3,3'-Thiodipropionic and 3,3'-Dithiodipropionic Acids

By Keith Prout

Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England

and Santiago Hernández-Cassou

Departamento de Química Analítica, Universidad Autónoma de Barcelona, Bellaterra, Barcelona, Spain

Abstract. $C_6H_{10}O_4S$ (TDPA), $M_r = 178\cdot2$, orthorhombic, *Pcan* (*Pbcn*), $a = 5\cdot063$ (1), $b = 8\cdot648$ (1), $c = 18\cdot073$ (2) Å, $U = 791\cdot3$ Å^3, $D_c = 1\cdot49$ Mg m^{-3} for $Z = 4$, Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å), $\mu = 0\cdot37$ mm^{-1}; final $R = 0\cdot038$ for 523 reflexions. $C_6H_{10}O_4S_2$ (DTDPA), $M_r = 210\cdot2$, monoclinic, $C2/c$, $a = 5\cdot466$ (3), $b = 8\cdot870$ (4), $c = 18\cdot906$ (3) Å, $\beta = 95\cdot99$ (3)°, $U = 911\cdot6$ Å^3, $D_c = 1\cdot53$ Mg m^{-3} for $Z = 4$, Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å), $\mu = 0\cdot54$ mm^{-1}; final $R = 0\cdot034$ for 626 reflexions. Both structures consist of infinite chains of molecules linked by intermolecular hydrogen bonds; the carboxylic acid groups and associated H bonds are coplanar, but they are not coplanar with the remaining non-hydrogen atoms of the molecule. O···O bond distances are 2·674 (3) Å for TDPA and 2·658 (3) Å for DTDPA.

Introduction. The crystal structures of the title compounds were determined as part of a series of investigations, comprising both solid and solution chemistry, on coordination compounds with potentially tridentate ligands containing a thioether or disulphide group. Colourless thin plates of 3,3'-thiodipropionic acid and 3,3'-dithiodipropionic acid were grown from a warm solution (aqueous for TDPA and ethanolic for DTDPA) which was left to evaporate at room temperature. Crystals were not air sensitive and precession photographs showed those of TDPA to be orthorhombic, with systematic absences: $hk0$: $h + k = 2n + 1$; $h0l$: $h = 2n + 1$; $0kl$: $l = 2n + 1$, corresponding to space group *Pcan* [non-standard setting $\pm(x,y,z; \frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z; \frac{1}{2} - x, \frac{1}{2} + y, z; x, \bar{y}, \frac{1}{2} + z)$], and those of DTDPA to be monoclinic, with systematic absences: hkl: $h + k = 2n + 1$; $h0l$: $l = 2n + 1$, consistent with space groups $C2/c$ and Cc (the structure was refined successfully in $C2/c$).

Single crystals, $0\cdot60 \times 0\cdot30 \times 0\cdot15$ mm for TDPA and $0\cdot75 \times 0\cdot50 \times 0\cdot15$ mm for DTDPA, were used for intensity-data collection on a Nonius CAD-4F automated diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Accurate unit-cell dimensions and the orientation matrix were obtained by least

squares from the setting angles of 25 reflexions. The intensities of reflexions with $\theta < 25°$ were measured by an $\omega/2\theta$ scan, a variable scan rate and an ω scan angle of $(1\cdot5 + 0\cdot35 \tan \theta)°$ for TDPA and $(1\cdot3 + 0\cdot35 \times \tan \theta)°$ for DTDPA. Some low-θ reflexions of DTDPA were so intense that they had to be recollected with one fifth of the usual filament current of the X-ray generator to avoid dead-time losses. 168 reflexions for TDPA and 174 for DTDPA with $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on simple counting statistics, were not included in the subsequent calculations, which were based on the remaining 523 and 626 independent reflexions for TDPA and DTDPA, respectively. Lorentz and polarization corrections were applied but no correction was made for absorption.

