it is not the commonest conformation in either (Sundaralingam, 1971). The torsion angle about the C1′—C1*P* bond defined by the end atoms O4′ and C6*P* is 126·2 (5)°.

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2,2,5,5-Tetramethyl-3-oxocyclohexyl *p*-Toluenesulfonate

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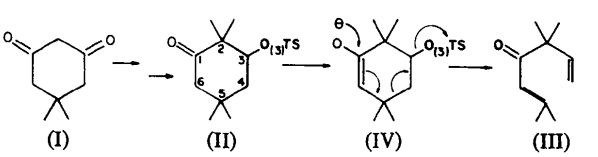
Abstract. $C_{17}H_{24}O_4S$, $M_r = 324{\cdot}4$, monoclinic, $P2_1/c$, $a = 9{\cdot}375$ (1), $b = 21{\cdot}334$ (4), $c = 9{\cdot}733$ (4) Å, $\beta = 113{\cdot}38$ (2)°, $V = 1786{\cdot}8$ (9) Å^3, $Z = 4$, $D_x = 1{\cdot}21$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}155$ mm^{-1}, $F(000) = 696$, $T = 296$ K, $R = 0{\cdot}054$ for 1964 reflections. The cyclohexane ring is in an almost ideal chair conformation and the relationship between the C(3)—O(Ts) and C(4)—C(5)$(CH_3)_2$ bonds is antiperiplanar, as required stereoelectronically for a successful occurrence of a fragmentation reaction. There are no unusual bond distances or angles.

Introduction. Commercially available dimedone (5,5-dimethyl-1,3-cyclohexanedione) (I) can be readily transformed into 2,2,5,5-tetramethyl-3-oxocyclohexyl *p*-toluenesulfonate (II) by standard methodology (Gaoni & Wenkert, 1966). The title compound (II) is the key intermediate in a synthetic sequence leading to Artemisia's ketone (III) (Simonsen & Owen, 1953) by fragmentation of the derived enolate (IV), as depicted in the scheme below. The success of such a fragmentation reaction (Brocksom, LaScala Teixeira, Kanawaga & Brocksom, 1987) is highly dependent upon the angular relationship that exists between the bonding electron pairs, and ideally should be antiperiplanar for the bonds C(3)—O(3) and C(4)—C(5) (II) (Marshall, 1969; Cookson, Edwards, Hudec & Kingsland, 1965). Therefore it became of interest to study the preferred conformation of the title compound (II), which has led to the present crystal structure determination.



Experimental. Prismatic colourless crystals 0·30 × 0·40 × 0·25 mm; Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$; cell parameters by

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least squares on setting angles for 22 reflections; $12 \le \theta < 20°$; ω–2θ scans, scan width $(0{\cdot}80 + 0{\cdot}35 \tan\theta)°$, scan speed $6{\cdot}7°$ min^{-1} max.; range of *hkl*: $0 < h < 11$, $0 < k < 25$, $-11 < l < 11$; standard reflections 008, 700 varied $\pm 1{\cdot}7\%$ of mean intensities over data collection; 3335 reflections measured, 3137 unique, $R_{int} = 0{\cdot}019$, 1966 observed above $3\sigma(I)$; Lp and absorption corrections (max. and min. transmission factors 0·962, 0·938). The structure was solved by direct methods; in final cycles of full-matrix least-squares refinement all non-H atoms anisotropic. H atoms located on geometrical grounds, methyl groups as rigid bodies, all with fixed $U = 0{\cdot}96$ Å^2. Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/|\sigma^2(F_o) + 0{\cdot}002\,|F_o|^2|$; 200 parameters refined; unobserved reflections and reflections 110 and 130 excluded; $R = 0{\cdot}054$; $wR = 0{\cdot}060$; inspection of F_c and F_o values indicated secondary-extinction correction required: $F_{corr} = F_c(1 - 10^{-4}\, x\, F_c^2/\sin\theta)$, where x refined to 0·13 in the final run; $(\Delta/\sigma)_{max} = 0{\cdot}002$; $\Delta\rho$ excursions within 0·2 and −0·3 e Å^{-3}. Scattering factors for non-H atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970) and for H from Stewart, Davidson & Simpson (1965); programs used: *SHELX*76 (Sheldrick, 1976), *ORTEP* (Johnson, 1965). Most of the calculations were performed on a VAX 11/780 computer from the Instituto de Física e Química de São Carlos.

Discussion. The molecule is shown in Fig. 1, together with atom labelling. Positional atomic parameters and equivalent isotropic temperature factors are given in Table 1.* Bond lengths and angles are given in Table 2; all values are within the expected range.

