connect each cation with all anions in the unit cell (Fig. 1). These bonds promote the localization of charges and, perhaps, account for the low electroconductivity of MT– and MS–TCNQ.

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Structure of (1*S**,5*S**,*SR**)-1-(3-*p*-Toluenesulfinyl-2-propenyl)-2-methylene-7,7-dimethylbicyclo[3.3.0]octan-3-one

BY DUY H. HUA,† IBRAHEEM BADEJO AND PEGGY J. MCCANN

Department of Chemistry, Kansas State University, Manhattan, KS 66506, *USA*

AND FUSAO TAKUSAGAWA†

Department of Chemistry, University of Kansas, Lawrence, KS 66045, *USA*

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Abstract. $C_{21}H_{26}O_2S$, $M_r = 342{\cdot}50$, monoclinic, $C2/c$, $a = 28{\cdot}345\ (5)$, $b = 12{\cdot}303\ (2)$, $c = 11{\cdot}638\ (2)$ Å, $\beta = 103{\cdot}75\ (2)°$, $V = 3942\ (1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}154$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}738$ cm^{-1}, $F(000) = 1472$, room temperature, final $R = 0{\cdot}044$ for all 2594 reflections. The calculated molecular structure discloses the stereochemistry of the title compound to be 1*S**, 5*S** and *SR**. The five-membered rings forming the bicyclo[3.3.0]-octanone moiety deviate from the geometry of cyclopentane [C(1)–C(2) = 1·5254, C(1)–C(8) = 1·515 (4), C(4)–C(5) = 1·512 (3) Å; the bridging bond C(1)–C(5) = 1·561 (3) Å]. Angle C(11)–S(12)–C(13) = 96·16 (11)°.

Introduction. As part of our continuing study of stereospecific addition reactions of sulfinylallyl anions with ambident electrophiles (Hua, Sinai-Zingde & Venkataraman, 1985; Hua, 1986) and their application in the asymmetric total synthesis of antibiotic pentalenolactone (Duchamp & Chidester, 1972) (an agent which is active against Gram-positive/negative baceteria and fungi and which inhibits the enzyme glyceraldehyde-3-phosphate dehydrogenase), 2-[(*tert*-butyldimethylsilyloxy)methyl]-7,7-dimethylbicyclo-[3.3.0]-$\Delta^{1,2}$-octen-3-one (2) was treated with 1 equiv. of the anion derived from racemic *p*-tolyl allyl sulfoxide (1) and lithium diisopropylamide (LDA) in THF at 195 K for 30 min to provide the 1,4-adduct, 1-(3-*p*-toluenesulfinyl-2-propenyl)-2-methylene-7,7-dimethylbicyclo-[3.3.0]octan-3-one, (3), in 85% yield (m.p. 371–372 K). This product resulted from the rapid elimination of *tert*-butyldimethylsilyloxy ion from the initially formed enolate ion adduct. Together with sharp m.p., ^{1}H and ^{13}C NMR spectra support a single diastereomeric structure of (3). The relative stereochemistry at the S atom, C(1) and C(5) of (3) was proven by X-ray study. This proof, in turn, provides firm evidence of the stereochemical course followed in asymmetric addition reactions of chiral sulfinylallyl anions with cyclopentenones. Several reports on the X-ray crystallography of sulfoxides have previously been reported (Bandoli, Panattoni, Clemente, Tondello, Dondoni & Mangini, 1971; Hine, 1962; Thorup, 1971; Watkin & Hamor, 1971).

Experimental. A colorless prism, 0·41 × 0·39 × 0·22 mm, obtained by recrystallization from ether, was mounted on a glass fiber oriented approximately along [110]. Cell constants determined using 15 centered

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† Authors to whom correspondence should be addressed.

