concluded that the C–S bond lengths in four-membered rings are clearly longer than in other environments. The C–S bond distance in tetrafluoro-1,3-dithietane, 1.820(2) Å, is shorter than that in thietane; however, the CSC angle is larger, 82.7(2)°. The corresponding parameters are 1.804(3) Å and 97.0(19)° in 4-thiacyclohexanone.[16]

The ED-data are consistent with D_{2h} symmetry for tetrafluoro-1,3-dithietane, a result which is in agreement with vibrational [4] and NMR [17] spectroscopy.

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1. Chang, C. H., Porter, R. F. and Bauer, S. H. *J. Mol. Struct. 7* (1971) 89.
2. Harris, W. C. and Yang, D. B. *J. Chem. Phys. 60* (1974) 4175.
3. Alekseev, N. V. and Barzdain, P. P. *J. Struct. Chem. 15* (1974) 171; Lemaire, H. P. and Livingston, R. L. *J. Am. Chem. Soc. 74* (1952) 5732.
4. Durig, J. R. and Lord, R. C. *Spectrochim. Acta 19* (1963) 769.
5. Karakida, K. and Kuchitsu, K. *Bull. Chem. Soc. Jpn. 48* (1975) 1691.
6. Harris, D. O., Harrington, H. W., Luntz, A. C. and Gwinn, W. D. *J. Chem. Phys. 44* (1966) 3467.
7. Zeil, W., Haase, J. and Wegmann, L. *Z. Instrumentenk. 74* (1966) 84.
8. Bastiansen, O., Graber, R. and Wegmann, L. *Balzers High Vacuum Report 25* (1969) 1.
9. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
10. Yates, A. C. *Comput. Phys. Commun. 2* (1971) 175.
11. Strand, T. G. and Bonham, R. A. *J. Chem. Phys. 40* (1964) 1686.
12. Tavard, C., Nicolas, D. and Rouault, M. *J. Chim. Phys. 64* (1967) 540.
13. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett. 15* (1972) 263.
14. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Lett. 3* (1969) 617.
15. Karakida, K., Kuchitsu, K. and Bohn, R. K. *Chem. Lett.* (1974) 159.
16. Seip, R., Seip, H. M. and Smith, Z. *J. Mol. Struct. 32* (1976) 279.
17. Long, R. C., Jr. and Goldstein, J. H. *J. Chem. Phys. 54* (1971) 1563.

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Hydrogen Bonding Effects on the Fluorescence of Methyl Salicylate

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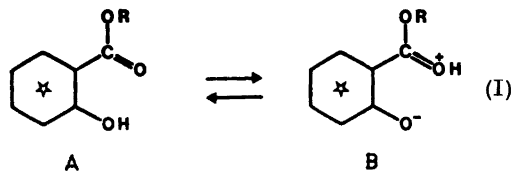
Some twenty years ago Weller [1] found that salicylic acid and methyl salicylate in methanol solution have unstructured fluorescence spectra both with a Stokes' shift about 5000 cm^{-1} greater than that of the corresponding methoxy compound, *o*-methoxy benzoic acid and its methyl ester. An additional weak fluorescence component with a Stokes' shift similar to that of the corresponding methoxy compound appeared in hydrocarbon solutions. The ratio between the intensities of the short and long wavelength components of the methyl salicylate fluorescence decreased as the temperature was reduced. Partial quenching of the fluorescence with carbon disulfide did not affect the intensity ratio. Weller interpreted the fluorescence properties of salicylic acid and methyl salicylate as a result of the following, at room temperature fully established, protolytic equilibrium in the excited state:



(I)

where R denotes H or CH_3. The short and long wavelength fluorescence components should emanate from A and B, respectively. This interpretation was supported by the fact that phenolic groups are much more acidic in the lowest excited singlet state than in the ground state, while excitation makes aromatic carbonyl and carboxyl groups much more basic. Excitation of intramolecularly hydrogen-bonded salicylic acid or methyl salicylate molecules would thus favour an intramolecular proton transfer. From the measurements on methyl salicylate in methylcyclohexane, Weller calculated the ΔH values for the proton transfer as -1.0 kcal mol^{-1} and 13.5 kcal mol^{-1} in the excited and ground states, respectively.*

A preliminary new study of the methyl salicylate fluorescence has revealed some unexpected effects of solvent and excitation wavelength, which indicate that the hitherto accepted reaction mechanism should be modified. As seen from Fig. 1, the ratio between the intensities of the short and long wavelength

* 1 kcal = 4.184 kJ.

