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Methyl 3,3,7,7-Tetramethyl-2-oxocycloheptanesulphinate, C12H22O3S

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Abstract. $M_r = 246.37$, triclinic, $P\bar{1}$, $a = 8.680$ (2), $b = 10.643$ (2), $c = 8.306$ (2) Å, $\alpha = 110.45$ (1), $\beta = 111.20$ (1), $\gamma = 79.97$ (2)°, $V = 669.3$ (3) Å^3, $Z = 2$, D_m(flotation, aqueous KI) = 1.224, $D_x = 1.222$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 2.2$ cm^{-1}, $F(000) = 268$, $T = 295$ K, $R = 0.036$ for 2971 observed reflections. The cycloheptane ring has a twist-chair conformation, with mean C–C = 1.538 (6) Å, mean C–C–C = 113.5 (16)°, C=O = 1.215 (2) Å. In the methyl sulphinate group, S has a pyramidal configuration, C–S = 1.824 (1), S=O = 1.466 (1), S–OCH$_3$ = 1.631 (1) Å. Packing of the molecules is governed by normal van der Waals contacts.

Introduction. In a study of the reactions of thioketones with singlet oxygen (Wasserman & Murray, 1979; Ramnath, Ramesh & Ramamurthy, 1983; Jayathirtha Rao, Ramamurthy, Schaumann & Nimmesgern, 1984), oxidation of the cyclohexane derivative (I) in methanol gave the ketone (II) and a novel product with proposed structure (III). The present X-ray analysis was undertaken to establish the structure of (III) and to determine the conformation of the cycloheptane ring.

(I)   (II)   (III)
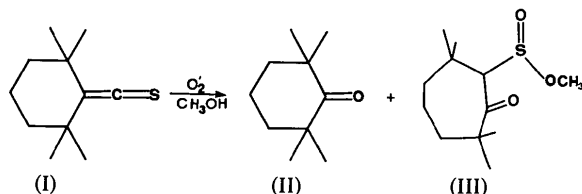
Experimental. Colourless crystals, $0.05 \times 0.38 \times 0.26$ mm, CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\theta \leq 32.5°$, ω–2θ

scan, ω-scan width $(0.90 + 0.35\tan\theta)°$ extended by 25% on either side of the peak for background measurement, horizontal aperture $(2 + \tan\theta)$ mm, vertical aperture 4 mm. Cell parameters by least-squares fit to observed $\sin^2\theta$ values for 21 centred reflections with $17 < \theta < 21°$, intensity and orientation controls regularly; decay of three standard intensities necessitated application of an isotropic decay correction. 4289 independent reflections (h –12 to 12, k –15 to 15, l 0 to 12), 2971 with $I \geq 3\sigma(I)$, $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, $S = $ total peak count and $B = $ time-averaged background, Lp corrections (no absorption corrections). Structure solved by direct methods with *SHELX*76 (Sheldrick, 1976), refined by full-matrix least squares on F with anisotropic thermal parameters, H atoms identified on a difference map and included in refinement with isotropic temperature factors; final $R = 0.036$, $wR = 0.039$ for 2971 observed reflections, 233 variables, $R = 0.076$ for all data, $w = 1/\sigma^2(F)$; $(\Delta/\sigma)_{max} = 0.05$, max. height in final difference map 0.3 e Å^{-3}. Scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), local adaptions of standard computer programs *ORFFE* (Busing, Martin & Levy, 1964) and *PLUTO* (Motherwell & Clegg, 1978).

Discussion. Final atomic parameters are in Table 1, bond lengths and angles in Table 2.*

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* Lists of structure factors, anisotropic thermal parameters, H coordinates, bond distances involving H atoms, torsion angles and the packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42017 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The cycloheptane ring (Fig. 1 and Table 3) has a twist-chair conformation (Bixon & Lifson, 1967; Hendrickson, 1967; Bocian, Pickett, Rounds & Strauss, 1975; Flapper & Romers, 1975), as found in other derivatives (Chacko, Srinivasan & Zand, 1971; Birnbaum, Buchanan & Morin, 1977; De Kok & Romers, 1980).