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reflections widely scattered throughout reciprocal space ($2\theta > 25°$). Preliminary counter data indicated a monoclinic system with systematic absences, $h + k = 2n + 1$ in hkl, $l = 2n + 1$ in $h0l$ and $k = 2n + 1$ in $0k0$, uniquely determining the space group as $C2/c$. Four octants ($h = -28 \rightarrow 28$, $k = -13 \rightarrow 13$, $l = -12 \rightarrow 0$) of data out to $2\theta = 45°$ collected using Nicolet $P2_1$ diffractometer (Mo $K\alpha$, graphite monochromator) with θ–2θ scan mode (scan angle: $0{\cdot}6894 \tan\theta + 2{\cdot}4°$, scan speed: 1·5 to 20·0° min^{-1}, background: 1/6 of total scan at the both edges). Total number of reflections measured 5530. Lorentz and polarization factors applied. Corrections made for 0·935 decline in intensity of two standard reflections monitored every 100 measurements. Semi-empirical χ-scan technique (±4·8%) used to correct for absorption (North, Phillips & Mathews, 1968). 2594 independent F_o^2 data obtained by merging equivalent reflections. $R_{\rm int}$ for merging is 0·022. The reflections with $F_o^2 < 0{\cdot}2\sigma(F_o^2)$ reset to $F_o^2 = 0{\cdot}2\sigma(F_o^2)$. The $\sigma(F_o^2)$ and $\sigma(F_o)$ values are defined as follows: $\sigma(F_o^2) = [\sigma^2_{\rm count} + (0{\cdot}02F_o^2)^2]^{1/2}$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$. All reflections used in subsequent calculations. The structure was solved by a direct method using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms located from difference Fourier maps. Full-matrix refinement, anisotropic for non-hydrogen and isotropic for hydrogen. Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma(F_o)^2$. Convergence to $R = 0{\cdot}044$, $wR = 0{\cdot}053$, $S = 1{\cdot}088$ for 2594 reflections. Final difference Fourier map featureless ($\pm 0{\cdot}22$ e Å^{-3}, $\Delta/\sigma < 0{\cdot}32$). Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). All calculations performed on a Honeywell 66/6000 computer at the University of Kansas using programs of the *KUDNA* system (Takusagawa, 1984).

Discussion. Final fractional coordinates with equivalent isotropic temperature factors are in Table 1; Table 2 contains some molecular dimensions (bond distances and bond angles).*

The molecule (Fig. 1) has a *cis*-fused bicyclo[3.3.0]octane. The framework bonds, at C(1)—C(2), C(1)—C(8) and C(4)—C(5), are somewhat shorter, and at C(1)—C(5) somewhat longer, than the 1·546 Å value determined for cyclopentane (Adams, Geise & Bartell, 1970). The bond angle C(11)—S(12)—C(13) is smaller than the 100° value determined for dimethyl sulfoxide (Bastiansen & Viervoll, 1948). The stereochemistry determined at C(1), C(5) and S is in line with the prediction that the anion derived from (+)-(R)-allyl p-tolyl sulfoxide approaches 2-cyclopentenone from the *si* face (Hua, Sinai-Zingde & Venkataraman, 1985; Hua, 1986).

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Table 1. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters*

