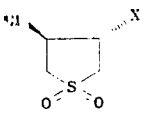
3. Z. I. Zelikman and L. A. Falina, *Khim. Khim. Tekhnol., Tr. Krasnodarsk. Politekh. In-ta*, No. 63, 3 (1974).
4. Z. I. Zelikman, L. A. Falina, V. G. Kul'nevich, G. N. Dorofeenko, and L. V. Mezheritskaya, *Khim. Geterotsikl. Soedin.*, No. 7, 891 (1973).
5. Z. I. Zelikman, L. A. Falina, A. I. Shkrebets, and V. G. Kul'nevich, *Izv. Vuzov. Khim. Khim. Tekhnol.*, **16**, 1381 (1973).

# REVERSE INDUCTIVE EFFECT IN THE SERIES OF trans-3,4-DISUBSTITUTED THIOLANE 1,1-DIOXIDES

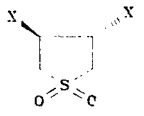
**A. B. Rozhenko and V. M. Bzhezovskii**

UDC 547.73:543.422+519.272

Series of trans-4-substituted 3-chlorothiolane 1,1-dioxides (Ia-h) and trans-3,4-disubstituted thiolane 1,1-dioxides (IIa-j) were studied by $^{33}S$ NMR spectroscopy (solutions in acetone-$D_6$ and DMSO-$D_6$, respectively).



Ia-b



IIa-j

I a X=H, b X=OH, c X=$OCH_3$, d X=$OCOCH_3$, e X=$SC_4H_9$, f X=$SO_2Cl$, g X=Cl, h X=Br; II a X=H, b X=$N(CH_3)_2$, c X=$N^+H(CH_3)_2$, d X=OH, e X=$OCH_3$, f X=$OCOCH_3$, g X=$OSO_2C_6H_5$, h X=F, i X=Cl, j X=Br

It was found that increase in the inductive acceptor power of the substituent X is accompanied by increase in screening of the $^{33}S$ nuclei, and not descreening, as should have been expected according to the classical concepts on the inductive effect of substituent X.

Statistically reliable correlational dependences of $\delta_S$ in compounds Ia-h and IIa-j [Eqs. (1) and (2), respectively] on $\sigma_I$ (without taking into account $\delta_S$ in compounds Ie and IIb) were observed:

$$\delta_S = -23{,}40(\pm 0{,}99)\sigma_I + 361{,}03(\pm 0{,}42),\ r = 0{,}996,\ s_0 = 0{,}604,\ n = 7; \quad (1)$$

$$\delta_S = -41{,}70(\pm 3{,}96)\sigma_I + 368{,}99(\pm 1{,}68),\ r = 0{,}970,\ s_0 = 2{,}282,\ n = 9. \quad (2)$$

We believe that the character of the dependences indicates the influence of a field factor of substituent X on the screening of the $^{33}S$ nuclei, consisting in a dipole–dipole interaction of the C–X and S=O bonds with the resulting polarization of the latter in the direction of the sulfur atom.

TABLE 1. Characteristics of Compounds Ia-h and IIa-j*

| Compound | $\delta_S$ | $\nu_{1/2}$, Hz | $\sigma_I$ | Compound | $\delta_S$ | $\nu_{1/2}$, Hz | $\sigma_I$ | Compound | $\delta_S$ | $\nu_{1/2}$, Hz | $\sigma_I$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | 361,5 | 10 | 0,00 | Ig | 349,8 | 50 | 0,46 | IIe | 357,2 | 5 | 0,25 |
| Ib | 354,8 | 25 | 0,25 | Ih | 351,4 | 15 | 0,44 | II f | 353,6 | 9 | 0,27 |
| Ic | 355,5 | 28 | 0,25 | IIa | 370,6 | 5 | 0,00 | IIg | 344,2 | 240 | 0,58 |
| Id | 353.9 | 65 | 0,27 | II b | 345,8 | 38 | 0,17 | IIh | 345,8 | 30 | 0,52 |
| Ie | 351,8 | 40 | 0,13 | II c | 344,0 | 300 | 0,65 | IIi | 350,2 | 40 | 0,46 |
| If | 342,5 | 60 | 0,80 | II d | 361,2 | 7 | 0,25 | IIj | 351,5 | 15 | 0,44 |

*$\delta_S$ are NMR chemical shifts of the $^{33}S$ nuclei relative to $\delta_S$ in $CS_2$; $\nu_{1/2}$ is the width of the signals at half height; $\sigma_I$ are the Taft inductive constants of substituent X.

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 993, July, 1990. Original article submitted August 10, 1989.

 0009-3122/90/2607-0832$12.50 