A Conformational Study of the 3-*p*-Tolylsulphonylbutan-2-ol and 1,2-Diphenyl-2-*p*-tolylsulphonylethanol Diastereoisomeric Pairs

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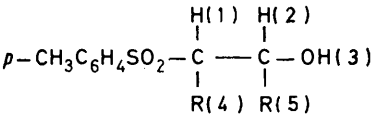
Solvent and temperature effects upon the conformation of *erythro*- and *threo*-3-*p*-tolylsulphonylbutan-2-ol (I) and (III), and of *erythro*- and *threo*-1,2-diphenyl-2-*p*-tolylsulphonylethanol (II) and (IV) have been studied by i.r. and ^{1}H n.m.r. spectroscopic techniques. All compounds form an intramolecular hydrogen bond in chloroform and carbon tetrachloride solutions, whereas in dimethyl sulphoxide, pyridine, and acetone hydrogen bond formation with the solvent occurs. Steric requirements control the conformational preference of (II) and (IV) in all solvents. The conformation of (I) and (III) in polar solvents may be determined primarily by a *gauche* attractive interaction between oxygen and sulphur atoms. In low polarity solvents the conformations which facilitate intramolecular hydrogen bonding are preferred.

SULPHUR compounds bearing an ethyl fragment have been the subject of mechanistic and spectroscopic investigations in these laboratories.[1-3] We now report an i.r. and ^{1}H n.m.r. study dealing with conformational aspects of *erythro*- and *threo*-3-*p*-tolylsulphonylbutan-2-ol and *erythro*- and *threo*-1,2-diphenyl-2-*p*-tolylsulphonylethanol (I)—(IV).

During our investigation, complementary results have been presented on similar compounds (*i.e.*, some 2-thio-derivatives of 1-phenylethanol and 1,2-diphenylethanol).[4] This allows us to compare our conclusions with those reported for the latter compounds, leading



(I) R = Me *erythro*
(II) R = Ph *erythro*
(III) R = Me *threo*
(IV) R = Ph *threo*

eventually to a better understanding of the relative importance of steric, polar, and hydrogen bonding interactions.

RESULTS AND DISCUSSION

Combination of i.r. and ^{1}H n.m.r. spectroscopic techniques provides evidence for extensive intramolecular hydrogen bond formation for both diastereoisomeric pairs in $CHCl_3$ and CCl_4 solutions. For the sake of comparison both i.r. and ^{1}H n.m.r. spectra have been recorded in the same concentration range, 0.06—0.30M for compounds (I) and (III), and 0.09—0.50M for compounds (II) and (IV).

The i.r. spectra of the *threo*-isomers display two sharp absorptions, with very different intensity, in the O–H stretching region (Table 1). Spectra which were recorded in $CHCl_3$ at different concentrations (0.06—0.30M) show that (i) the two absorption frequencies are concentration independent, (ii) their intensity ratio remains constant, and (iii) no broad absorption suggesting a solute–solute hydrogen bond appears at higher concentrations.

TABLE 1

I.r. stretching vibration frequencies [a] of OH and SO_2 groups for compounds (I)—(VII). Values of $\varepsilon_{max.}$ are in parentheses

Compound	Concentration (M)	Free OH	Intramolecular bonded OH	Symmetric SO_2	Antisymmetric SO_2
(I)	0.09	3 610 (21)	3 540 (95)	1 310 (350)	1 140 (750)
(II)	0.06	3 600 (67)	3 550 (85)	1 310 (465)	1 140 (850)
(III)	0.09	3 620 (28)	3 520 (118)	1 310 (390)	1 140 (710)
(IV)	0.06	3 600 (27)	3 500 (124)	1 310 (445)	1 140 (850)
(V)	0.05			1 320 (515)	1 145 (710)
(VI)	0.05			1 320 (470)	1 145 (735)
(VII)	0.05			1 320 (470)	1 145 (740)

[a] In cm^{-1}, chloroform solutions.

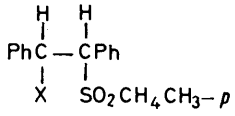
The *erythro*-isomers show an i.r. absorption with a shoulder at higher frequency. The effect of dilution is generally similar to that observed for the *threo*-isomers.

The presence of two bands may be attributed to intramolecular hydrogen bonding, *i.e.* the higher frequency band is due to the free hydroxy group and the lower frequency one is ascribed to the presence of a hydrogen-bonded hydroxy group. The proof that the hydrogen bond is intra- rather than inter-molecular is given by the near invariance of the intensity ratio in the above mentioned concentration range. If the bonding were intermolecular, the lower frequency band would decrease and the higher frequency band increase with dilution, thus influencing their intensity ratio.