The mean C—C(ring) bond length of 1.538 (6) Å and the mean C—CH$_3$ distance of 1.534 (1) Å are close to the value of 1.534 (2) Å in n-alkanes (Bartell & Kohl, 1963); the C(sp^3)—C(sp^3) ring bonds at the methyl-substituted atoms C(3) and C(7) are slightly longer than the average, with mean 1.555 (5) Å. The bond angles in the ring vary from 108.3 (1) to 118.1 (1)°, with the mean of 113.5 (16)° being close to the theoretical values of 114.1 and $114.7°$ given for the twist-chair conformation (Bixon & Lifson, 1967;
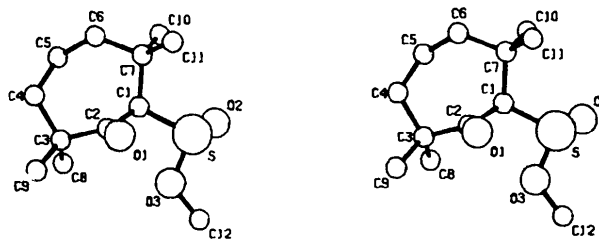

Fig. 1. Stereoview of the molecule of methyl 3,3,7,7-tetramethyl-2-oxocycloheptanesulphinate, showing the atom numbering.

Table 3. *Conformation of the cycloheptane ring*

Displacement of atoms from mean plane (Å, $\sigma = 0.001$–0.002 Å)			Bond torsion angles (°, $\sigma = 0.1°$)		
	This work	Bixon & Lifson (1967)		This work	Bixon & Lifson (1967)
C(1)	−0.443	−0.45	C(1)—C(2)	+100.5	+94
C(2)	+0.418	+0.44	C(2)—C(3)	−73.1	−74
C(3)	−0.096	−0.10	C(3)—C(4)	+45.8	+51
C(4)	+0.040	+0.09	C(4)—C(5)	−69.9	−70
C(5)	−0.431	−0.40	C(5)—C(6)	+92.8	+90
C(6)	+0.461	+0.45	C(6)—C(7)	−38.5	−40
C(7)	+0.072	−0.01	C(7)—C(1)	−42.1	−40

Table 1. *Final positional (fractional* $\times 10^4$*) and equivalent isotropic thermal parameters* (Å $\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
S	5701.4 (4)	2684.4 (3)	1353.0 (5)	42
O(1)	2604 (1)	4393 (1)	1234 (1)	47
O(2)	6802 (1)	1508 (1)	870 (2)	62
O(3)	5390 (1)	2697 (1)	3181 (1)	50
C(1)	3606 (1)	2191 (1)	−75 (2)	32
C(2)	2410 (1)	3199 (1)	761 (2)	32
C(3)	960 (1)	2660 (1)	899 (2)	36
C(4)	−319 (2)	2179 (2)	−1033 (2)	46
C(5)	352 (2)	1326 (1)	−2564 (2)	48
C(6)	1343 (2)	2106 (2)	−3057 (2)	46
C(7)	3240 (2)	2101 (1)	−2097 (2)	40
C(8)	1538 (2)	1498 (2)	1709 (2)	47
C(9)	128 (2)	3798 (2)	2100 (3)	58
C(10)	4031 (3)	779 (2)	−3051 (3)	62
C(11)	3887 (3)	3294 (2)	−2238 (3)	60
C(12)	6608 (3)	3381 (4)	4820 (3)	96

$$* \ U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S—O(2)	1.466 (1)	C(3)—C(4)	1.551 (2)
S—O(3)	1.631 (1)	C(3)—C(8)	1.535 (2)
S—C(1)	1.824 (1)	C(3)—C(9)	1.535 (3)
O(1)—C(2)	1.215 (2)	C(4)—C(5)	1.525 (2)
O(3)—C(12)	1.427 (3)	C(5)—C(6)	1.529 (2)
C(1)—C(2)	1.524 (2)	C(6)—C(7)	1.549 (2)
C(1)—C(7)	1.564 (2)	C(7)—C(10)	1.535 (3)
C(2)—C(3)	1.526 (2)	C(7)—C(11)	1.530 (3)
O(2)—S—O(3)	107.6 (1)	C(4)—C(3)—C(8)	110.2 (1)
O(2)—S—C(1)	106.1 (1)	C(4)—C(3)—C(9)	108.4 (1)
O(3)—S—C(1)	92.5 (1)	C(8)—C(3)—C(9)	109.5 (1)
S—O(3)—C(12)	113.3 (1)	C(3)—C(4)—C(5)	117.0 (1)
S—C(1)—C(2)	107.6 (1)	C(4)—C(5)—C(6)	113.7 (1)
S—C(1)—C(7)	112.5 (1)	C(5)—C(6)—C(7)	117.3 (1)
C(2)—C(1)—C(7)	111.7 (1)	C(1)—C(7)—C(6)	108.6 (1)
O(1)—C(2)—C(1)	119.6 (1)	C(1)—C(7)—C(10)	109.2 (1)
O(1)—C(2)—C(3)	122.3 (1)	C(1)—C(7)—C(11)	111.7 (1)
C(1)—C(2)—C(3)	118.1 (1)	C(6)—C(7)—C(10)	108.8 (1)
C(2)—C(3)—C(4)	108.3 (1)	C(6)—C(7)—C(11)	108.2 (1)
C(2)—C(3)—C(8)	111.2 (1)	C(10)—C(7)—C(11)	110.2 (1)
C(2)—C(3)—C(9)	109.3 (1)		

Hendrickson, 1967). The carbonyl group is approximately planar [C(2) displaced from mean plane by 0.013 (1) Å], with normal C=O bond length, 1.215 (2) Å.

