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ORGANOSULPHUR COMPOUNDS—IX[1]

NMR AND STRUCTURAL ASSIGNMENTS IN α,β-UNSATURATED SULPHOXIDES USING ADDITIVE INCREMENTS METHOD

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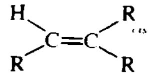
Abstract—Additive shielding increments for the sulphinyl group, RS(O)-, have been estimated ($Z_{RSO\text{-}gem}$ 1·27; $Z_{RSO\text{-}cis}$ 0·67; $Z_{RSO\text{-}trans}$ 0·41) and their utility in making NMR and structural assignments in α,β-unsaturated sulphoxides is presented.

Among the various NMR spectroscopic approaches to identify the configuration about double bond the additive shielding increments method[2-5] has been shown to be general and very useful in practice. This method is based on the independence and additivity of vinyl substituent shielding effects. The resonance position of an olefinic proton can be calculated by the eqn (1)

$$\delta_{ppm} = 5{\cdot}25 + Z_{gem} + Z_{cis} + Z_{trans} \qquad (1)$$



where 5·25 represents the chemical shift of ethylene and Z_{gem}, Z_{cis} and Z_{trans} are the respective increments for substituents R in the *gem*, *cis* and *trans* relationship to the protons. Additive shielding parameters for olefinic protons have been computed[3] from the 4298 cases investigated for 43 functional groups covering a large number of substituted ethylenes. The list of the additive shielding increments given by Matter *et al.*[3] in their original work include also the sulphur containing substituents like RS– and RSO_2– as well as SF_5– and CH_3COS–. The latter two are less common groups attached to the ethylene residue. Until now, however, the shielding increments for the sulphinyl group, RS(O)–, occupying the middle position between the mercapto and sulphonyl group, have not been estimated. In view of the growing interest in the chemistry and stereochemistry of α,β-unsaturated sulphoxides[6-9] in the past few years and because of our recent studies[10,11] in this field we decided to calculate the corresponding shielding increments for the sulphinyl group with the hope that they may be very useful in structural assignments.

Using the Z values derived by Matter *et al.*[3] we calculated according to the equations given below the average Z values for the sulphinyl group based on the 64 proton chemical shifts in α,β-unsaturated sulphoxides drawn from the literature.

$$Z_{RSO\text{-}gem} = \delta - (5{\cdot}25 + Z_{cis} + Z_{trans}) \qquad (2)$$

$$Z_{RSO\text{-}cis} = \delta - (5{\cdot}25 + Z_{gem} + Z_{trans}) \qquad (3)$$

$$Z_{RSO\text{-}trans} = \delta - (5{\cdot}25 + Z_{cis} + Z_{gem}). \qquad (4)$$

The chemical shift values of olefinic protons in vinyl sulphoxides taken for calculations refer to the carbon tetrachloride and deuterochloroform solutions and TMS as internal standard. It has been found that the difference ($\Delta\delta$) between the experimental and calculated values of the proton chemical shift in vinyl sulphoxides does not exceed 0·15 ppm for 83% of the examples taken into account.

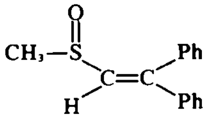
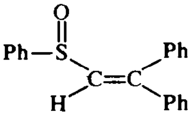
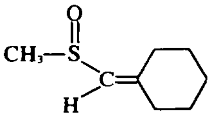
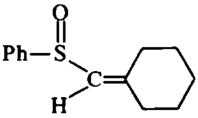
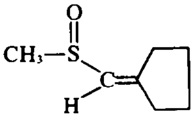
Table 1 illustrates the good agreement between the calculated and observed vinyl proton resonance positions in some α,β-unsaturated sulphoxides. In this context we would like to point out that the additive shielding increments for the RS(O)-group derived here are practically independent on the nature of the substituent R bonded to the S atom. As it can be seen from Table 1 excellent results are obtained for aliphatic as well as for aromatic vinyl sulphoxides (compare the examples 1 and 2 and 3 and 4).

By calculating absolute values of the proton chemical shift in suitably substituted vinyl sulphoxides it is also possible to assign configuration to geometrical isomers providing that the difference between the observed resonance positions in these isomers is greater than the uncertainty limit of the method under discussion (±0·1 ppm). This approach provides a rapid method for establishing the geometric structures of mono-, di- and tri-substituted vinyl sulphoxides and it is, of course, most advantageous for such systems in which the stereospecific coupling constants (especially $^3J_{H\text{-}H}$) are not available or in case where only one isomer is accessible and characterized by PMR spectroscopy. Some examples illustrating this are given in Table 2 and discussed below.