The hydroxy group absorption of the *threo*-isomers shows (Table 1) stronger intramolecular hydrogen

bonding ($\Delta\nu$ 100 cm^{-1}) than observed for *erythro*-isomers ($\Delta\nu$ 50 and 70 cm^{-1}). It is suggested that deviation from dihedral angle of 60°, to diminish the Ph/Ph [5] or Me/Me *gauche*-interaction energy (0.8 kcal mol^{-1} in both cases [6]), strengthens the hydrogen bond in the *threo*-isomers but weakens it in the *erythro*-isomers [7] (see rotamers Ta, Eb, and Ec in the Scheme).

The ability of the sulphonyl group to form hydrogen bonds is well documented. The formation of hydrogen bond shifts the SO_2 symmetrical and antisymmetrical stretching frequencies to lower values.[8] In order to obtain the frequencies of the symmetrical and antisymmetrical stretching of a sulphonyl group not involved in hydrogen bond formation, the i.r. spectra of *erythro*- and *threo*-1-bromo-1,2-diphenyl-2-*p*-tolylsulphonylethane (V) and (VI) and of *threo*-1-chloro-1,2-diphenyl-2-*p*-tolylsulphonylethane (VII) have been recorded in



(V) X = Br *erythro*
(VI) X = Br *threo*
(VII) X = Cl *threo*

$CHCl_3$ solution. Table 1 reveals that in the sulphonyl-substituted alcohols the frequencies of the antisymmetrical and symmetrical stretching vibrations occur at lower wavenumbers than in (V)—(VII). The magnitudes of the respective shifts are in good agreement with those reported [8] in similar cases, thus indicating that the sulphonyl group is involved in the formation of a hydrogen bond.

In order to obtain further evidence for intramolecular hydrogen bonding the i.r. spectra of (III) in CCl_4–DMSO and CCl_4–pyridine mixed solvents were investigated. Since DMSO and pyridine are known to form stronger hydrogen bonds than sulphones, solute–solvent interactions would be expected to replace intramolecular interactions. In fact, we have observed that, in the mixed solvents, the sharp free OH stretching band becomes very weak or even disappears and a new broad band appears at considerably lower frequency, in addition to the narrow band due to intramolecular hydrogen-bonded O–H stretching. The new band should be due to the intermolecularly hydrogen-bonded O–H stretch of the alcohol–DMSO (or of the alcohol–pyridine) complex. Upon enrichment of the mixed solvent with DMSO or pyridine the intra- and inter-molecular hydrogen-bonded bands become weaker and stronger, respectively, reflecting the replacement of intramolecular by intermolecular hydrogen bonding. This effect is more pronounced in CCl_4–DMSO mixtures.

TABLE 2

^1H N.m.r. parameters for compound (I). Chemical shifts (at 100 MHz) and coupling constants are given in Hz

	$CDCl_3$ (−30 to +40 °C; 6) [a]	CCl_4 (−20 to +40 °C; 5)	$(CH_3)_2SO$ (+30 to +90 °C; 8)	$(CH_3)_2CO$ 30 °C	C_6H_5N 30 °C
ν_1	$298.1 - 0.04_3\Delta t$ [b]	282.6 [c]	$314.7 - 0.08_0\Delta t$	312.3	334.0
ν_2	$444.6 - 0.01_2\Delta t$	430.3 [c]	$425.7 - 0.07_5\Delta t$	430.3	489.1
ν_3	$304.4 - 0.32_8\Delta t$	$287.9 - 0.32_0\Delta t$	$466.9 - 0.56_7\Delta t$	355.9	
ν_4	$132.6 - 0.05_1\Delta t$	124.0 [c]	$113.3 + 0.04_8\Delta t$	124.5	147.3
ν_5	120.4 [c]	112.4 [c]	$111.3 - 0.04_0\Delta t$	117.6	133.4
$^3J_{12}$	$1.2_6 + 0.002\Delta t$	$1.3_6 + 0.002\Delta t$	$2.7_0 + 0.002\Delta t$	2.2	2.4
$^3J_{23}$	$2.6_8 + 0.006\Delta t$	2.3_0 [c]	5.6_0 [c]	4.4	
$^3J_{14}$	7.3 [c]	7.3 [c]	7.2 [c]	7.1	7.3
$^3J_{25}$	6.6 [c]	6.7 [c]	6.5 [c]	6.7	6.7
$^4J_{35}$	0.7 [c]	0.7 [c]			

[a] Number of points and temperature range used to determine the ν and J temperature relationships. [b] $\Delta t = (t - 30)$ °C. [c] Within the limit of experimental error no temperature dependence was observed.

