The Structure of Methylidynetrithiotriacetic Acid

By Joël Canonne and Guy Nowogrocki

Laboratoire de Physicochimie des Solutions, Ecole Nationale Supérieure de Chimie de Lille, BP 40, 59650 Villeneuve d'Ascq, France

and Jean-Claude Boivin and Daniel Thomas

Laboratoire de Cristallochimie, UER et ENS de Chimie, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq CEDEX, France

Abstract

Methylidynetrithiotriacetic acid (MTTA), $C_7H_{10}O_6S_3$, is triclinic, space group $P\bar{1}$, with $a = 9.701$ (4), $b = 5.366$ (2), $c = 11.744$ (4) Å, $\alpha = 97.16$ (4), $\beta = 90.33$ (4), $\gamma = 110.39$ (4)°, $Z = 2$. The structure was refined to $R = 0.027$ for 2554 counter reflexions [$I \geq 3\sigma(I)$]. Short distances occur between S atoms, average 2.953 Å. The molecules are linked through intermolecular hydrogen bonds to form rings. One of these connects four carboxyl groups to form a cyclic planar tetramer.

Introduction and experimental

The present investigation is part of a series of structural studies of polythiopolycarboxylic acids and their corresponding metal complexes to compare their molecular conformations and to define some relations between conformation and reactivity of the acids (Canonne, Boivin, Nowogrocki & Thomas, 1977, 1978a,b). The title compound was obtained by the procedure described by Holmberg (1907). A mixture of mercaptoacetic acid (0·5 mol) and formic acid (0·16 mol) was saturated with dry hydrogen chloride and left to stand at room temperature. Deposition of small white crystals started after one day. The compound was recrystallized twice from water, m.p. 443 K. Suitable single crystals for the structure investigation were obtained by evaporation from a saturated solution at room temperature (solubility in water at 298 K: 10·8 g dm⁻³). Chemical analysis of the crystals confirms the expected composition: found: C 29·27, H 3·47, O 33·79, S 33·73%; calculated: C 29·36, H 3·52, O 33·52, S 33·60%.

Cell dimensions and intensities were measured on the Philips PW 1100 four-circle diffractometer of the University of Lille I with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). During the data

Table 1. *Crystal data*

$a =$	9.701 (4) Å	Crystal system: triclinic
$b =$	5.366 (2)	Space group: $P\bar{1}$
$c =$	11.744 (4)	$Z = 2$
$\alpha =$	97.16 (4)°	$d_m = 1.67$ Mg m⁻³
$\beta =$	90.33 (4)	$d_c = 1.67$
$\gamma =$	110.39 (4)	$M_r = 286.3$
$V =$	567.8 Å³	

collection three reference reflexions were periodically monitored to check crystal stability. Crystal data are listed in Table 1. 3010 reflexions were collected in a half of reciprocal space explored to $\theta = 30°$. 2554 reflexions with $I \geq 3\sigma(I)$ were considered observed and were subsequently corrected for Lorentz–polarization effects. No correction was made for absorption ($\mu = 0.6$ mm⁻¹).

Structure determination and refinement

Preliminary investigation by Weissenberg photographs showed the crystals to be triclinic. The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). Wilson statistics gave no information about the symmetry. With the 250 strongest normalized E and 1850 unique phase relations, the best phases, with ABS FOM = 1·077, PSI ZERO = 0·684 × 10³ and COMB FOM = 3·0, revealed 24 non-H atoms of the 32 expected in $P1$. Refinement of the atomic coordinates by full-matrix least squares, followed by a difference synthesis, revealed the last eight non-H atoms. Refinement with isotropic thermal parameters converged to $R = 0.11$. Examination of atomic coordinates showed the structure to be centrosymmetric. Refinement in $P\bar{1}$ was successful: with anisotropic thermal parameters, R fell to 0·045. All the H atoms were located from a difference map and were assigned the same isotropic thermal parameters as the atoms to which they were

