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THE INFLUENCE OF AN ADJACENT SULPHUR ATOM ON GEMINAL COUPLING CONSTANTS IN METHYLENE GROUPS

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Abstract—The values of geminal coupling constants in methylene groups linked to a sulphur atom are reviewed. Eclipsing of the lone pairs on a sulphur atom with the C—H bonds of an adjacent methylene group (as in a ring of 5 atoms) makes the coupling constant 2 or 3 c/s less negative.

INTEREST has recently centred on the influence on geminal coupling constants (J) of p-orbitals of adjacent heteroatoms.[1-3] The influence of the p-orbitals of the oxygen atom has been studied in a variety of compounds but very little work has been published on the effect of sulphur p-orbitals on the J of an adjacent methylene group.

Previous work[1] has demonstrated the marked increase in J which is observed in going from 6-membered ring compounds of type I to the corresponding 5-membered ring compounds of type II. Assuming the X—CH_2—Y angle in I to be similar to that in II the increase in J may be explained on the basis of eclipsing of the lone pair electron orbitals on X and Y with the adjacent C—H orbitals in the near-planar 5-membered ring. This eclipsing results in transfer of electrons into the antisymmetric molecular orbital of the CH_2 with a corresponding increase in J.[2]

TABLE 1

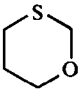
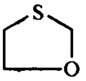
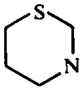
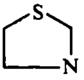
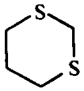
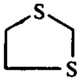
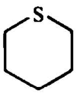
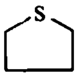
Compound	$-J$ (c/s)	Compound	$-J$ (c/s)	Difference in J (c/s)	"Eclipsing effect" of sulphur atom (c/s)
	11		5	6	2·5
	13·8		9·4	4·4	1·9
	14		9·7	4·3	2·1
	13		10	3	3

TABLE 2

Compound		Solvent	Chemical shift (τ)		J (c/s)	Other coupling constants
			—S—CH$_2$— protons			
III		CH$_3$CN	5·13	5·24	—11·1	$J_{2e,6e} = 1·6$
IV	R = Me. R′ = H	Benzene	5·29	5·50	− 5·2	$J_{44'} = -10, J_{45} = 8·1, J_{4'5} = 5·8$
IV	R = H, R′ = Me	Benzene	spectrum of mixture		− 5·2	
V		Benzene	5·14	5·29	− 4·6	
VI	R = Me$_2$CH—	Pyridine	5·21	5·44	−13·8	$J_{2e,4e} = 0·8$
VI	R = cyclohexyl	Pyridine	5·22	5·37	−13·5	$J_{2e,4e}$ = ca 0·8
VII[6]		CCl$_4$	6·10	6·42	−12	$J_{2e,4e} = 1·5$
VIII[7]	R = Me, R′ = PhCH$_2$	—	6·02	6·16	ca −9	
VIII	R = COOMe, R′ = H	CDCl$_3$	5·61	5·85	− 9·4	$J_{55'} = -10, J_{45} = 8·0. J_{45'} = 7·2$
IX		CCl$_4$	6·03	6·54	−14	$J_{2e,6e}$ = ca 1·2
X	R = Me	PhCN	singlet	6·18		$J_{44'} = -12, J_{45} = 6·5. J_{4'5} = 4·7$
X	R = Ph	CH$_3$CN	5·94	5·95	− 9·7	$J_{44'} = -11·4, J_{45} = 8·3, J_{4'5} = 5·3$ (CDCl$_3$)
XI		Pyridine	5·89	6·33	−15·5	$J_{52} = 1·5$
XII		Pyridine	6·04	6·31	−15	
XIII		Pyridine	5·35	5·55	−16·1	$J_{52} = 0$