The structures were solved by the heavy-atom method and Fourier techniques, and refined using full-matrix least-squares methods. The S atom in TDPA is located in the special position 2(*c*). After refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, difference maps clearly indicated H-atom positions, which were included with isotropic temperature factors in the next cycles, C—H bonds being constrained to have the same length and angles as in sp^3 hybridization. In the last stage of refinement, each reflexion was assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r(X)$ where n is the number of coefficients A_r for a Chebyshev series, T_r is the polynomial function and $X = |F_o|/|F_o(\text{max.})|$. Three coefficients A_r were used, with values 101·1, 136·9 and 39·9 for TDPA and 15·1, 18·1 and 5·2 for DTDPA (Rollett, 1965; Carruthers & Watkin, 1979). The use of the weighting-scheme function shortened hydrogen-bond lengths by 0·04–0·06 Å. Final difference maps had no peaks higher than 0·3 e Å^{-3} and the refinement converged for TDPA at $R = 0\cdot038$ ($R_w = 0\cdot044$) for 523 reflexions and for DTDPA at $R = 0\cdot034$ ($R_w = 0\cdot042$) for 626 reflexions.

Scattering factors were taken from Cromer & Mann (1968). Correction was made for the real and imaginary parts of the anomalous dispersion of S (Cromer & Liberman, 1970). All calculations were

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors, with e.s.d.'s in parentheses*

	x	y	z	U_{eq}^* ($\text{Å}^2 \times 10^2$)
TDPA				
S(1)	0·2105 (2)	0·0000	0·2500	3·13 (5)
C(1)	0·4407 (5)	−0·0624 (3)	0·1788 (1)	3·0 (1)
C(2)	0·5274 (6)	0·0721 (3)	0·1317 (1)	3·4 (1)
C(3)	0·7320 (5)	0·0344 (3)	0·0744 (1)	2·9 (1)
O(1)	0·7474 (4)	0·1344 (2)	0·0212 (1)	4·3 (1)
O(2)	0·8766 (4)	−0·0795 (2)	0·0793 (1)	4·1 (1)
H(11)	0·357 (4)	−0·136 (2)	0·149 (1)	2·7 (3)
H(12)	0·588 (4)	−0·108 (2)	0·200 (1)	2·9 (3)
H(13)	0·588 (4)	0·151 (2)	0·161 (1)	3·0 (3)
H(14)	0·378 (4)	0·118 (3)	0·109 (1)	4·2 (3)
H(15)	0·881 (7)	0·111 (4)	−0·013 (2)	3·3 (3)
DTDPA				
S(1)	0·3664 (1)	0·1131 (1)	0·2084 (1)	4·36 (4)
C(1)	0·4505 (5)	−0·0404 (3)	0·1523 (2)	3·8 (1)
C(2)	0·7000 (5)	−0·0224 (3)	0·1252 (1)	3·7 (1)
C(3)	0·7145 (5)	0·0991 (3)	0·0713 (1)	3·4 (1)
O(1)	0·9404 (3)	0·1258 (2)	0·0579 (1)	4·5 (1)
O(2)	0·5357 (3)	0·1653 (2)	0·0419 (1)	4·5 (1)
H(11)	0·330 (4)	−0·048 (2)	0·113 (1)	3·5 (3)
H(12)	0·449 (3)	−0·131 (2)	0·178 (1)	2·9 (3)
H(13)	0·822 (4)	−0·005 (2)	0·164 (1)	3·6 (3)
H(14)	0·746 (3)	−0·113 (2)	0·106 (1)	3·2 (3)
H(15)	0·936 (6)	0·195 (4)	0·019 (2)	3·8 (3)

* $U_{eq} = (U_1 U_2 U_3)^{1/3}$ where U_1, U_2, U_3 are the mean-square displacements of the principal axes of the thermal ellipsoid.