Table 2. *Atomic positional parameters* $(\times 10^5$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

|	x	y	z
C(1)	16106 (18)	−24711 (34)	29161 (17)
C(2)	23240 (23)	−11246 (41)	52618 (19)
C(3)	35559 (20)	15056 (38)	51401 (18)
C(4)	40429 (21)	−25669 (37)	17144 (21)
C(5)	46906 (19)	3238 (34)	15018 (17)
C(6)	−4412 (24)	−7966 (47)	19598 (24)
C(7)	−17584 (18)	−17393 (34)	11405 (16)
O(1)	36825 (17)	33436 (31)	60195 (14)
O(2)	43205 (15)	19010 (28)	43184 (13)
O(3)	60451 (15)	15192 (28)	19658 (13)
O(4)	40898 (16)	14284 (27)	9488 (15)
O(5)	−16442 (15)	734 (28)	4539 (14)
O(6)	−28067 (15)	−38085 (28)	11117 (14)
S(1)	21295 (5)	−38096 (9)	41180 (5)
S(2)	20551 (5)	−40453 (9)	15873 (5)
S(3)	−3607 (5)	−31535 (10)	29023 (5)
H(1)	438 (3)	478 (6)	594 (2)
H(2)	640 (3)	298 (5)	181 (2)
H(3)	−239 (3)	−33 (5)	3 (2)
H(4)	256 (3)	−167 (5)	595 (2)
H(5)	137 (3)	−86 (5)	528 (2)
H(6)	438 (3)	−355 (5)	120 (2)
H(7)	441 (2)	−275 (4)	244 (2)
H(8)	47 (3)	−27 (6)	160 (3)
H(9)	−16 (4)	99 (7)	229 (3)
H(10)	213 (2)	−49 (4)	301 (2)
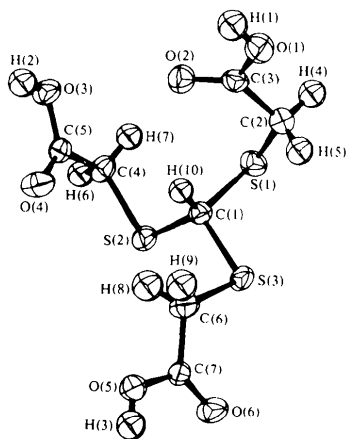
Fig. 1. Perspective view of the molecule with the atomic numbering and 50% probability thermal ellipsoids.

bonded. The final refinement converged to $R = 0.027$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.029$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Anomalous-scattering corrections were applied to S (Cromer, 1965). Final atomic parameters are listed in Table 2.* The atomic numbering is defined in Fig. 1.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35384 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

The molecular conformation is shown in Fig. 1, drawn by a local version of *ORTEP* (Johnson, 1965) adapted for a Hewlett–Packard 9825A computer. Bond lengths and angles are listed in Table 3.

Equivalent bond lengths and angles in the three carboxyl groups show no significant differences. The average C=O 1.210, C–O(H) 1.376 Å, O=C–O 123.3° are in good agreement with those tabulated by Leiserowitz (1976). The best planes for the C–COOH groups and the angles between the planes are given in Table 4. As in crystals of saturated monocarboxylic acids, where the synplanar C^β–C^α–C=O arrangement is adopted without exception, the S^α substituent is in the *syn* position with respect to C=O in the three thioacid portions of the molecule. The torsion angles are reported in Table 5. The S(2) thioacetic group torsion angles are different from the others, showing in this group a deformation of the synplanar arrangement. The C(2)–C(3), C(4)–C(5) and C(6)–C(7) distances are 1.522, 1.511 and 1.493 Å respectively, and are shorter than the standard C–C single bond. Such a shortening has been found in similar compounds where a C–C bond lies between a carboxyl group and a C–S bond (Canonne, Boivin, Nowogrocki & Thomas, 1977, 1978a,b). The S–C–C angles vary from 114.9 to 115.8°. The average, 115.3°, is somewhat larger than