TABLE 2—*continued*

Compound	J	Compound	J
XIV[8]	−13 (−65°)	XV[10] (R = SMe)	−15
XV[9] (R = Ar)	−13·3	XVI[11] (S—O axial)	−13·7
		(S—O eq)	−11·7
XVII	−13·9	XVIII[12]	−19
XVIII[12] (sulphoxide)	−18	XIX[13] (R = H)	< 0·4
XIX[14] (R = Ph)	− 1·37	XX[15]	−12·5
XXI[16]	−11	XXII[17]	−15
XXIII[17] A'B'	−13	XXIV[18] (R = EtS)	−17
A"B"	−12	(R = (Me$_2$)CHO)	−17
		(R = EtO)	−15
XXV[19]	−14·8	XXVI[20] (R = alk)	−14·6
		(R = Ph)	−15·2
XXVII[21] (R = Et, R' = Me)	−12		
(R = n-Pr. R' = Et)	−12		
(R = Me. R' = Et)	−12		
(R = Me. R' = Ph)	−12		

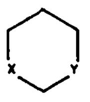
Table 1 shows in a comparative manner the values of J for 6- and 5-membered rings containing S. The difference in J shown in column 3 of the Table represents the combined "eclipsing effects" of the heteroatoms. Subtracting from these values the "eclipsing effects" of the oxygen atom (3·5 c/s) or the N atom (2·5 c/s)[4] gives the "eclipsing effect" of the S atom and, as shown in Table 1, this is found to vary between 2·0–3 c/s. In support of this, J for the CH_2 adjacent to CO in cyclopentanones is normally -17 to -18 whereas in XII J is -15 c/s and in XI $-15{\cdot}5$ c/s. Thus the S atom here too has an "eclipsing effect" of ca. 2–2·5 c/s.

Table 2 shows coupling constant data on S compounds obtained from our own measurements and values taken from the literature.

J_{gem} in 3-methyldithian (IX) is -14, 1·4 c/s more negative than J_{gem} in cyclohexane. Two factors would perhaps be expected to influence J_{gem} in this case: the transfer of non-bonding electrons on S into the antisymmetric methylene molecular orbital producing a positive change in J_{gem} and a withdrawal of electrons from the same molecular orbital into the empty d-orbitals of the sulphur atom with an opposite effect. Similar effects should operate in XIV and XV (R = Ar) where J is found to be -13 and $-13{\cdot}3$ respectively. In this connection it is noteworthy that electron diffraction[5] has shown the S—C—C angle in 1,4-dithian to be 111° and the S—C—S angle in s-trithian is 114·5°. Thus it seems unlikely that changes in angle give rise to these slightly more negative J_{gem} values since the C—C—C angle in cyclohexane is 111·5° ($J_{gem} = -12{\cdot}6$). If the value of -15 for J_{gem} of XV (R = SMe)[10] is not in error then XV is probably not in a chair conformation.

That the change in orientation of the S orbitals to an adjacent CH_2 produces changes in J_{gem} is borne out by the example of XXIV[18] (R = SEt, and R = $OCHMe_2$) with $J = -17$. Increase in S—C—C angle could be responsible for part of this decrease in J but it would seem that the compound is probably in a twist boat conformation in which overlap of lone pair orbitals with the adjacent CH_2 would not be as efficient as in the chair conformation assumed to predominate in the 6-membered ring compounds. XXIV (R = OEt) with $J = -15$ is presumably in a different conformation (if the difference is significant).

Sulphones and sulphoxides generally give rise to slightly more negative values of J than the parent compounds, thus J is $-15{\cdot}5$ for XI and $-16{\cdot}1$ for the corresponding



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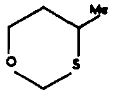

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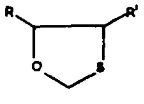

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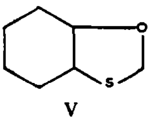

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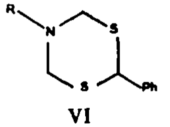

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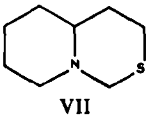

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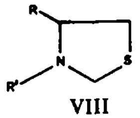

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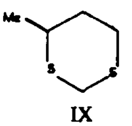

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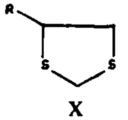

