0.1713 (1)	4.38 (6)
O(2)	0.5416 (6)	0.0901 (2)	0.1178 (1)	7.39 (7)
C(3)	0.2258 (6)	0.2887 (3)	0.1704 (1)	4.51 (6)
C(4)	0.2855 (6)	0.3995 (3)	0.1163 (1)	4.92 (6)
C(5)	0.1190 (6)	0.5560 (3)	0.1120 (1)	4.86 (6)
O(5)	-0.0668 (7)	0.5937 (3)	0.1580 (1)	8.20 (8)
O(6)	0.1972 (5)	0.6462 (2)	0.0501 (1)	5.88 (5)
C(7)	0.0479 (10)	0.8019 (3)	0.0403 (2)	6.48 (9)
N(11)	0.2058 (3)	0.0765 (2)	0.3029 (1)	3.48 (4)
C(12)	0.3713 (4)	0.1291 (2)	0.3576 (1)	3.95 (5)
O(12)	0.6267 (4)	0.1528 (3)	0.3451 (2)	7.70 (8)
C(13)	0.2197 (5)	0.1634 (2)	0.4328 (1)	3.96 (5)
C(14)	0.3240 (5)	0.2556 (3)	0.4824 (2)	4.90 (6)
C(15)	0.1663 (6)	0.2924 (3)	0.5557 (1)	4.63 (6)
O(15)	-0.0293 (7)	0.2206 (3)	0.5846 (1)	7.59 (8)
O(16)	0.2572 (5)	0.4191 (2)	0.5849 (1)	6.10 (6)
C(17)	0.1170 (11)	0.4669 (4)	0.6564 (2)	6.57 (9)

≤ 21 . Three standard reflections measured every hour showed changes of intensity below 5% and the data were scaled accordingly. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (Sheldrick, 1986) and refined by full-matrix least squares (Sheldrick, 1976) with anisotropic thermal parameters for O, N and C atoms and isotropic thermal parameters for H atoms. Isotropic extinction was taken into consideration according to Larson (1967) and refined in the final cycles of calculations to 0.044 (10). 229 parameters refined in final cycles. The final agreement factors R (wR) of 0.060 (0.084) were based on 2276 reflections having $F > 3\sigma(F)$. $(\Delta/\sigma)_{\max} = 0.05$ for H(101) z. The function minimized was $\sum w|F_o| - |F_c|^2$ where $w^{-1} = \sigma^2(F_o) + 0.0038F_o^2$. The maximum peak of 0.15 e \AA^{-3} in the final difference Fourier synthesis was located 0.35 \AA from O(6) and $\Delta\rho_{\min}$ was -0.16 e \AA^{-3} . Scattering factors were those in *SHELX76*.

A view of molecule and the atomic labeling scheme are shown in Fig. 1. The final atomic coordinates and equivalent isotropic temperature parameters are given in Table 1,* while bond distances, valency and torsion angles for these atoms are listed in Table 2.

Discussion. The molecule of (1) comprises two methyl 4-oxo-2-butenoate moieties joined by a methylhydrazine link. Although the two 4-amino-4-oxo-2-butenoate fragments are in the extended form

* Lists of H-atom coordinates, anisotropic thermal parameters for non-H atoms and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53379 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and valency and torsion angles (°)

N(1)—N(11)	1.387 (2)	N(1)—C(1)	1.457 (3)
N(1)—C(2)	1.361 (3)	N(11)—C(12)	1.331 (2)
C(2)—O(2)	1.212 (3)	C(12)—O(12)	1.220 (3)
C(2)—C(3)	1.492 (3)	C(12)—C(13)	1.483 (3)
C(3)—C(4)	1.307 (3)	C(13)—C(14)	1.313 (4)
C(4)—C(5)	1.491 (4)	C(14)—C(15)	1.473 (4)
C(5)—O(5)	1.193 (3)	C(15)—O(15)	1.203 (3)
C(5)—O(6)	1.314 (3)	C(15)—O(16)	1.320 (3)
O(6)—C(7)	1.453 (3)	O(16)—C(17)	1.438 (4)
C(1)—N(1)—C(2)	120.5 (2)	C(1)—N(1)—N(11)	116.2 (2)
N(11)—N(1)—C(2)	120.3 (2)	N(1)—N(11)—C(12)	120.7 (2)
N(1)—C(2)—O(2)	120.1 (2)	N(11)—C(12)—O(12)	121.9 (2)
N(1)—C(2)—C(3)	117.4 (2)	N(11)—C(12)—C(13)	115.3 (2)
O(2)—C(2)—C(3)	122.5 (2)	O(12)—C(12)—C(13)	122.8 (2)
C(2)—C(3)—C(4)	120.7 (2)	C(12)—C(13)—C(14)	122.1 (2)
C(3)—C(4)—C(5)	121.1 (2)	C(13)—C(14)—C(15)	121.4 (2)
C(4)—C(5)—O(5)	124.3 (2)	C(14)—C(15)—O(15)	124.9 (2)
C(4)—C(5)—O(6)	111.6 (2)	C(14)—C(15)—O(16)	111.8 (2)
O(5)—C(5)—O(6)	124.1 (2)	O(15)—C(15)—O(16)	123.3 (2)
C(5)—O(6)—C(7)	116.1 (2)	C(15)—O(16)—C(17)	116.7 (2)
C(1)—N(1)—C(2)—O(2)	4.7 (3)	C(1)—N(1)—N(11)—C(12)	77.3 (2)
C(1)—N(1)—C(2)—C(3)	-178.3 (2)	C(2)—N(1)—N(11)—C(12)	-83.3 (2)
N(11)—N(1)—C(2)—O(2)	164.6 (2)	N(1)—N(11)—C(12)—O(12)	9.5 (3)
N(11)—N(1)—C(2)—C(3)	-18.5 (3)	N(1)—N(11)—C(12)—C(13)	-173.2 (2)
N(1)—C(2)—C(3)—C(4)	174.0 (2)	N(11)—C(12)—C(13)—C(14)	-160.1 (2)
O(2)—C(2)—C(3)—C(4)	-9.1 (4)	O(12)—C(12)—C(13)—C(14)	17.1 (3)
C(2)—C(3)—C(4)—C(5)	176.4 (2)	C(12)—C(13)—C(14)—C(15)	178.1 (2)
C(3)—C(4)—C(5)—O(5)	3.3 (4)	C(13)—C(14)—C(15)—O(15)	16.0 (4)
C(3)—C(4)—C(5)—O(6)	-175.2 (2)	C(13)—C(14)—C(15)—O(16)	-161.4 (2)
C(4)—C(5)—O(6)—C(7)	-180.0 (2)	C(14)—C(15)—O(16)—C(17)	179.6 (2)
O(5)—C(5)—O(6)—C(7)	1.6 (4)	O(15)—C(15)—O(16)—C(17)	2.2 (4)