Table 3. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–S(1)	1.805 (2)	S(2)–C(4)–C(5)	115.8 (2)
C(1)–S(2)	1.808 (2)	C(4)–C(5)–O(4)	125.2 (4)
C(1)–S(3)	1.817 (2)	C(4)–C(5)–O(3)	112.0 (3)
S(1)–C(2)	1.800 (2)	O(4)–C(5)–O(3)	122.8 (4)
C(2)–C(3)	1.522 (3)	C(1)–S(3)–C(6)	98.4 (2)
C(3)–O(1)	1.309 (3)	S(3)–C(6)–C(7)	115.3 (3)
C(3)–O(2)	1.215 (3)	C(6)–C(7)–O(6)	126.6 (4)
S(2)–C(4)	1.809 (2)	C(6)–C(7)–O(5)	109.5 (3)
C(4)–C(5)	1.511 (3)	O(6)–C(7)–O(5)	123.9 (3)
C(5)–O(4)	1.202 (3)	S(1)–C(1)–S(2)	109.9 (1)
C(5)–O(3)	1.324 (2)	S(1)–C(1)–S(3)	108.8 (1)
S(3)–C(6)	1.802 (3)	S(2)–C(1)–S(3)	109.3 (1)
C(6)–C(7)	1.493 (3)	S(1)–C(1)–H(10)	109 (2)
C(7)–O(6)	1.213 (2)	S(2)–C(1)–H(10)	111 (2)
C(7)–O(5)	1.315 (3)	S(1)–C(1)–H(10)	109 (2)
S(1)–S(2)	2.958 (1)	S(2)–C(1)–H(10)	111 (2)
S(1)–S(3)	2.946 (1)	S(3)–C(1)–H(10)	108 (2)
S(2)–S(3)	2.957 (1)	S(1)–C(2)–H(5)	106 (3)
C(4)–H(7)	0.96 (3)	S(1)–C(2)–H(4)	108 (2)
C(4)–H(6)	0.89 (3)	C(3)–C(2)–H(5)	110 (3)
O(3)–H(2)	0.78 (2)	C(3)–C(2)–H(4)	106 (3)
C(2)–H(4)	0.95 (3)	H(4)–C(2)–H(5)	112 (6)
C(2)–H(5)	0.98 (3)	C(3)–O(1)–H(1)	111 (3)
O(1)–H(1)	0.85 (2)	S(2)–C(4)–H(7)	111 (2)
C(6)–H(8)	0.95 (3)	S(2)–C(4)–H(6)	107 (3)
C(6)–H(9)	0.93 (4)	C(5)–C(4)–H(7)	110 (3)
O(5)–H(3)	0.82 (2)	C(5)–C(4)–H(6)	108 (3)
C(1)–H(10)	1.00 (2)	H(6)–C(4)–H(7)	105 (5)
S(1)–C(2)–C(3)	114.9 (2)	C(5)–O(3)–H(2)	112 (3)
C(1)–S(1)–C(2)	100.9 (2)	S(3)–C(6)–H(8)	106 (3)
C(2)–C(3)–O(1)	112.1 (3)	S(3)–C(6)–H(9)	116 (4)
C(2)–C(3)–O(2)	124.6 (4)	C(7)–C(6)–H(8)	114 (4)
O(1)–C(3)–O(2)	123.3 (4)	C(7)–C(6)–H(9)	115 (4)
C(1)–S(2)–C(4)	99.9 (2)	H(8)–C(6)–H(9)	86 (5)
		C(7)–O(5)–H(3)	112 (3)

the ideal tetrahedral angle. The S—C lengths and C—S—C angles have the expected magnitudes (average 100°, in accordance with the repulsion due to electron pairs) as do the S—C—S angles (average 109·3°, close to tetrahedral). The average S···S distance (2·953 Å) is shorter than those in similar compounds: methylenedithiodiacetic acid, MDDA, 3·062 Å, methylenedithiodipropionic acid, MDDP, 3·069 Å, ethanediylidenetetrathiotetraacetic acid, ETTA, 3·131 Å (Canonne, Boivin, Nowogrocki & Thomas, 1977, 1978a,b), hexakis(phenylthio)ethane 3·09 Å

(Roelofsen, Kanters & Seebach, 1974). However, shorter non-bonding S···S distances have been found in some compounds, e.g. in 1,2,4-dithiazolidine derivatives (Letten, 1975) where S···S distances range from 2·571 to 2·675 Å. Despite the difference in the average S···S distances, calculations performed with the CNDO2 program (Pople & Beveridge, 1970) do not

Table 4. *Equations of least-squares planes, deviations* (Å) *of the atoms from the planes and angles* (°) *between the planes*

X, Y, Z are orthogonal coordinates obtained by:

$$\begin{vmatrix} X \\ Y \\ Z \end{vmatrix} = \begin{vmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha^* \\ 0 & 0 & c\sin\beta\sin\alpha^* \end{vmatrix} \times \begin{vmatrix} x \\ y \\ z \end{vmatrix}.$$

The atoms indicated by asterisks were used to define the plane. E.s.d.'s are 2×10^{-3} for deviations of non-H and 3×10^{-2} Å for H atoms.