In the methyl sulphinate group, S has a pyramidal configuration, with the methyl C atom, C(12), deviating by 0.349 (4) Å from the C(1), S, O(3) plane. The C(1)—S, 1.824 (1) Å, and S=O(2), 1.466 (1) Å, distances are close to normal values (Sutton, 1965), and S—O(3), 1.631 (1) Å, is slightly longer than a normal S—OC bond (1.60 Å, Cruickshank, 1961); angles involving the doubly bonded O(2) are slightly larger, 106.1 (1) and 107.6 (1)°, than C(1)—S—O(3), 92.5 (1)°, as expected. All these dimensions may be slightly influenced by steric interaction [O(3)···C(2) $= 2.743$ (2), O(3)···O(1) = 3.068 (2) Å].

Intermolecular distances correspond to van der Waals interactions; the shortest non-hydrogen contacts are O(1)···C(12) = 3.214 (2) Å and O(2)···C(8) = 3.569 (2) Å.

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N-Acetyl-DL-methionine, $C_7H_{13}NO_3S$

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Abstract. $M_r = 191·25$, monoclinic, $P2_1/c$, $a = 5·882$ (1), $b = 9·285$ (1), $c = 21·934$ (3) Å, $\beta = 124·88$ (5)°, $V = 982·7$ (2) Å^3, $Z = 4$, $D_x = 1·292$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2·8$ cm^{-1}, $F(000) = 408$, $T = 295$ K, $R = 0·041$ for 2131 observed reflections. The peptide group is planar within about 0·03 Å. The carboxyl group, also approximately planar, exists in the un-ionized form, with N out of the plane by 0·536 (1) Å. Bond lengths and angles are normal. Molecules are linked by N—H···O [2·953 (2) Å] and O—H···O [2·550 (2) Å] hydrogen bonds.

Introduction. Sulphur-centred radicals produced in crystals of N-acetyl-DL-methionine show well characterized thirteen-line hyperfine splitting in the ESR spectra and clear optical absorption bands (Kominami, Akasaka, Umegaki & Hatano, 1971; Kominami, 1972). The intensity ratios of these hyperfine lines are difficult to explain on the basis of a proposed radical structure. ENDOR (electron nuclear double resonance) measurements were made to establish the detailed electronic structures of these sulphur-centred radicals (Naito, Akasaka & Hatano, 1981), and to aid this study the crystal structure was determined by X-ray methods.

Experimental. Colourless crystals, 0·28 × 0·30 × 0·18 mm, CAD-4 diffractometer, graphite-

monochromatized Mo $K\alpha$ radiation, $\theta \leq 32·5°$, ω–2θ scan, ω-scan width $(0·70 + 0·35 \tan\theta)°$ extended by 25% on either side of the peak for background measurement, horizontal aperture $(2 + \tan\theta)$ mm, vertical aperture 4 mm. Cell parameters by least-squares fit to observed $\sin^2\theta$ values for 25 centred reflections with $15 < \theta < 21°$, absent reflections $0k0$, k odd, $h0l$, l odd $(P2_1/c)$; intensity and orientation checks for three standard reflections showed little $(< \pm 0·9\%)$ variation or decay throughout data collection. 3533 independent reflections $(h$ −7 to 7, k 0 to 14, l 0 to 31), 2131 (60·3%) with $I \geq 3\sigma(I)$, $\sigma^2(I) = S + 2B + [0·04(S-B)]^2$, $S =$ total peak count and $B =$ time-averaged background, Lp corrections (no absorption corrections). Structure solved by $MULTAN$80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares by $SHELX$76 (Sheldrick, 1976), anisotropic, H atoms from a difference synthesis, isotropic; function minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$, three reflections with high F_c/F_o ratios, possibly due to extinction, removed; max. electron density in final difference map 0·29 e Å^{-3}, final $R = 0·041$, $wR = 0·047$ for 2131 observed reflections, 161 variables, $R = 0·079$ for all data; $(\Delta/\sigma)_{max} = 0·04$. Scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), local adaptations of standard computer programs $ORFFE$ (Busing, Martin & Levy, 1964), $ORTEP$II (Johnson, 1976), and $PLUTO$ (Motherwell & Clegg, 1978).