* Lists of H-atom positions, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44088 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

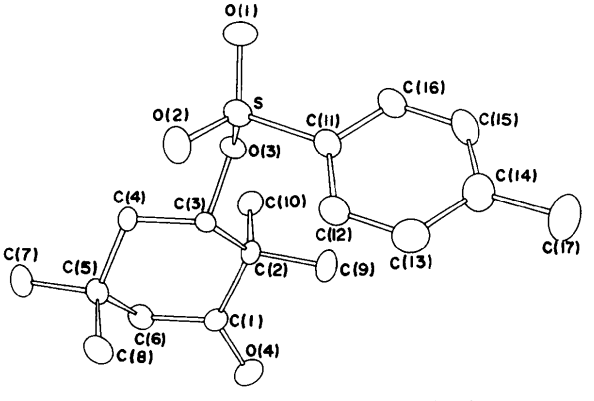

Fig. 1. A perspective view of the molecule.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
S	0·3804 (1)	0·1319 (0)	0·1290 (1)	4·35 (3)
O(1)	0·4264 (3)	0·0983 (1)	0·2653 (3)	6·2 (1)
O(2)	0·4830 (3)	0·1766 (1)	0·1078 (3)	5·70 (9)
O(3)	0·3422 (3)	0·0793 (1)	0·0063 (2)	3·82 (7)
O(4)	0·1094 (3)	0·0785 (2)	−0·5193 (3)	6·18 (9)
C(1)	0·2197 (4)	0·0636 (2)	−0·4087 (4)	4·0 (1)
C(2)	0·2052 (3)	0·0568 (2)	−0·2577 (4)	3·62 (9)
C(3)	0·3379 (3)	0·0954 (2)	−0·1432 (3)	3·32 (9)
C(4)	0·4970 (3)	0·0825 (2)	−0·1432 (3)	3·40 (9)
C(5)	0·5014 (4)	0·0924 (2)	−0·2974 (3)	3·9 (1)
C(6)	0·3762 (4)	0·0515 (2)	−0·4106 (4)	4·3 (1)
C(7)	0·4710 (5)	0·1614 (2)	−0·3456 (5)	5·5 (1)
C(8)	0·6613 (5)	0·0733 (2)	−0·2897 (5)	5·6 (1)
C(9)	0·2208 (4)	−0·0140 (2)	−0·2179 (4)	4·6 (1)
C(10)	0·0484 (4)	0·0810 (2)	−0·2677 (5)	5·8 (1)
C(11)	0·2013 (4)	0·1681 (2)	0·0928 (4)	4·1 (1)
C(12)	0·0994 (5)	0·1427 (2)	0·1484 (5)	5·1 (1)
C(13)	−0·0400 (5)	0·1719 (2)	0·1214 (5)	5·7 (1)
C(14)	−0·0797 (5)	0·2270 (2)	0·0430 (5)	5·5 (1)
C(15)	0·0238 (5)	0·2519 (2)	−0·0136 (5)	5·6 (1)
C(16)	0·1633 (5)	0·2231 (2)	0·0100 (4)	4·9 (1)
C(17)	−0·2268 (6)	0·2610 (2)	0·0224 (6)	7·6 (2)

* $B_{eq} = \frac{4}{3}\sum_i \sum_j B_{ij}(\mathbf{a}_i.\mathbf{a}_j)$ (Hamilton, 1959).

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

S–O(1)	1·416 (3)	C(4)–C(5)	1·532 (5)
S–O(2)	1·426 (3)	C(5)–C(6)	1·525 (5)
S–O(3)	1·573 (2)	C(5)–C(7)	1·537 (5)
S–C(11)	1·752 (4)	C(5)–C(8)	1·526 (6)
C(1)–C(2)	1·536 (5)	C(11)–C(12)	1·382 (6)
C(1)–C(6)	1·497 (6)	C(11)–C(16)	1·388 (5)
C(1)–O(4)	1·202 (4)	C(12)–C(13)	1·376 (7)
C(2)–C(3)	1·539 (5)	C(13)–C(14)	1·370 (6)
C(2)–C(9)	1·552 (5)	C(14)–C(15)	1·397 (7)
C(2)–C(10)	1·524 (5)	C(14)–C(17)	1·500 (7)
C(3)–C(4)	1·517 (5)	C(15)–C(16)	1·379 (7)
C(3)–O(3)	1·480 (4)		