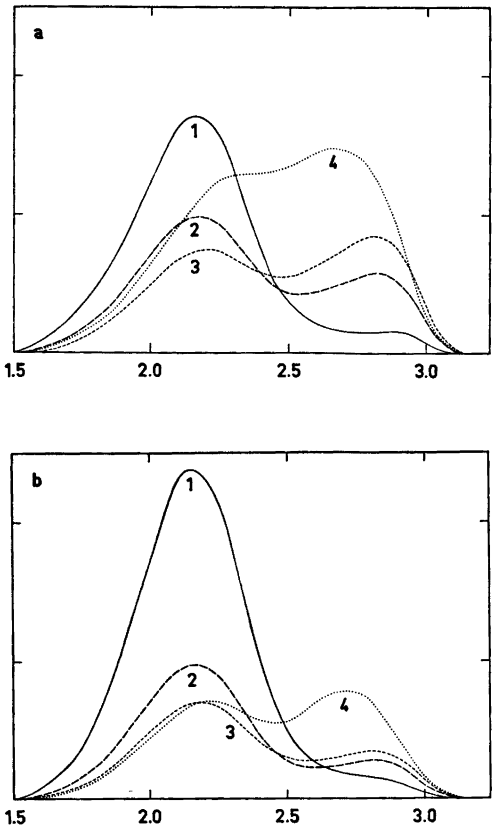
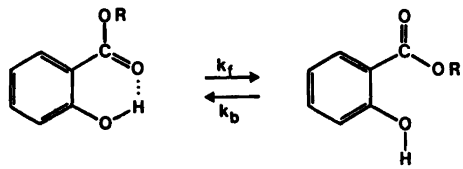


Fig. 1. Fluorescence spectra of 2×10^{-4} mol dm^{-3} methyl salicylate in cyclohexane (——), ethanol (– – –), methanol (- - -), and 2,2,2,-trifluoroethanol (···). The spectra are shown in relative numbers of quanta *vs.* wave number in μm^{-1}. The excitation wavelengths are 286 nm and 316 nm in *a* and *b*, respectively.

fluorescence components depends on the excitation wavelength, and, contrary to the earlier findings, this ratio is much greater in the alcoholic solvents than in cyclohexane. The ratio increases in the same order as do the stabilities of the hydrogen bond complexes between the alcohols and esters. For, *e.g.*, the ethyl acetate complex with ethanol, methanol, or 2,2,2-trifluorethanol, the values of the stability constants are:[2,3] 1.0, 1.4, and 6.9 dm^3 mol^{-1} in carbon tetrachloride at 25 °C. The position of the short wavelength maximum is seen to be solvent dependent. The fluorescence maximum of methyl *o*-methoxybenzoate shows similar solvent shifts.

The fact that the fluorescence spectrum of methyl salicylate depends on the excitation wavelength indicates at least two forms of ground state molecules and that the relative steady state concentrations of the fluorescing species depend on the proportions in which the ground state forms are excited. It seems tempting to assume that the relevant ground state forms are those with and without an established intramolecular hydrogen bond. Yasunaga *et al.*[4] have, by means of ultrasonic absorption measurements, performed a kinetic study of the ground state equilibrium:



(II)

cis *trans*

The rate constants found in neat methyl salicylate at 25 °C were $k_f = 9.5 \times 10^5$ and $k_b = 2.6 \times 10^7$ s^{-1}. If excited methyl salicylate in cyclohexane solution has a similar value of k_b, the formation of the *cis* form, a prerequisite for the intramolecular proton transfer, cannot efficiently take place during the lifetime of the excited *trans* form. In air saturated solution this lifetime is most probably less than 10^{-8} s. It might well be that the proton transfer in excited *cis* form molecules is very efficient, *i.e.* that equilibrium (I) is almost totally displaced to the right. The temperature effect on equilibrium (II) should then be the main cause of the fluorescence temperature dependence in methylcyclohexane solution found by Weller. In the alcoholic solvents a proton transfer is evidently inhibited by the formation of an intermolecular hydrogen bond between the ester group and the solvent. It may also be noted that for salicylic acid in cyclohexane or benzene, the intensity ratio between the short and long wavelength fluorescence components increases with the acid concentration in a way that may be quantitatively accounted for as caused by dimer formation. The cyclic hydrogen bonding of the carboxyl groups in the dimer inhibits a proton transfer.