The thermal parameters are of the form $B = 8\pi^2U$ and $B_{\rm eq} = \frac{8}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B/B_{\rm eq}$(Å^2)
C(1)	0·13535 (9)	0·2118 (2)	0·3259 (2)	5·24
C(2)	0·1631 (1)	0·2275 (3)	0·4542 (3)	6·64
C(3)	0·20101 (9)	0·1395 (2)	0·4772 (2)	5·28
C(4)	0·20458 (8)	0·0932 (2)	0·3616 (2)	4·14
C(5)	0·17079 (8)	0·1535 (2)	0·2618 (2)	4·12
C(6)	0·13841 (9)	0·0790 (2)	0·1686 (2)	5·18
C(7)	0·08618 (9)	0·0905 (2)	0·1812 (2)	5·76
C(8)	0·0930 (1)	0·1334 (3)	0·3076 (3)	6·13
C(9)	0·19985 (9)	0·2378 (2)	0·2072 (2)	4·47
C(10)	0·23902 (9)	0·1908 (2)	0·1581 (2)	4·50
C(11)	0·28476 (9)	0·2200 (2)	0·1908 (2)	4·92
S(12)	0·32924 (2)	0·16011 (7)	0·12822 (6)	6·20
C(13)	0·36930 (9)	0·1208 (2)	0·2658 (2)	4·79
C(14)	0·3585 (1)	0·0309 (2)	0·3252 (3)	6·60
C(15)	0·3881 (1)	0·0043 (3)	0·4311 (3)	7·73
C(16)	0·4285 (1)	0·0656 (3)	0·4828 (3)	6·87
C(17)	0·4393 (1)	0·1527 (3)	0·4193 (3)	6·52
C(18)	0·4101 (1)	0·1795 (2)	0·3106 (3)	5·54
O(19)	0·22454 (8)	0·1104 (2)	0·5733 (1)	7·28
C(20)	0·2339 (1)	0·0107 (2)	0·3553 (2)	5·24
C(21)	0·0590 (2)	0·1730 (4)	0·0920 (4)	8·91
C(22)	0·0586 (2)	−0·0170 (4)	0·1621 (5)	9·37
O(23)	0·35501 (8)	0·2473 (3)	0·0809 (2)	9·28
C(24)	0·4595 (2)	0·0414 (5)	0·6045 (4)	10·90
H(1)	0·124 (1)	0·280 (2)	0·288 (2)	6·79
H(2*A*)	0·144 (1)	0·222 (3)	0·508 (3)	8·93
H(2*B*)	0·180 (1)	0·296 (2)	0·468 (3)	7·34
H(6*A*)	0·148 (1)	0·003 (2)	0·184 (2)	6·12
H(6*B*)	0·140 (1)	0·094 (2)	0·088 (3)	8·06
H(8*A*)	0·065 (1)	0·166 (2)	0·321 (3)	7·67
H(8*B*)	0·1022 (9)	0·075 (2)	0·361 (2)	6·05
H(9*A*)	0·2147 (9)	0·292 (2)	0·271 (2)	5·88
H(9*B*)	0·1772 (9)	0·276 (2)	0·142 (2)	5·48
H(10)	0·2279 (9)	0·135 (2)	0·103 (2)	6·21
H(11)	0·2969 (9)	0·278 (2)	0·251 (2)	5·58
H(14)	0·328 (1)	−0·009 (3)	0·291 (3)	9·33
H(15)	0·380 (1)	−0·061 (3)	0·478 (4)	11·96
H(17)	0·468 (1)	0·197 (2)	0·452 (3)	8·31
H(18)	0·4169 (9)	0·241 (2)	0·270 (2)	5·84
H(20*A*)	0·2553 (9)	−0·025 (2)	0·427 (2)	5·63
H(20*B*)	0·2348 (9)	−0·021 (2)	0·276 (2)	6·12
H(21*A*)	0·028 (2)	0·181 (3)	0·104 (4)	10·93
H(21*B*)	0·055 (1)	0·152 (3)	0·009 (4)	9·65
H(21*C*)	0·071 (1)	0·247 (3)	0·111 (3)	10·49
H(22*A*)	0·027 (2)	−0·005 (3)	0·178 (4)	11·73
H(22*B*)	0·077 (1)	−0·073 (3)	0·220 (3)	9·29
H(22*C*)	0·055 (1)	−0·047 (3)	0·082 (4)	10·21
H(24*A*)	0·495 (2)	0·068 (4)	0·607 (4)	13·31
H(24*B*)	0·462 (2)	−0·025 (4)	0·612 (5)	14·08
H(24*C*)	0·442 (3)	0·076 (5)	0·683 (6)	20·38