S–O(3)–C(3)	119·3 (2)	C(3)–C(4)–C(5)	112·6 (3)
S–C(11)–C(12)	120·3 (3)	C(4)–C(3)–O(3)	108·3 (2)
S–C(11)–C(16)	119·6 (3)	C(4)–C(5)–C(7)	110·9 (3)
O(1)–S–O(2)	120·1 (2)	C(4)–C(5)–C(8)	108·8 (3)
O(1)–S–O(3)	104·1 (2)	C(6)–C(1)–O(4)	122·2 (3)
O(1)–S–C(11)	108·8 (2)	C(6)–C(5)–C(4)	108·5 (3)
O(2)–S–O(3)	109·3 (2)	C(6)–C(5)–C(7)	109·3 (3)
O(2)–S–C(11)	108·9 (2)	C(6)–C(5)–C(8)	110·0 (3)
O(3)–S–C(11)	104·5 (2)	C(7)–C(5)–C(8)	109·3 (3)
C(1)–C(2)–C(9)	107·2 (3)	C(9)–C(2)–C(10)	109·8 (3)
C(1)–C(2)–C(10)	110·9 (3)	C(11)–C(12)–C(13)	120·0 (4)
C(1)–C(6)–C(5)	111·7 (3)	C(11)–C(16)–C(15)	118·8 (4)
C(2)–C(1)–C(6)	117·1 (3)	C(12)–C(11)–C(16)	120·1 (4)
C(2)–C(1)–O(4)	120·7 (3)	C(12)–C(13)–C(14)	121·5 (4)
C(2)–C(3)–C(4)	114·5 (3)	C(13)–C(14)–C(15)	117·9 (4)
C(2)–C(3)–O(3)	106·7 (2)	C(13)–C(14)–C(17)	121·4 (4)
C(3)–C(2)–C(1)	106·8 (3)	C(14)–C(15)–C(16)	121·7 (4)
C(3)–C(2)–C(9)	111·8 (3)	C(15)–C(14)–C(17)	120·6 (4)
C(3)–C(2)–C(10)	110·3 (3)		

The cyclohexane ring is in an almost ideal chair conformation as indicated by the Cremer & Pople (1975) parameters: $q_2 = 0{\cdot}042$ (4), $q_3 = -0{\cdot}543$ (4) Å, $\varphi_2 = 44$ (5)°, $Q_T = 0{\cdot}544$ (4) Å, $\theta = 175{\cdot}6$ (4)°. Fig. 2 is a Newman projection down C(5)–C(6) showing the cyclohexane ring conformation and also that the

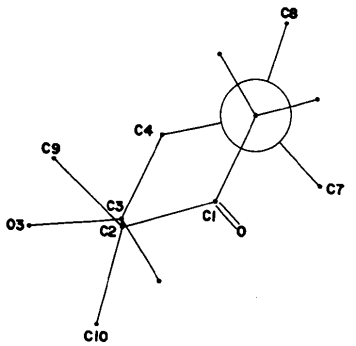

Fig. 2. A Newmann projection of the molecule, down C(5)–C(6).

relationship between C(3)–O(3) and C(4)–C(5) bonds is antiperiplanar. Therefore, the stereoelectronic requirements are met and the fragmentation reaction should occur with a relatively low activation energy.

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Nucleic Acid Binding Drugs. XVII. Structures of 4-Substituted Analogues of the Antitumour Drug Amsacrine

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Abstract. 4′-(9-Oxo-4-acridinyl)methanesulfonanilide monohydrate (I), $C_{20}H_{16}N_2O_3S.H_2O$, $M_r = 382$, monoclinic, $P2_1/c$, $a = 7{\cdot}373$ (1), $b = 11{\cdot}266$ (4), $c = 20{\cdot}925$ (3) Å, $\beta = 94{\cdot}59$ (2)°, $V = 1732{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}466$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 18{\cdot}76$ cm^{-1}, $F(000) = 800$, $T = 293$ K, $R = 0{\cdot}078$ for 1238 observed reflections. 4′-(9-Amino-4-acridinyl)-methanesulfonanilide hydrochloride (II), $C_{20}H_{18}N_3O_2S^+.Cl^-$, $M_r = 399{\cdot}4$, monoclinic, $P2_1/c$, $a = 10{\cdot}437$ (2), $b = 16{\cdot}092$ (3), $c = 10{\cdot}866$ (1) Å, $\beta = 91{\cdot}28$ (2)°, $V = 1824{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}456$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 30{\cdot}99$ cm^{-1}, $F(000) = 832$, $T = 293$ K, $R = 0{\cdot}047$ for 1501 observed reflections. The acridone and acridine rings in (I) and (II) are highly planar. The methanesulfonanilide substituent groups are oriented in a similar manner in both structures, although the methanesulfonanide groups adopt different orientations with respect to the phenyl ring.

Introduction. A large number of acridines substituted at the 9 position have been synthesized and evaluated for antitumour activity (Baguley, Denny, Atwell & Cain, 1981; Denny, Cain, Atwell, Hansch, Panthananickal & Leo, 1982). The compound 4′-(9-acridinylamino)-3′-methoxymethanesulfonanilide (ansacrine) has outstanding experimental *in vivo* activity in the series, and is

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