Table 2. *Final interatomic distances (Å) and bond angles (°)*

	TDPA	DTDPA
S(1)—S(1^i)		2·032 (2)
S(1)—C(1)	1·818 (2)	1·815 (3)
C(1)—C(2)	1·507 (4)	1·514 (4)
C(2)—C(3)	1·500 (4)	1·492 (4)
C(3)—O(1)	1·296 (3)	1·308 (3)
C(3)—O(2)	1·230 (3)	1·222 (3)
C(1)—H(11)	0·94 (2)	0·94 (2)
C(1)—H(12)	0·93 (2)	0·94 (2)
C(2)—H(13)	0·92 (2)	0·95 (2)
C(2)—H(14)	0·95 (3)	0·93 (2)
O(1)—H(15)	0·94 (3)	0·95 (2)
O(1)···O(2^{ii})	2·674 (3)	2·658 (3)
H(15)···O(2^{ii})	1·74 (3)	1·71 (3)
C(1)—S(1)—C(1^{iii})	100·3 (2)	
S(1^i)—S(1)—C(1)		104·3 (1)
S(1)—C(1)—C(2)	110·9 (2)	114·2 (2)
C(1)—C(2)—C(3)	115·0 (2)	114·9 (2)
C(2)—C(3)—O(1)	114·1 (2)	112·4 (2)
C(2)—C(3)—O(2)	122·4 (2)	124·1 (2)
O(1)—C(3)—O(2)	123·5 (2)	123·5 (3)
C(3)—O(1)—H(15)	113 (2)	108 (2)
H(11)—C(1)—H(12)	109 (2)	108 (2)
H(13)—C(2)—H(14)	102 (2)	104 (2)

Symmetry code: none	x,y,z	x,y,z
(i)		$1 - x, y, 0·5 - z$
(ii)	$2 - x, \bar{y}, \bar{z}$	$1·5 - x, 0·5 - y, \bar{z}$
(iii)	$x, \bar{y}, 0·5 - z$	

performed on the Oxford University ICL 2980 computer with the rewritten Oxford *CRYSTALS* package (Carruthers & Watkin, 1976–77).

The final positional parameters are given in Table 1,* and interatomic distances and interbond angles with e.s.d.'s calculated from the full variance–covariance matrix are in Table 2.

Discussion. The structure of TDPA is shown in Fig. 1 and of DTDPA in Fig. 2. The twofold axis is located at the S atom for TDPA and at the middle of the S—S bond for DTDPA; in consequence, the asymmetric unit in each case is one half of the molecule. Both structures are composed of infinite chains of molecules along the *c* axis, linked by hydrogen bonds between carboxylic groups. This confirms the intermolecular hydrogen bonds suggested by the bands in the infrared spectra between 2400–3200 cm^{-1} (Pimentel & McClellan, 1960). There can be no bifurcated hydrogen-bonded network in three dimensions similar to that in oxydiacetic acid (Herbertsson & Boman, 1973) because the O···O distance between parallel chains exceeds 3·1 Å.

The S—C bond length in TDPA (1·818 Å) is similar to distances previously found by Paul (1967) and Herbertsson (1976) for the thiodiacetate system, but the C—S—C angle is larger and nearer to those in other aliphatic compounds (Stam, 1962). The S—S bond length in DTDPA (2·032 Å) agrees with that in the Cu^{II} complex of this ligand (Thich, Lalancette, Potenza & Harvey, 1976) and also with the accepted value for non-cyclic disulphides (Jones, Bernal, Frey & Koetzle, 1974; Rahman, Safe & Taylor, 1970). The observed
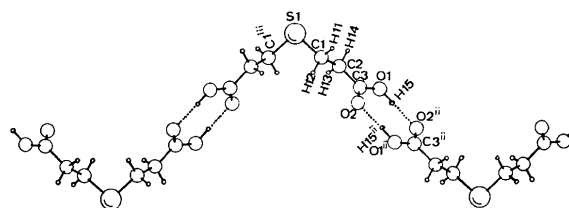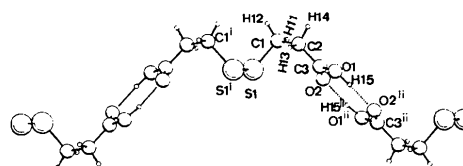
Fig. 1. Thiodipropionic acid, best-plane view.

Fig. 2. Dithiodipropionic acid, best-plane view.