Recently, we have obtained[10] both E and Z isomers of 1-methylsulphinyl-2-methyl-2-phenyl-ethylene (**6**). Their geometry has unambiguously been established on the basis of the stereo-specific synthesis. Thus, the isomer with δ_H 6·54 ppm and $^4J_{H\text{-}CH_3}$ – 1·0 Hz was assigned the E configuration whereas the configuration Z was given to the isomer with δ_H 6·30 ppm and $^4J_{H\text{-}CH_3}$ – 1·5 Hz. Simple calculations using the additive shielding increments shown in Table 2 lead to the same conclusion providing an additional proof of this assignment.

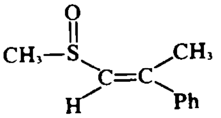
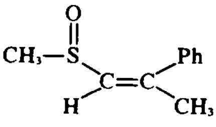
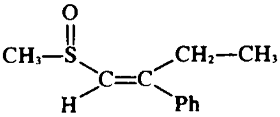
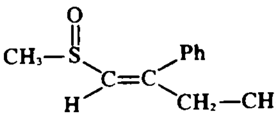
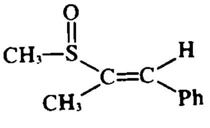
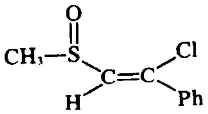
The E and Z geometry has also been assigned to the isomers of sulphoxide (**7**) on the basis of the allylic coupling observed in one isomer the olefinic proton of which absorbs at δ 6·32 ppm. The resonance signal of the vinyl proton in the second isomer appears at δ 6·46 ppm as a singlet. This observation led Russell and Ochrymowycz[12] to suggest the E configuration for the former isomer. However, they have neglected the sign of the allylic coupling constant which is known to be negative. Accordig to Barfield[13] the *trans* $^4J_{H\text{-}CH_3}$ should be

Table 1. Chemical shifts of olefinic protons in α,β-unsaturated sulphoxides

No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
1	10	 6·81	5·25 1·27 (RSO *gem*) 0·36 (aromatic *cis*) −0·07 (aromatic *trans*) 6·81 (Δ = 0)
2	6	 6·78	as for 1 6·81 (Δ = −0·03)
3	10	 6·01	5·25 1·27 (RSO *gem*) −0·25 (alkil ring *cis*) −0·28 (alkil ring *trans*) 5·99 (Δ = 0·02)
4	6	 5·95	as for 3 5·99 (Δ = −0·04)
5	10	 6·12	as for 3 5·99 (Δ = 0·13)

All chemical shifts are in ppm ex TMS.
Δ denotes experimental value—calculated value.

Table 2. Structural assignments to geometrical isomers in α,β-unsaturated sulphoxides using additive shielding increments

No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
6-E	10	 6·54	5·25 1·27 (RSO *gem*) −0·28 (alkil *trans*) 0·36 (aromatic *cis*) 6·60 (Δ = −0·06) Reversing assignment 6·23 (Δ = 0·31)
6-Z	10	 6·30	5·25 1·27 (RSO *gem*) −0·22 (alkil *cis*) −0·07 (aromatic *trans*) 6·23 (Δ = 0·07) Reversing assignment 6·60 (Δ = −0·30)
7-E	12	 6·46	as for 6-E 6·60 (Δ = −0·14) Reversing assignment 6·23 (Δ = 0·23)
7-Z	12	 6·32	as for 6-Z 6·23 (Δ = 0·09) Reversing assignment 6·60 (Δ = −0·28)
8	12	 7·10	for isomer E 5·25 0·67 (RSO *cis*) 1·38 (aromatic *gem*) −0·28 (alkil *trans*) 7·02 (Δ = 0·08) for isomer Z 5·25 0·41 (RSO *trans*) 1·38 (aromatic *gem*) −0·22 (alkil *cis*) 6·82 (Δ = 0·28)
9	12	 6·89	for isomer E 5·25 1·27 (RSO *gem*) 0·18 (Cl *cis*) −0·07 (aromatic *trans*) 6·63 (Δ = 0·26) for isomer Z 5·25 1·27 (RSO *gem*) 0·13 (Cl *trans*) 0·36 (aromatic *cis*) 7·01 (Δ = −0·12)

greater, i.e. less negative than the *cis* $^4J_{H-CH_3}$ which means that the *trans*-allylic coupling should be less visible than the *cis* one. Therefore, one may expect that the reversed assignments should be correct. In full agreement with this reasoning are the calculations with the aid of the additive increments given in Table 2.