The conclusions reached from the i.r. studies were corroborated by ^1H n.m.r. investigations on the changes of the chemical shift and coupling constant of the OH proton (i) upon dilution in weak hydrogen bonding solvent and (ii) on going from a non-hydrogen bonding to a hydrogen bonding solvent. In $CDCl_3$ solution, little or no effect of concentration on the $^3J_{23}$ values and on the chemical shift of the OH proton was observed for the concentration ranges 0.06—0.30M for (II) and (IV), and 0.1—0.5M for (I) and (III), in agreement with the presence of an intramolecular hydrogen bond. Because of the Karplus-type relation between the H–C–O–H coupling constant and the corresponding dihedral angle,[9] the small and constant $^3J_{23}$ values in $CDCl_3$ and CCl_4 (see Tables 2—5) reflect the existence to a large extent of a preferred H–C–O–H rotamer, as a result of intramolecular hydrogen bonding. In acetone, pyridine,

TABLE 3

^1H N.m.r. parameters for compound (II). Chemical shifts (at 100 MHz) and coupling constants are given in Hz

	$CDCl_3$ (−60 to +55 °C; 21) [a]	$(CH_3)_2SO$ (+30 to +130 °C; 10)	$(CH_3)_2CO$ 30 °C	C_6H_5N 30 °C
ν_1	415.4 [c]	$460.7 - 0.16_7\,\Delta t + 0.000\,7_5\,(\Delta t)^2$	592.8	493.1
ν_2	$598.8 - 0.04_5\,\Delta t$ [b]	$570.0 + 0.01_9\,\Delta t$	447.7	653.9
ν_3	$357.7 - 0.38_4\,\Delta t$	$595.8 - 0.51_8\,\Delta t - 0.000\,9_3\,(\Delta t)^2$	491.3	815.4
$^3J_{12}$	$2.4_4 + 0.003\,\Delta t$	$3.2_8 - 0.002\,\Delta t$	3.0	3.0
$^3J_{23}$	$2.7_8 + 0.007\,\Delta t$	4.9_0 [c]	4.3	4.6
$^4J_{13}$		0.6 [c]	0.5	

[a–c] As Table 2.

and DMSO the values of $^3J_{23}$ increase significantly. This fact is consistent with the breaking of the intramolecular hydrogen bonds and concomitant hydrogen bonding of the hydroxy hydrogens to solvent molecules. Important parameters which cause a variation in the $^3J_{23}$ values such as the orbital hybridization of carbon and oxygen, the H–C–O and C–O–H bond angles, and the C–O bond length are assumed to remain essentially constant in the solvents employed.

Conformational Analysis.—Aiming at a proper understanding of the factors governing the conformational distribution among the rotamers in the Scheme, we examined the temperature and solvent dependence of both vicinal proton–proton coupling constants, $^3J_{12}$ and $^3J_{23}$.

erythro-3-p-*Tolylsulphonylbutan-2-ol* (I). The small $^3J_{12}$ values in $CDCl_3$ and CCl_4 (Table 2) are indicative of predominantly *gauche*-protons as in rotamers Eb and Ec. The four-bond coupling constant between the hydroxy proton and the methyl protons indicates that the rotamer Eb is predominant. This conformation displays a favourable CH_3–C–O–H coupling pattern, *i.e.* the hydrogen bond to the sulphonyl group holds the hydroxy hydrogen in an *anti*-relationship with respect to the methyl group at position 1 of the carbon skeleton. Furthermore, as Dreiding models show, the small value of $^3J_{23}$ is consistent with an arrangement of the hydroxy and sulphonyl groups conducive to intramolecular hydrogen bond formation.