Table 3. *Some selected torsion angles* (°) *and deviations* (Å) *from the least-squares best planes*

	TDPA	DTDPA
C(1^{iii})–S(1)–C(1)–C(2)	−85·0 (2)	
C(1^{i})–S(1^{i})–S(1)–C(1)		−78·5 (2)
S(1^{i})–S(1)–C(1)–C(2)		−60·1 (2)
S(1)–C(1)–C(2)–C(3)	176·0 (2)	−70·1 (2)
C(1)–C(2)–C(3)–O(1)	160·4 (2)	170·0 (2)
C(1)–C(2)–C(3)–O(2)	−21·6 (2)	−11·0 (2)

Plane (1): C(3), O(1), O(2), O(1^{ii}) and O(2^{ii})
Plane (2): S(1), C(1), C(2), C(3), O(1) and O(2)

	Plane (1)		Plane (2)	
	TDPA	DTDPA	TDPA	DTDPA
S(1)	0·160 (1)	−1·864 (1)	0·066 (1)	0·663 (1)
C(1)	0·386 (3)	−0·164 (3)	−0·205 (3)	−0·571 (3)
C(2)	−0·063 (3)	0·059 (3)	0·125 (3)	−0·132 (3)
C(3)	−0·003 (3)	0·007 (3)	0·022 (3)	−0·036 (3)
O(1)	0·002 (3)	−0·004 (3)	−0·089 (3)	0·541 (3)
O(2)	0·002 (3)	−0·004 (3)	0·080 (3)	−0·465 (3)
H(15)	0·01 (4)	0·07 (3)	−0·12 (4)	0·48 (3)
O(1^{ii})	0·000 (3)	0·001 (3)		
O(2^{ii})	0·000 (3)	0·001 (3)		

The symmetry code is as in Table 2.

dihedral angle (−78·5°) about the S—S bond shows a tendency to minimize S lone-pair repulsions. Both molecules are twisted about the thioether and disulphide group, respectively. Some torsion angles are given in Table 3.

C—O distances are in the range quoted for single C—O and double C=O bonds in carboxylic acids (Pimentel & McClellan, 1960). The least-squares best planes for carboxylic groups and for the independent halves of the molecules are shown in Table 3. The non-hydrogen atoms are not coplanar (apart from the C attached to the C of the carboxyl group) with the carboxylic plane (plane 1), but H(15) is very close to the plane for TDPA and deviates only slightly from the plane for DTDPA. The atoms of the TDPA molecule define better planes than do those of DTDPA. Hydrogen-bonded O···O distances (2·674 Å for TDPA and 2·658 Å for DTDPA) are longer than those obtained for the acid salts (Herbertsson, 1976) but analogous to those in the free acids (Paul, 1967; Herbertsson & Boman, 1973).

References

CARRUTHERS, J. R. & WATKIN, D. J. (1976–77). *CRYSTALS User Manual.* Oxford Univ. Computing Laboratory.
CARRUTHERS, J. R. & WATKIN, D. J. (1979). *Acta Cryst.* A35, 698–699.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
HERBERTSSON, H. (1976). *Acta Cryst.* B32, 3107–3109.
HERBERTSSON, H. & BOMAN, C. E. (1973). *Acta Chem. Scand.* 27, 2234–2236.
JONES, D. D., BERNAL, I., FREY, M. N. & KOETZLE, T. F. (1974). *Acta Cryst.* B30, 1220–1227.
PAUL, S. (1967). *Acta Cryst.* 23, 491–494.
PIMENTEL, G. C. & McCLELLAN, A. L. (1960). In *The Hydrogen Bond.* San Francisco and London: Freeman.
RAHMAN, R., SAFE, S. & TAYLOR, A. (1970). *Q. Rev. Chem. Soc.* 24, 208–237.
ROLLETT, J. S. (1965). Editor. *Computing Methods in Crystallography,* p. 40. Oxford: Pergamon Press.
STAM, C. H. (1962). *Acta Cryst.* 15, 317–322.
THICH, J. A., LALANCETTE, R. A., POTENZA, J. A. & HARVEY, J. S. (1976). *Inorg. Chem.* 15, 2731–2734.