In the case of sulphoxide (**8**) only one isomer has been isolated. The comparison of the calculated and the observed resonance positions indicate that it should have the configuration E. Similarly, from the predicted resonance positions the Z configuration can confidently be assigned to the isomer of sulphoxide (**9**) reported. It is interesting to note that in the latter case there is no other possibility of configurational assignments.

From the point of view of the proton NMR spectroscopy it is of great importance to know the proton resonance positions in AB systems. Usually, this problem can be solved with the help of the specifically deuterated compounds. Here we wish to demonstrate that simple application of the additive shielding increments permits rapid and reliable assigning the chemical shifts to H_A and H_B protons in various α,β-unsaturated sulphoxides (Table 3).

Finally, in Table 4 we have summarized the examples of α,β-unsaturated sulphoxides where the chemical shifts of olefinic proton show considerable deviations from the values calculated by means of the additive shielding

Table 3. Assignments of proton resonance position in AB systems in α,β-unsaturated sulphoxides

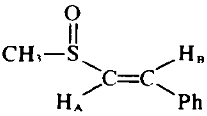
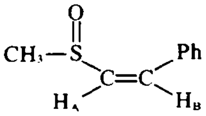
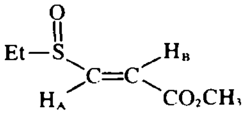
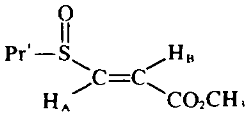
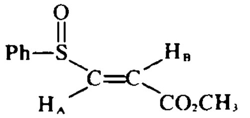
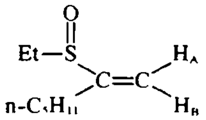
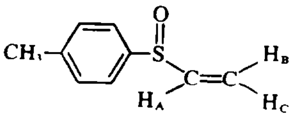
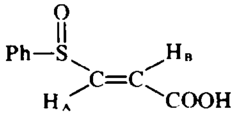
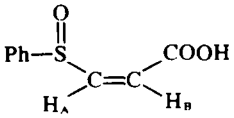
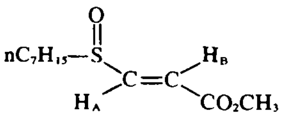
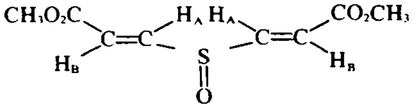
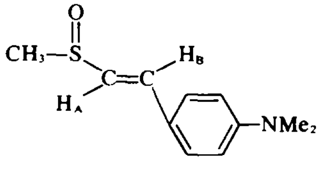
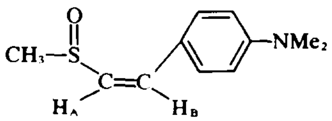
No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
10E	10	 6·88; 7·23	H_A: 5·25 1·27 (RSO *gem*) 0·36 (aromatic *cis*) 6·88 (Δ = 0) H_B: 5·25 0·67 (RSO *cis*) 1·38 (aromatic *gem*) 7·30 (Δ = −0·07)
10Z	10	 6·44; 7·02	H_A: 5·25 1·27 (RSO *gem*) −0·07 (aromatic *trans*) 6·45 (Δ = −0·01) H_B: 5·25 0·41 (RSO *trans*) 1·38 (aromatic *gem*) 7·04 (Δ = −0·02)
11	7	 6·46; 7·62	H_A: 5·25 1·27 (RSO *gem*) 1·01 (COOR conjugated *cis*) 7·53 (Δ = 0·09) H_B: 5·25 0·41 (RSO *cis*) 0·78 (COOR conjugated *gem*) 6·44 (Δ = 0·02)
12	7	 6·47; 7·55	H_A: as for 11 7·53 (Δ = 0·02) H_B: as for 11 6·44 (Δ = 0·03)
13	8	 6·33; 7·43	H_A: as for 11 7·53 (Δ = −0·10) H_B: as for 11 6·44 (Δ = −0·11)
14	7	 5·56; 5·72	H_A: 5·25 0·67 (RSO *cis*) −0·28 (alkil *trans*) 5·64 (Δ = 0·08) H_B: 5·25 0·41 (RSO *trans*) −0·22 (alkil *cis*) 5·44 (Δ = 0·12)
15	14	 5·72; 5·97; 6·60	H_A: 5·25 1·27 (RSO *gem*) 6·52 (Δ = 0·08) H_B: 5·25 0·67 (RSO *cis*) 5·92 (Δ = 0·05) H_C: 5·25 0·41 (RSO *trans*) 5·66 (Δ = 0·06)