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

C(1)—C(2)	1·525 (4)	C(5)—C(9)	1·551 (3)
C(1)—C(5)	1·561 (3)	C(11)—S(12)	1·760 (2)
C(1)—C(8)	1·515 (4)	S(12)—C(13)	1·795 (3)
C(4)—C(5)	1·512 (3)	S(12)—O(23)	1·476 (3)
C(5)—C(6)	1·544 (4)		
C(2)—C(1)—C(5)	106·56 (21)	C(1)—C(5)—C(6)	105·40 (19)
C(2)—C(1)—C(8)	115·11 (24)	C(1)—C(5)—C(9)	110·67 (18)
C(5)—C(1)—C(8)	102·68 (21)	C(11)—S(12)—C(13)	96·16 (11)
C(1)—C(5)—C(4)	102·75 (18)	C(11)—S(12)—O(23)	108·46 (14)

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* Lists of complete molecular dimensions (bond distances, bond angles and torsion angles), anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43727 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

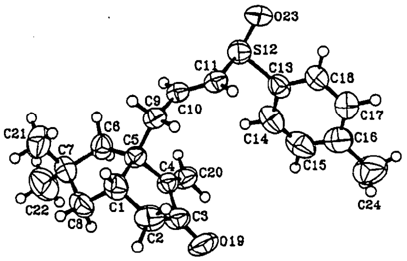

Fig. 1. View of the title compound with atom numbering.

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The Structure of 1,5-Bis(salicylidene)carbonohydrazide Monohydrate

By J. Dan

Department of Physics, Sri Ramkrishna Sarada Vidyamahapit, PO Kamarpukur, Hooghly – 712612, *WB, India*

S. Seth

Department of Physics, Durgapur Government College, Durgapur – 713214, *Burdwan, WB, India*

and S. Chakraborty*

Department of Physics, University of Burdwan, Burdwan – 713104, *WB, India*

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Abstract. $C_{15}H_{14}N_4O_3.H_2O$, $M_r = 316{\cdot}3$, orthorhombic, $C222_1$, $a = 12{\cdot}229\,(2)$, $b = 4{\cdot}553\,(1)$, $c = 27{\cdot}371\,(13)$ Å, $V = 1523{\cdot}98$ Å^3, $Z = 4$, molecular symmetry 2 (C_2), $D_m = 1{\cdot}39\,(1)$, $D_x = 1{\cdot}379$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}109$ mm^{-1}, $F(000) = 664$, $T = 298$ K. Final $R = 0{\cdot}042$ for 510 observed diffractometer data. The ligand as a whole is planar to within 0·081 (7) Å. The salicyl ring is planar to within 0·012 (7) Å with normal dimensions and is tilted by 3·0 (2)° from the remainder of the molecule. Bond lengths and angles suggest delocalization of π electrons in the part of the molecule adjacent to the salicyl ring. In addition to van der Waals forces, hydrogen bonding of the water O atom with the carbonyl O atom [O···O 2·730 (4) Å] stabilizes the molecular packing.

Introduction. Recently, Dutta & Hossain (1983) have synthesized bis(salicylidene)carbonohydrazide which acts a chelating ligand. Although several metal chelates of bis(salicylidene)thiocarbonohydrazide have been studied, there is no report on the complexing behaviour of its oxygen analogue. A number of coordination complexes of the latter ligand with nickel(II), cobalt(II), copper(II), oxovanadium(IV) and lead(II) have been synthesized. A comparison of the structural parameters of the free ligand with those of its metal complexes allows a discussion of the bonding in the metal complexes and hence a rationalization of some of their properties (Calligaris, Nardin & Randaccio, 1972).

Experimental. Title compound synthesized by mixing carbonohydrazide and salicylaldehyde and refluxing on a steam bath. Thin plate-shaped colourless crystals obtained by slow evaporation from alcohol at room

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* To whom correspondence should be addressed.

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