the whole molecule is bent at the central N—N bond [C(2)—N(1)—N(11)—C(12) = -83.3 (2)°]. The configurations at the C(3)=C(4) and C(13)=C(14) bonds are *trans* and all four carbonyl groups are *syn* in relation to the double C=C bonds. Similar geometries have been observed in the crystal structures of funaltrexamines (Griffin, Larson & Porthoghese, 1986) and in dimethyl 4,4'-(2,5-dioxo-1,4-piperazinediyl)bis(4-oxo-2-butenoate) (Głowska &

Iwanicka, 1990). The bond lengths and angles in the two equivalent 4-oxo-2-butenoate moieties agree to within 3σ except for N(1)—C(2), N(1)—C(2)—O(2), N(1)—C(2)—C(3) and C(2)—C(3)—C(4) (Table 2) which differ by about 10σ. These differences result from methyl substitution at N(1), from different crystallographic environments of the moieties and from N(11)—H...O(12) (x - 1, y, z) hydrogen bonds which join molecules of (1) into infinite chains running in the [100] direction. N...O, H...O distances and the N—H...O angle are 2.796 (2), 2.07 (3) Å and 147 (3)°, respectively.

The authors wish to thank the Polish Ministry of National Education (research project RP.II.10) for financial support.

References

- GŁOWKA, M. L. & IWANICKA, I. (1990). *Acta Cryst.* **C46**, 1262–1264.
- GRACZYK, J., PAKULSKA, W., GROSZKOWSKI, S. & NAJMAN, L. (1980). *Acta Pol. Pharm.* **37**, 249–254.
- GRIFFIN, J. F., LARSON, D. L. & PORTHOGESE, P. S. (1986). *J. Med. Chem.* **29**, 778–783.
- GROSZKOWSKI, S. & NAJMAN, L. (1979). *Pol. J. Pharmacol. Pharm.* **31**, 157–159.
- GROSZKOWSKI, S. & NAJMAN, L. (1983). *Pol. J. Pharmacol. Pharm.* **35**, 517–521.
- GROSZKOWSKI, S. & NAJMAN, L. (1986). *Acta Pol. Pharm.* **43**, 327–330.
- GROSZKOWSKI, S., NAJMAN, L. & SIENKIEWICZ, J. (1972). *Rocz. Chem.* **46**, 269–273.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Acta Cryst. (1991). **C47**, 620–623

Structure of 8-Chloro-6-(2-chlorophenyl)-2*H*,4*H*-[1,2,3]triazolo[5,4-*d*][2]-benzazepinium Methanesulfonate Methanol Solvate*

BY HELEN J. KEMMISH AND THOMAS A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

(Received 8 January 1990; accepted 2 July 1990)

Abstract. [C₁₆H₁₁Cl₂N₄]⁺. [CH₃O₃S]⁻. 0.25CH₄O, *M*_r = 433.3, monoclinic, *C*2/*c*, *a* = 23.234 (5), *b* =

10.624 (2), *c* = 16.552 (6) Å, β = 100.95 (4)°, *V* = 4011 Å³, *Z* = 8, *D*_x = 1.435 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 4.42 cm⁻¹, *F*(000) = 1780, *T* = 293 K, *R* = 0.041 for 2340 observed reflections. The benzazepine N atom is protonated, causing a signifi-

* Contribution from the Crystallography Unit, Universities of Aston and Birmingham, England.