Symmetry code
(i) x,y,z (ii) $x + 1, y + 1, z$
(iii) $\bar{x} + 1, \bar{y} + 1, \bar{z}$ (iv) $\bar{x} + 1, \bar{y} + 1, \bar{z} + 1$

Plane (I): $-0·5174X + 0·1802Y + 0·8365Z + 0·8812 = 0$

C(4)*	−0·003	O(4)*	−0·004
C(5)*	0·012	O(3)*	−0·004
H(2)	−0·053		

Plane (II): $-0·8104X + 0·3702Y - 0·4540Z + 5·2692 = 0$

C(2)*	0·002	O(1)*	0·002
C(3)*	−0·007	O(2)*	0·003
H(1)	−0·016		

Plane (III): $0·6671X - 0·3716Y - 0·6457Z + 1·4003 = 0$

C(6)*	−0·003	O(6)*	−0·004
C(7)*	0·009	O(5)	−0·003
H(3)	−0·061		

Plane (IV): $-0·8405X + 0·3007Y - 0·4507Z + 5·3674 = 0$

C(3)*	0·021	C(3ⁱᵛ)*	−0·021
O(1)*	−0·014	O(1ⁱᵛ)*	0·014
O(2)*	−0·015	O(2ⁱᵛ)*	0·015
C(2)	0·145	H(1)	−0·096

Plane (V): $-0·5795X + 0·3768Y - 0·7227Z + 1·3277 = 0$

O(4)*	0·199	O(4ⁱⁱⁱ)*	−0·187
O(3)*	−0·075	O(3ⁱⁱⁱ)*	0·087
C(5)*	−0·034	C(5ⁱⁱⁱ)*	0·046
O(6ⁱⁱ)*	0·001	O(6ⁱ)*	0·011
O(5ⁱⁱ)*	−0·013	O(5ⁱ)*	0·025
C(7ⁱⁱ)*	0·050	C(7ⁱ)*	−0·038
H(2)	0·038	H(2ⁱⁱⁱ)	−0·026
H(3ⁱ)	0·056	H(3ⁱⁱ)	−0·044

Angles (°) between the planes

(I)—(II)	83·9 (1)	(II)—(III)	112·6 (1)
(I)—(III)	162·2 (3)	(IV)—(V)	22·2 (1)

Table 5. *Torsion angles* (°)

The torsion angle $A(1)-A(2)-A(3)-A(4)$ is viewed along $A(2)-A(3)$ with a clockwise rotation of $A(1)$ to $A(4)$ taken to be positive.

S(1)—C(2)—C(3)—O(2)	4·1 (3)
S(2)—C(4)—C(5)—O(4)	−23·2 (3)
S(3)—C(6)—C(7)—O(6)	5·9 (3)
S(1)—C(2)—C(3)—O(1)	−177·3 (2)
S(2)—C(4)—C(5)—O(3)	159·5 (2)
S(3)—C(6)—C(7)—O(5)	−176·0 (2)

Table 6. *Intermolecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

The symmetry code is as in Table 4.

O(1)—O(2ⁱᵛ)	2·690 (2)	C(3)—O(1)—O(2ⁱᵛ)	111·3 (2)
H(1)—O(2ⁱᵛ)	1·85 (3)	O(1)—H(1)—O(2ⁱᵛ)	171 (22)
O(1)—O(1ⁱᵛ)	3·660 (3)	C(3)—O(2)—O(1ⁱᵛ)	125·3 (3)
O(2)—O(2ⁱᵛ)	3·310 (3)		
O(4)—O(5ⁱ)	2·699 (2)	C(5)—O(4)—O(5ⁱ)	136·2 (4)
O(3)—O(6ⁱⁱ)	2·688 (2)	O(4)—O(5ⁱ)—C(7ⁱ)	110·2 (2)
O(4)—H(3ⁱ)	1·88 (2)	C(7ⁱ)—O(5ⁱ)—H(3ⁱ)	112 (3)
O(6ⁱⁱ)—H(2)	1·92 (3)	C(5)—O(3)—O(6ⁱⁱ)	107·0 (2)
O(4)—O(6ⁱ)	3·298 (2)	C(5)—O(3)—H(2)	112 (3)
O(4)—O(6ⁱⁱ)	3·185 (2)	O(3)—O(6ⁱⁱ)—C(7ⁱⁱ)	145·8 (4)
C(5)—C(7ⁱ)	4·504 (3)		
C(5)—C(7ⁱⁱ)	4·520 (2)		
O(3)—O(5ⁱ)	4·873 (2)		
O(3)—O(5ⁱⁱ)	4·915 (2)		
O(4)—O(4ⁱⁱⁱ)	4·498 (3)		
O(6ⁱ)—O(6ⁱⁱ)	4·670 (3)		