In polar solvents hydrogen bonding to solvent occurs. The variation of the ^{1}H n.m.r. parameters with temperature has been investigated for DMSO solution. The temperature dependence is greater for ν_{OH} than for ν_1, ν_2, ν_4, and ν_5, and it is not significant for the coupling constants. It is reasonable to ascribe the slight decrease of ν_{OH} with increasing temperature to a decrease of the degree of hydrogen bonding of the OH group to the solvent. The behaviour of the other parameters suggests the presence of a predominant rotamer which, as the $^3J_{12}$ values show, again has *gauche*-protons. The conformational preference between Eb and Ec is difficult to assess. However, according to the dependence of the magnitude of J_{HH}(*gauche*) upon the orientation of the electronegative substituents, small values of $^3J_{12}$ favour rotamer Eb. It should be noted that the Ec conformation displays an unfavourable interaction between the 2-methyl group and the sulphonyl oxygen atoms. By considering (i) that the population of Ea appears to be quite small even though space-filling

TABLE 4

^{1}H N.m.r. parameters for compound (III). Chemical shifts (at 100 MHz) and coupling constants are given in Hz

	$CDCl_3$ (−60 to +40 °C; 10) [a]	CCl_4 (−20 to +70 °C; 10)	$(CH_3)_2SO$ (+30 to +90 °C; 7)	$(CH_3)_2CO$ 30 °C	C_6H_5N 30 °C
ν_1	$310.9 - 0.08_7\Delta t$ [b]	$301.3 - 0.06_3\Delta t$	$331.3 - 0.03_5\Delta t$	372.5	367.3
ν_2	$417.2 - 0.02_0\Delta t$	$408.7 - 0.03_5\Delta t$	$408.6 + 0.01_0\Delta t$	426.2	473.3
ν_3	$405.7 - 0.60_2\Delta t$	$373.8 - 0.57_8\Delta t$	$491.6 - 0.53_2\Delta t$	410.2	
ν_4	$114.5 - 0.04_0\Delta t$	$107.0 + 0.02_2\Delta t$	$114.5 - 0.01_7\Delta t$	119.0	144.4
ν_5	$124.6 - 0.03_8\Delta t$	$115.5 + 0.02_3\Delta t$	111.7 [c]	120.4	149.3
$^3J_{12}$	7.9_0 [c]	$6.9_0 + 0.002\Delta t$	3.9_5 [c]	4.9	4.4
$^3J_{23}$	$2.4_0 + 0.004\Delta t$	$2.3_4 - 0.004\Delta t$	4.8 [c]	4.2	
$^3J_{14}$	7.4 [c]	7.4 [c]	7.3 [c]	7.2	7.3
$^3J_{25}$	6.5 [c]	6.5 [c]	6.5 [c]	6.3	6.5

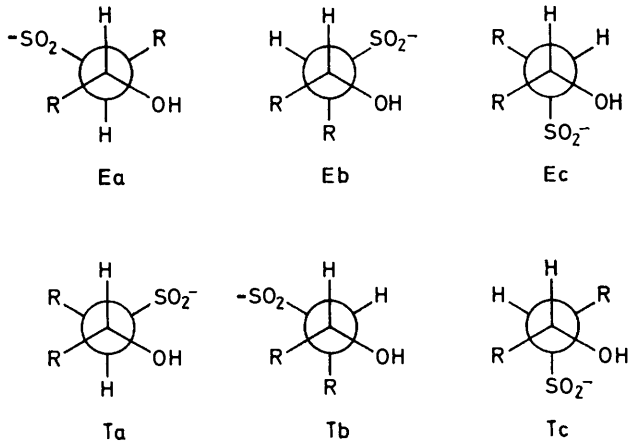
[a–c] As Table 3.

TABLE 5

^{1}H N.m.r. parameters for compound (IV). Chemical shifts (at 100 MHz) and coupling constants are given in Hz

	$CDCl_3$ (−60 to +55 °C; 13) [a]	$(CH_3)_2SO$ (+30 to +170 °C; 14)	$(CH_3)_2CO$ 30 °C	C_6H_5N 30 °C
ν_1	$443.6 - 0.08_8\ \Delta t$ [b]	$491.9 - 0.11_9\ \Delta t$	481.7	529.4
ν_2	$572.4 - 0.07_6\ \Delta t$	$545.2 + 0.06_5\ \Delta t$	566.5	613.1
ν_3	$469.8 - 0.25_0\ \Delta t$	$569.4 - 0.44_6\ \Delta t$	484.7	770.9
$^3J_{12}$	$9.8_8 - 0.004\ \Delta t$	$9.8_8 - 0.004\ \Delta t$	10.1	9.9
$^3J_{23}$	$1.6_1 + 0.007\ \Delta t$	4.6 [c]	2.6	3.0
$^4J_{13}$		0.7 [b]		

[a–c] As Table 2.



