Crystal structure of dithioacetic acid trimers, (CH₃C(SH)S)₃

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Abstract

C₆H₁₂S₆, orthorhombic, *Pnma* (No. 62), *a* = 9.954(3) Å, *b* = 12.617(3) Å, *c* = 9.716(2) Å, *V* = 1220.2 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.035, *wR*_{obs}(*F*²) = 0.097, *T* = 153 K.

Source of material

Dithioacetic acid is prepared following the process described in [1,2] by condensing CS₂ on commercial CH₃MgCl at 250 K in tetrahydrofuran distilled on benzophenon-sodium. Dithioacid is liberated by treating the organic layer by HCl-H₂O, and extracted by diethyl ether. Pure dithioacid is obtained after elimination of solvent, by distillation under vacuum.

Discussion

In a previous paper [3], we have reported the formation of a solid when dithioacetic acid is kept at low temperature for several days. Analyses (elemental, mass spectra, ¹H NMR) were consistent with the formation of a mixture of two isomeric cyclic trimers of the dithioacid. Traces of tetramethylhexathiaadamantane were also identified. Later on, the two trimers were isolated and characterized by their ¹³C-NMR spectra [4]. In a ¹H- and ¹³C-NMR study of the conformational equilibrium of dithioacetic acid, the appearance of weak extra signals in the expected region was observed and the possible formation of the same trimers was mentioned [5]. We tried to complement the characterization of these trimers by alkylation of the thiol functions in basic medium, as it

was done for the trimers of the dithioformic acid [6]. However, this was not possible due to the unstability of the compounds in basic medium. Therefore, we decided to confirm the structure of each isomer by a low temperature X-ray study of a single crystal isolated from the solid formed from a sample of dithioacetic acid left at 254 K for one month.

The figure shows a general view of the molecule. The substituted 1,3,5-trithiacyclohexane heterocycle has a chair conformation. The molecule occupies a special position in the mirror plane which passes through the S(1) and C(3) atoms. The substituents at the C(2) and C(3) atoms are disordered over two positions with different occupancies which indicates the presence of two diastereoisomers, one of them, namely that with the equatorial sulphur and axial carbon atoms, being predominant. The structure was refined by the full-matrix least-squares technique in the anisotropic approximation except for the disordered S(3'), S(4'), C(1'), and C(4') atoms which were refined isotropically. Taking into account the severe disorder no attempts to locate the H atoms were undertaken. Bond lengths and angles in the title molecule as determined in this X-ray study are unexceptional [7] and comparable with those reported in unsubstituted 1,3,5-trithiacyclohexane [8–10].

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.3 × 0.3 × 0.2 mm
Wavelength:	Mo K _α radiation (0.71073 Å)
μ:	10.71 cm ⁻¹
Diffractometer, scan mode:	Siemens P3/PC, θ/2θ
2θ _{max} :	54.08°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	1147, 1147
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 0 σ(<i>I</i> _{obs}), 1109
<i>N</i> (<i>param</i>) _{refined} :	75
Program:	SHELXTL-plus [11]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
C(1')	8d	0.27	0.820(6)	0.534(4)	0.066(5)	0.03(1)
C(4')	4c	0.18	0.454(4)	3/4	-0.265(3)	0.030(9)
S(3')	8d	0.27	0.6006(7)	0.6168(4)	0.2127(5)	0.029(1)
S(4')	4c	0.18	0.387(2)	3/4	0.009(1)	0.065(5)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(1)	4c		0.81900(9)	3/4	0.09851(7)	0.0200(6)	0.0210(4)	0.0156(3)	0	-0.0027(3)	0
S(2)	8d		0.62891(7)	0.62921(4)	-0.09329(5)	0.0270(5)	0.0224(3)	0.0194(3)	-0.0005(2)	-0.0053(2)	-0.0037(2)
S(3)	8d	0.73	0.8316(5)	0.5253(3)	0.0640(4)	0.036(2)	0.0225(8)	0.032(1)	0.0091(7)	-0.0069(6)	-0.0025(5)
S(4)	4c	0.82	0.4918(2)	3/4	-0.2946(2)	0.036(1)	0.0407(7)	0.0244(7)	0	-0.0163(7)	0
C(1)	8d	0.73	0.6253(8)	0.6039(5)	0.2037(7)	0.036(5)	0.020(2)	0.035(2)	0.010(2)	0.012(2)	0.009(2)
C(2)	8d		0.7135(3)	0.6337(2)	0.0742(2)	0.025(2)	0.0181(9)	0.0164(8)	-0.0002(8)	-0.0020(8)	0.0011(7)
C(3)	4c		0.5287(4)	3/4	-0.1085(3)	0.023(2)	0.027(1)	0.023(1)	0	-0.008(1)	0
C(4)	4c	0.82	0.3949(9)	3/4	-0.027(1)	0.023(4)	0.041(3)	0.038(4)	0	-0.009(3)	0

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