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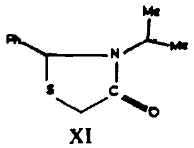

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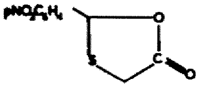

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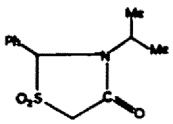

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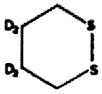

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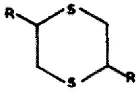

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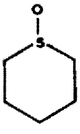

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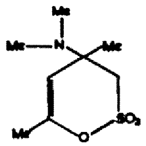
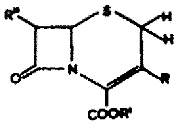
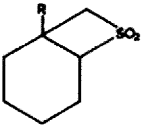


XVII



XVIII

XIX



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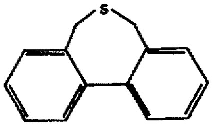
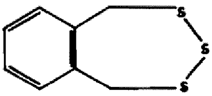


XXI

sulphone XIII. In these oxidized compounds the inductive removal of the electrons from the CH_2 should make J more positive but this effect is counteracted by the loss of the non-bonded electrons on S (completely only in the sulphones) which were available for transfer into the antisymmetric CH_2 molecular orbital in the unoxidized precursors. However an exceptional value of J is that of $-11{\cdot}7$ observed[11] for XVI in the chair conformation with the lone pair orbital axial compared with a J of $-13{\cdot}7$ for the other chair conformation with the lone pair orbital equatorial. This is reasonable since the axial lone pair is able to transfer its electrons into the antisymmetric CH_2 molecular orbital producing a positive change in J whereas for an equatorially situated lone pair this transfer should be nil.



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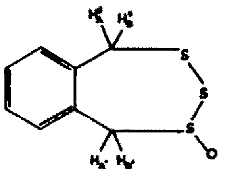

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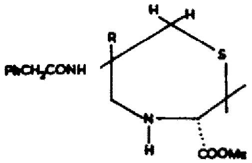

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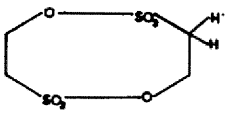

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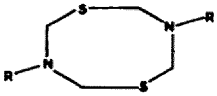

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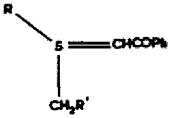

XXVII

In addition. removal of electrons from the CH_2 by the S = O group will be different in the two conformers and this will also contribute to the value of J. This presents us with an analogy to the Barfield–Grant J_x–ϕ relationship observed for cyclic ketones.

Long range coupling

The spectra of the 6-membered ring compounds III. VI, VII, IX all show the signals of the high field part of the S—CH_2— quartet to be long range coupled. These signals must arise from the equatorial protons.

Long range coupling is normally expected to occur between equatorially situated protons and so in these compounds. unlike analogous compounds in which the S atom has been replaced by N or O. the equatorial protons absorb at higher field than the axial protons.* Equatorial protons in substituted 1,3,5-trithianes[22] also absorb at higher field than do axial protons and this has been attributed to the different shielding properties of the C—S as against the C—C bond. The long range coupled signals in III. VI, VII appear as sharp doublets showing coupling between the equatorial proton and only one other, i.e. equatorial proton four bonds removed. The signals in IX are broad. the peak width at half-height being 2·4 c/s, thus in addition to long range coupling between H_{2e} and H_{6e} there is probably coupling to H_{5e} as is the case in 4-phenyl-1.3-dioxan. In XI, the H_5 proton giving rise to the low field signals of the C_5 methylene quartet shows additional splitting of J = 1·5 c/s to the C_2 proton. This coupling disappears in the corresponding sulphone XIII.

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* Naturally, the difference in chemical shift depends on the solvent: e.g. in CCl_4 the equatorial proton of the S—CH_2—O group (long-range coupled) in III still appeared at slightly higher field than the axial one (sharp doublet), whereas in benzene the chemical shifts were almost identical, with the equatorial proton at fractionally lower field.

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