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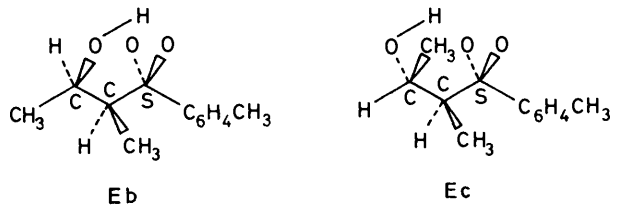
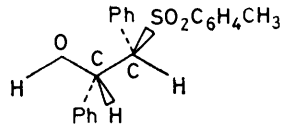


molecular models indicate the absence of appreciable steric hindrance, and (ii) the results of studies carried out on 2-thio-derivatives of phenylethanols,[4] we suggest that a *gauche*-attractive electrostatic interaction of the partially charged sulphur atom with the hydroxy oxygen atom may have an influence in controlling the rotamer preference of (I). The larger values of $^3J_{23}$ are attributed to the weighted average between H–C–O–H rotamers showing a favourable geometry for hydrogen bonding to the solvent molecules.

erythro-1,2-*Diphenyl*-2-p-*tolylsulphonylethanol* (II). The i.r. spectrum shows a substantial free hydroxy absorption and a relatively small hydroxy splitting ($\Delta\nu$ 50 cm^{-1}) which indicate the presence of a weak intramolecular hydrogen bond. As for (I), the $^3J_{12}$ and $^3J_{23}$ values in $CDCl_3$ solution (Table 3) allow us to select two conformations involving C–C and C–O bonds which are consistent with intramolecular hydrogen bond formation. The vicinal coupling constants and the H(1) and H(2) chemical shifts display practically no temperature dependence in the range −60 to +55 °C, thus suggesting the predominant presence of only one rotamer which probably corresponds to Eb. Indeed, owing to the large steric requirement of $SO_2C_6H_4CH_3$ compared with that of OH, Ec is much more sterically hindered than Eb.

In DMSO, acetone, and pyridine the *gauche*-relationship between the protons of the ethane fragment is maintained. The existence of a long-range coupling constant, $^4J_{13}$ resulting from a W conformation adopted by the H–C–C–O–H fragment, provides us with the opportunity of indicating the Eb as the most populated



conformation for the ethane fragment, thus confirming the conclusions achieved in $CDCl_3$ solution. In contrast, Ec lacks the proper orientation to show H–C–C–O–H coupling in its ^1H n.m.r. spectrum. It can be argued that in Ec the steric factors overcome the oxygen–sulphur attractive interaction.

threo-3-p-*Tolysulphonylbutan*-2-*ol* (III). $^3J_{12}$ Values in $CDCl_3$ and CCl_4 (Table 4) indicate that (III) is conformationally mixed. However, the i.r. hydroxy absorption shows in both solvents an intense and strong intramolecular hydrogen bonding ($\Delta\nu$ 100 cm^{-1}) with a very weak free hydroxy absorption. This indicates that both rotamers which facilitate hydrogen bonding (Ta and Tc) are populated. The $^3J_{12}$ values permit a rough approximation of rotamer population at equilibrium using relationship (1) where X is the rotamer population expressed as a mole fraction.

$$^3J_{12} = X_{(Ta)}{}^3J_{anti} + X_{(Tc)}{}^3J_{gauche} \qquad (1)$$

Literature data [2,10] on acylic compounds with an SO_2 group as substituent and a sum of substituent electronegativities comparable with that for (III) indicate the value 11.4 ± 0.4 Hz and the range 1.2—2.9 Hz as possible magnitudes for $^3J_{anti}$ and $^3J_{gauche}$, respectively. Employing equation (1) one obtains an $X_{(Ta)}$ range of 0.58—0.65 in $CDCl_3$ and of 0.47—0.56 in CCl_4. Replacement of CCl_4 and $CDCl_3$ by hydrogen bonding solvents causes $^3J_{12}$ to decrease with increasing hydrogen bonding ability of the solvent. The breaking of intramolecular hydrogen bonding results in a decrease in the relative population of rotamer Ta. This observation is unexpected since (i) it seems reasonable to predict that the division of the four bulkiest groups into pairs separated from one another by hydrogen should contribute to a reduction in the energy of the system and (ii) the Ta conformation, like Tc, should be favoured by oxygen–sulphur interactions.[4]

