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PROTON MAGNETIC RESONANCE SPECTRA OF ETHYLENE EPISULFOXIDES. ANOMALY IN MAGNITUDES OF SPIN-COUPLING CONSTANTS BETWEEN RING PROTONS*[1],*[2]

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In the course of the chemical study of episulfoxides (1, 2), we have found in the PMR spectra of ethylene episulfoxide (I)*[3] and propylene episulfoxide (II) that the J-values between ring protons are abnormal in comparison with those obtained in other three-membered heterocyclic compounds.

The spectrum of I consists of AA'BB' multiplets both in a neat sample and in solutions in various solvents, showing its S→O bond to lie out of the plane of the ring. The assignment of the signals was established by observing the relaxation effect of paramagnetic species (5); line broadenings of the signals of I were observed when a paramagnetic metal chelate, nickel (II) acetylacetonate, was added to a $CDCl_3$ solution of I. With increase of the chelate concentration, the observed chemical shifts of I are linearly changed; the exchange rate of I with the metal chelate was proved to be rapid. The low-field signal becomes broader than the high-field one. Thus the former is due to the syn protons provided that the coordination site is the oxygen atom. This signal assignment is also consistent with that based on the anisotropic shielding effect of the S→O group (1, 6).

The PMR spectrum of propylene episulfoxide (II) (1) was also taken in order to aid the analysis of.

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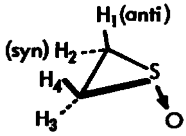
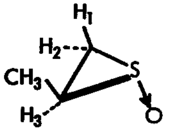
*[1] This paper was preliminarily accounted at the 7th Symposium on NMR Spectroscopy in Japan (Nagoya), Abstract p. 55 (1968).

*[2] We thank Mr. A. Negishi of Sagami Chemical Research Center for providing us with the samples used.

*[3] Recent reports (3,4) have described the AA'BB' spectrum of I with no signal assignments and no special references.



(I)



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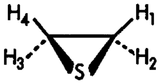

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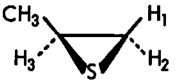

(IV)

the spectrum of I. The ring protons in II were assigned on the assumption that $J_{\underline{cis}} > J_{\underline{trans}}$ as generally accepted in three-membered rings. The PMR parameters of I and II are shown in the Table together with those of ethylene sulfide (III) and propylene sulfide (IV) reinvestigated in the present study. The relative signs of J's were determined from spin-tickling experiments; the analyses were carried out by using NMRENI and NMRIT programs (7). The fact that methyl substituent effects on chemical shifts of ring protons in the case of I→II are similar to those in the case of III→IV also supports the signal assignment.

The magnitude of J_{gem} is remarkably changed with a change from a sulfide to an episulfoxide ring. J_{gem} in three-membered heterocyclic compounds is known to show a positive trend dependent on the electronegativity of the hetero atom (8), although in the case of a sulfur atom, J_{gem} has a more positive value than that expected from its electronegativity. The J_{gem}'s in I and II have large negative values in spite of the higher group-electronegativity of S→O than S (9). According to Pople and Bothner-By (10), this fact can be understood in terms of the following three factors: (a) withdrawal of electrons from the antisymmetric orbital of a ring CH_2 group by the effect of the electronegative oxygen atom (hyperconjugative oxygen as a β-substituent), (b) transfer of electrons from the antisymmetric CH_2 orbital into the π-electron system of S→O (hyperconjugation of the C-H bonds with an a π-bond), and (c) withdrawal of electrons from the antisymmetric CH_2 orbital into the vacant d-orbitals of the sulfur atom. The second factor might be conjectured to play an important role. The vicinal couplings in episulfoxide rings are also unusual, probably due to similar reasons.

Benzene-induced solvent shifts (11) of I relative to CCl_4 were found to be 0.65 and 1.08 ppm for the syn- and the anti-proton signals, respectively. The result is compatible with the effect seen with many other compounds having an S→O bond (6b-e, 12).

TABLE

PMR Parameters in CCl_4[a]

Compound	Chemical shift (τ)					Coupling constant (Hz)				Reference
						J_{gem}		J_{vic}		
	H_1	H_2	H_3	H_4	CH_3	$J_{1,2}$ ($J_{3,4}$)	$J_{1,3}$ ($J_{2,4}$)	$J_{1,4}$	$J_{2,3}$	
I	8.08	7.58	7.58	8.08	-	-6.4_7	10.5_5	11.5_1[b]	11.7_2[b]	This work
						11.3_3	10.2_6	-6.1_2	-6.1_2	c
II	8.18	7.40	7.14	-	8.81	-6.0	8.8_5	-	10.3	This work
III[d]	7.73	7.73	7.73	7.73	-	-0.7_6	5.7_4	6.8_9	6.8_9	This work
	7.75	7.75	7.75	7.75	-	e	5.6_5	7.1_5	7.1_5	f
IV	7.99	7.60	7.21	-	8.50	-0.8_6	5.4_0	-	6.2_2	This work
						$\lesssim 0.4$	5.4	-	6.3	g

[a] All spectra were taken with a Varian HA-100 spectrometer operating at 100 M Hz in the frequency-swept and TMS-locked mode. Calibration of all charts was carried out to accuracies within ±0.1 Hz by using a Hewlett-Parkard HP-5212A electronic counter. [b] Although the values of $J_{^{13}C,H_1}$ (171.8) and $J_{^{13}C,H_2}$ (171.9 Hz) as well as $J_{1,4}$ and $J_{2,3}$ are slightly different from each other, the differences are not so large as those found in aziridine [T. Yonezawa and I. Morishima, J. Mol. Spectroscopy, 27, 210 (1967)]. [c] Reference (2). [d] Neat sample. [e] Not reported. [f] F. S. Mortimer, J. Mol. Spectroscopy, 5, 199 (1960). [g] J. I. Musher and R. G. Gordon, J. Chem. Phys., 36, 3097 (1962).

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