Table 4. Examples of α,β-unsaturated sulphoxides with discrepancies between the experimental and calculated values of chemical shifts

No.	Ref.	Structure and observed chemical shifts	Calculated chemical shifts
16-E	15	 6·55; 7·75	H_A: 5·25 1·27 (RSO *gem*) 0·98 (COOH conjugated *cis*) 7·50 (Δ = 0·25) H_B: 5·25 0·67 (RSO *cis*) 0·80 (COOH conjugated *gem*) 6·72 (Δ = 0·17)
16-Z	15	 6·38; 6·87	H_A: 5·25 1·27 (RSO *gem*) 0·32 (COOH conjugated *trans*) 6·84 (Δ = 0·03) H_B: 5·25 0·41 (RSO *trans*) 0·98 (COOH conjugated *cis*) 6·64 (Δ = 0·26)
17	8	 6·47; 7·24	H_A: as for 11 7·53 (Δ = 0·29) H_B: as for 11 6·44 (Δ = 0·03)
18	8	 6·59; 7·04	H_A: as for 11 7·53 (Δ = −0·49) H_B: as for 11 6·44 (Δ = 0·15)
19-E	10	 6·65; 7·14	H_A: as for 10-E 6·88 (Δ = −0·23) H_B: as for 10-E 7·30 (Δ = −0·26)
19-Z	10	 6·20; 6·87	H_A: as for 10-Z 6·45 (Δ = −0·25) H_B: as for 10-Z 7·02 (Δ = −0·15)

parameters. In the case of *cis* and *trans* β-phenylsulphinyl acrylic acid (**16**) it may be due to ability of this compound to hydrogen bond formation. In sulphoxides **17** and **18** these discrepancies may be related to the nature of the substituent attached to the sulphinyl S atom (long aliphatic chain, unsaturated residue) as a cause of lower chemical shifts of protons H_A in these systems. In the last case (**19**) the differences between the calculated and experimental values of H_A and H_B protons are undoubtedly caused by the electronic effect of the *p*-dimethylamino group present in aromatic ring. As it is a general problem we defer the discussion of such cases to a separate communication.

REFERENCES

[1] Part VIII: M. Mikołajczyk, P. Kiełbasinski and H. M. Schiebel, paper submitted to *J. Chem. Soc.*, Perkin I.
[2] C. Pascual, J. Meier and W. Simon, *Helv. Chim. Acta* **49**, 164 (1966).
[3] U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon and S. Sternhell, *Tetrahedron* **25**, 691 (1969).
[4] U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon and S. Sternhell, *Ibid.* **25**, 2023 (1969).
[5] S. W. Tobey, *J. Org. Chem.* **34**, 1281 (1969).
[6] F. A. Carey and D. Hernandez, *Ibid.* **38**, 2670 (1973).
[7] E. Block, *J. Am. Chem. Soc.* **94**, 642 (1972); E. Block and J. O'Connor, *Ibid.* **96**, 3929 (1974).

[8] I. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.* **8**, 197, 205, 217 (1973).

[9] D. H. R. Barton, J. H. Coates and P. G. Sammes, *J. Chem. Soc., Perkin I* 1459 (1974).

[10] M. Mikolajczyk, S. Grzejszczak and A. Zatorski, *J. Org. Chem.* **40**, 1979 (1975).

[11] M. Mikolajczyk, S. Grzejszczak, W. Midura and A. Zatorski, *Synthesis* 278 (1975).

[12] G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.* **35**, 2106 (1970).

[13] M. Barfield and B. Chakrabarti, *Chem. Revs.* **69**, 757 (1969).

[14] E. J. Mulvaney and R. A. Ottaviani, *J. Polymer Sci.* **8**, Part A-1, 2293 (1970).

[15] H. Hogeveen, G. Maccagnani and F. Taddei, *Rec. Trav. Chim.* **83**, 937 (1964).