threo-1,2-*Diphenyl*-2-p-*tolylsulphonylethanol* (IV). The large values of $^3J_{12}$ in all solvents employed (Table 5) are indicative of predominantly *anti*-protons. Space-filling models show that rotamers with vicinal protons constrained in a *gauche*-relationship are disfavoured. π–π or *n*–π repulsions between the aryl ring or the oxygen atoms of the *p*-tolylsulphonyl group and the phenyl rings on carbon atoms of the ethane backbone destabilize rotamers Tb and Tc. In $CDCl_3$ the magnitude of $^3J_{23}$ is in accord with intramolecular hydrogen bonding. In DMSO solution hydrogen bonding to solvent occurs resulting in larger values for $^3J_{23}$. Intermediate values for $^3J_{23}$ in acetone and pyridine are considered to be a weighted mean of the inter- and intra-molecularly bound hydroxy resonances.

To summarize, in compounds (I) and (II) the absence of Ec is due to steric factors which predominate over the oxygen–sulphur *gauche* interaction. On the other hand this interaction stabilizes rotamer Eb in respect to Ea, both displaying a lower degree of steric hindrance. Intramolecular hydrogen bonding and S–O *gauche* interaction are competitive in controlling the conformational preference (Ta and Tc) of compound (III) in low polarity solvents. Indeed, in polar solvents the breaking of the intramolecular hydrogen bond shifts the conformational populations toward the rotamer Tc. Substitution of the two methyl with phenyl groups [compound (IV)] gives a low population of Tc rotamer and Ta appears to be the most abundant, in agreement with the steric requirements of phenyl and *p*-tolylsulphonyl groups.

These results lead to the conclusion that, besides the oxygen–sulphur *gauche* attraction,[4] other factors, such as hydrogen bonding and Ph/Ph steric interaction, can be effective in determining the rotamer population.

EXPERIMENTAL

Synthesis of Compounds (I)—(VII).—*erythro*-3-*p*-Tolylsulphonylbutan-2-ol (I), m.p. 71—72° (from hexane),[11] *threo*-3-*p*-tolylsulphonylbutan-2-ol (III), b.p. 164—165° at 0.2 mmHg,[11] *erythro*-1,2-diphenyl-2-*p*-tolylsulphonylethanol (II), m.p. 156—157° (from ethanol),[3] *erythro*-1-bromo-1,2-diphenyl-2-tolylsulphonylethane (V), m.p. 205—206° (from

ethanol),[3] *threo*-1-bromo-1,2-diphenyl-2-*p*-tolylsulphonylethane (VI), m.p. 134—135° (from ethanol),[3] and *erythro*-1-chloro-1,2-diphenyl-2-*p*-tolylsulphonylethane (VII), m.p. 183—184° (from ethanol),[12] were prepared according to reported methods. *threo*-1,2-Diphenyl-2-*p*-tolylsulphonylethanol (IV) was prepared as follows. Hydrogen peroxide (36% v/v; 6 ml) was added to solution of *threo*-1,2-diphenyl-2-*p*-tolylthioethanol [3] (10 g, 0.31 mol) in acetic acid. The mixture was heated on a steam-bath for 2 h, then diluted with water, and extracted with ether. After the solvent had been removed the residue was crystallized from ethanol to give *product* (IV) (9.9 g, 90%), m.p. 151—152° (Found: C, 72.0; H, 5.8; S, 9.0. $C_{21}H_{20}O_3S$ requires C, 71.6; H, 5.7; S, 9.1%).

^{1}H N.m.r. spectra were recorded at 100 MHz on a Varian HA 100 instrument using the following conditions: recording scale 2 Hz cm^{-1}, sweep rate 0.2 Hz s^{-1}. Tetramethylsilane was used to generate the reference and the lock signal. Calibration at 10 Hz intervals was made by frequency counter. Non-first-order spectra were analysed using the LAOCOON 3 program. The parameters are accurate to 0.2 Hz. In order to observe the hydroxy splitting, the n.m.r. samples were kept over molecular sieves (type 3A; pellets 1/8 in; Union Carbide). Before recording the spectra at various temperatures, the temperature of the probe was checked. In DMSO solution the higher limit of temperature was determined by the onset of decomposition of the compound.

I.r. spectra were recorded on a Perkin-Elmer model 257 instrument standardized *versus* polystyrene. Measurements were made in 0.2 and 0.5 mm cells. The extinction coefficients ε, accurate to $\pm 10\%$, are maximum values and are equal to $(1/cl)\ \log_{10}\ (I_0/I)$ with l in cm and c in mol l^{-1}. Strictly, the integrated band area should be used in quoting values of ε, but this was not considered necessary for the purpose of the present work.

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