It may be expected that spectrally resolved fluorescence lifetime measurements will give more conclusive information regarding the processes which determine the fluorescence behaviour of methyl salicylate.

Experimental. The methyl salicylate was purified by fractional distillation at 1.6 kPa. Gas chromatography of the distilled sample indicate a purity of 99.96 %. The fluorescence spectra at 25 °C obtained with an Aminco Bowman spectrophotofluorometer were transformed to relative quantum spectra on a wave number scale.

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1. Weller, A. *Z. Elektrochem. 60* (1956) 1144.
2. Becker, E. D. *Spectrochim. Acta 17* (1961) 436.
3. Sherry, A. D. and Purcell, K. F. *J. Phys. Chem. 74* (1970) 3535.
4. Yasunaga, T., Tatsumoto, N., Inoue, H. and Miura, M. *J. Phys. Chem. 73* (1969) 477.

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NMR Experiments on Cyclic Sulfites. VII. Lanthanide Induced Chemical Shifts in Trimethylene Sulfites with Respect to the Orientation of the S=O Bond

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Lanthanide induced chemical shifts (LIS) in sulfoxides have been published.[1] The LIS chemical shift increases linearly with the concentration of the shift reagent for a given sulfoxide concentration. Several workers have attempted to correlate the shifts with the internuclear distance between the proton studied and the lanthanide ion on the basis of assumed models. Apparently the lanthanide induced shifts should make it possible to distinguish between an axial and an equatorial functional group in cyclic compounds since the internuclear distance is changed substantially when the coordination site is moved from one position to the other. Accordingly, the shift induced on complexing the substrate will depend on the relative contributions of rotamers or conformers. The trimethylene (TM) sulfites have been shown to exist in a rigid chair conformation preferably with the S=O group in the axial position.[2-7] However, equatorial S=O groups have been observed for some substituted TM sulfites.[4] A study of LIS of TM sulfites with either S=O equatorial or axial should give additional information with regard to the stereochemistry of cyclic sulfites.

Results and discussion. The following TM sulfites have been prepared and examined with regard to the lanthanide induced shifts of the 4- and 5-protons and 4- and 5-substituted methyl groups: TM sulfite (I), 5-methyl-TM sulfite (II), 5,5-dimethyl-TM sulfite (III), 4-methyl-TM sulfite (IV), 5-phenyl-TM sulfite (V), 5-*tert*-butyl-TM sulfite (VI), 4,6-dimethyl-TM sulfite (with axial S=O bond VII a, with equatorial S=O VII b, and a twisted form VII c) and *trans*-1,3,2-dioxathiadecalin-2-oxide (with axial S=O VIII a, with eq. S=O VIII b).

The compounds I–VI have been reported to be in a 100 % or close to a 100 % rigid chair conformation with axial S=O bond. VII b and VIII b are found to be in a rigid chair conformation with equatorial S=O bond.[5,15]

When the concentration of the LSR is plotted against the chemical shift for the discrete protons, the "shiftslope" will depend on the position of the proton in the molecule. This is shown by Fig. 1 for TM sulfite and *cis*-4,6-dimethyl-TM sulfite (S=O eq. and twisted) and in Table 1 the corresponding slopes are calculated together with the "shiftslopes", K^s, of the other molecules examined.

From each of the three conformational forms in Table 1 and Fig. 1, it is evident that we are able to differentiate between axial and equatorial groups or protons on the same carbon atom. Likewise, we can differentiate between the two rigid chair forms with axial and equatorial S=O bond and the twisted conformer by comparing the Eu-shift for the 4 (6) axial protons.

Under certain conditions for internal rotation or for axial symmetry in the susceptibility tensor, the pseudocontact contribution to the

Table 1. The "shiftslope" K^s (ν/x) for the methyl protons in the rigid chair conformations of the trimethylenesulfites with axial S=O bond, equatorial S=O bond, and the twisted form.

R/K^s (Hz)	S=O ax	S=O eq	Twist
$H_{4,6a}$	8.5 – 11.2	3.7 – 3.8	9.7 (H_{4a})
$H_{4,6e}$	3.5 – 4.4	5.7	4.4 (H_{6e})
H_{5a}	3.8 – 5.6	6.2 – 7.6	–
H_{5e}	3.1 – 3.8	3.2	–
$Me_{4,6e}$	2.1 – 2.6	2.8	5.7 (Me_{4e})
Me_{6a}	–	–	2.2
Me_{5a}	2.4 – 3.7	–	–
Me_{5e}	1.6 – 2.0	–	–

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