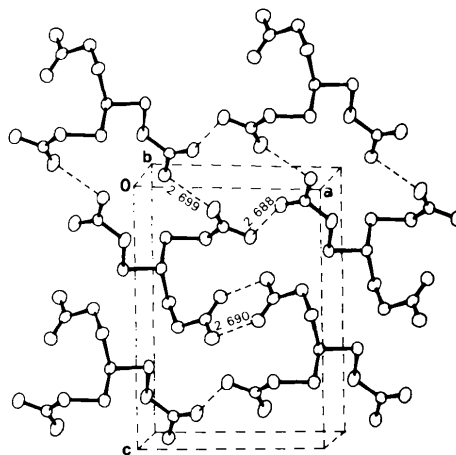

Fig. 2. Molecular packing with hydrogen-bonding scheme in a sheet parallel to the (1Ī0) plane. (Distances are in Å.)

exhibit significant differences for the interactions between the S atoms in MDDA and MTTA.

Hydrogen bonding

Intermolecular hydrogen-bond data are given in Table 6 and hydrogen bonds are shown as dashed lines in Fig. 2: a molecule of MTTA is hydrogen bonded through its carboxyl groups to four symmetry-related molecules.
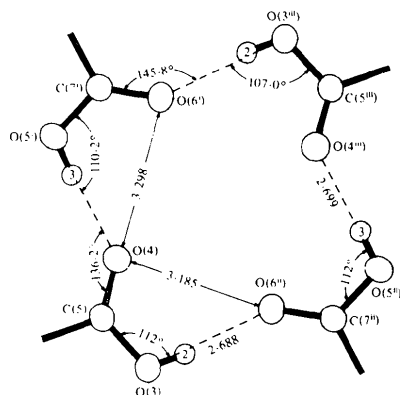

Fig. 3. Characteristics of the ring formed by intermolecular hydrogen bonding of four carboxyl groups (the symmetry code is as in Table 4). (Distances are in Å.)
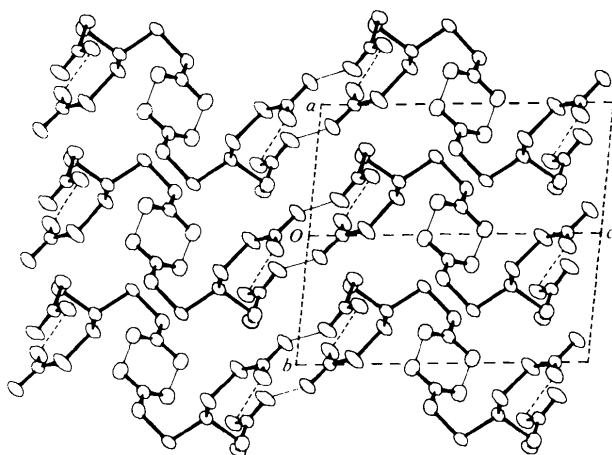

Fig. 4. Projection of the molecular packing viewed along |110|. a, b, c are the projections of the cell parameters. Dashed lines represent intermolecular hydrogen bonds of the type $O(4)\cdots O(5^i)$. Thin continuous lines represent projections of hydrogen bonds of the type $O(1)\cdots O(2^{iv})$ or $O(3)\cdots O(6^{ii})$.

The hydrogen-bond network is characterized by cyclic systems with rings of different sizes.

The $O(1)-C(1)-O(2)$ carboxyl group is linked to the equivalent group of the adjacent molecule at ($\bar{x}$ + 1, $\bar{y}$ + 1, $\bar{z}$ + 1) to form a planar cyclic hydrogen-bonded dimer where $O(1)\cdots O(2^{iv})$ = 2·690 and $H(1)\cdots O(2^{iv})$ = 1·85 Å.

The most interesting ring system contains four carboxyl groups which belong to four different molecules. Details of the geometry of the cyclic tetramer are given in Fig. 3. The cyclic system adopts a nearly planar arrangement, the maximum deviation from the least-squares plane (Table 4, plane V) being 0·2 Å for O(4). The four carboxyl groups are symmetry related by a pseudo-fourfold axis. A similar arrangement has already been observed in ETTA (Canonne, Boivin, Nowogrocki & Thomas, 1978b).

The $O(3)\cdots O(6^{iii})$ and $O(4)\cdots O(5^i)$ distances, respectively 2·688 and 2·699 Å, are similar, while the equivalent hydrogen bonds in ETTA are significantly different (2·633 and 2·729 Å); nevertheless, the two ring geometries agree well.

A projection of the molecular packing, viewed along |110|, is shown in Fig. 4. The molecules are interlinked through hydrogen bonds in sheets parallel to the (1 $\bar{1}$0) planes, contacts between sheets being of the van der Waals type.

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