Tetrahedron Letters No.34, pp. 3313-3315, 1967. Pergamon Press Ltd. Printed in Great Britain.

ON THE INTERACTION OF BENZENE WITH BIS(N,N-DIALKYLDITHIOCARBAMATO) DIMETHYLTIN AND BIS(N,N-DIMETHYLDITHIOCARBAMATO)METHYLTIN HALIDES

Masaru Honda, Yoshikane Kawasaki and Toshio Tanaka
Department of Applied Chemistry, Osaka University,
Miyakojima, Osaka, Japan.

(Received 1 May 1967; in revised form 25 May 1967)

Solvent shifts in proton magnetic resonance spectra induced by the ring current of benzene have widely been reported in many organic molecules (1-5). Ronayne and Williams interpreted these solvent shifts by a benzene-solute transient 1:1 collision complex at each electron-deficient site in the solute molecule (6). These studies on organometallic compounds are rather few (7,8). In the present note, the proton magnetic resonance spectra of bis(N,N-dimethyldithiocarbamato)dimethyltin, bis(N,N-diethyldithiocarbamato)dimethyltin and bis(N,N-dimethyldithiocarbamato)methyltin halides have been studied in chloroform and in benzene. The preparation of these compounds will be reported elsewhere (9).

The chemical shifts of the methyl protons attached to the tin atom and the N-methyl and N-ethyl protons in these complexes are shown in the Table.

The signals of the N-methyl and N-ethyl protons in benzene have been observed at higher magnetic field than in chloroform, but those of the methyl protons attached to the tin atom have shown the inverse behavior. Stereo-

TABLE

Chemical Shifts of Protons in $(CH_3)XSn(DMTC)_2$*, $(CH_3)_2Sn(DMTC)_2$ and $(CH_3)_2Sn(DETC)_2$**.

		Benzene τ	Chloroform τ	$\Delta^{C_6H_6}_{CHCl_3}$***
$(CH_3)ClSn(DMTC)_2$	$N-CH_3$	7.69	6.63	+1.06
	$Sn-CH_3$	8.14	8.48	-0.34
$(CH_3)BrSn(DMTC)_2$	$N-CH_3$	7.67	6.58	+1.09
	$Sn-CH_3$	7.99	8.30	-0.31
$(CH_3)ISn(DMTC)_2$	$N-CH_3$	7.35	6.41	+0.94
	$Sn-CH_3$	7.48	8.16	-0.68
$(CH_3)_2Sn(DMTC)_2$	$N-CH_3$	7.54	6.61	+0.93
	$Sn-CH_3$	8.17	8.49	-0.32
$(CH_3)_2Sn(DETC)_2$	$N-CH_2$	6.55	6.16	+0.39
	$C-CH_3$	9.10	8.69	+0.41
	$Sn-CH_3$	8.14	8.43	-0.29

The values are taken from an internal tetramethylsilane in ppm unit.

* DMTC : N,N-dimethyldithiocarbamate

** DETC : N,N-diethyldithiocarbamate

*** $\Delta^{C_6H_6}_{CHCl_3}$: $\tau_{C_6H_6} - \tau_{CHCl_3}$

specific interactions as shown in Figures 1,2 would account for the observed $\Delta^{C_6H_6}_{CHCl_3}$-values of these organotin complexes. In these interactions, the methyl protons attached to the tin atom are located in the paramagnetic region of the benzene molecule, and the N-methyl and N-ethyl protons in the diamagnetic region.

$\Delta^{C_6H_6}_{CHCl_3}$-values for the N-methylene and C-methyl protons in bis(N,N-diethyldithiocarbamato)dimethyltin are close each other and less than half of the $\Delta^{C_6H_6}_{CHCl_3}$-value for the N-methyl protons in bis(N,N-dimethyldithiocarbamato)

FIG.1

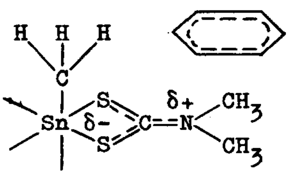


FIG.2

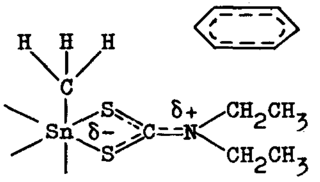
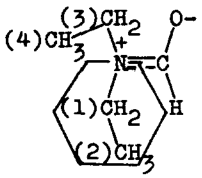


FIG.3



dimethyltin. The smaller $\Delta^{C_6H_6}_{CHCl_3}$-values in the former complex may be due to a steric effect of the N-ethyl group. The above results of $\Delta^{C_6H_6}_{CHCl_3}$-values for the N-methylene and C-methyl protons are contrasted with those obtained for N,N-diethylformamide (Fig.3), in which the order of decreasing $\Delta^{C_6H_6}_{CHCl_3}$-values is $CH_2(1) > CH_3(2) > CH_2(3) > CH_3(4)$; the mean value of $C\text{-}CH_3$ shifts is smaller than that of $N\text{-}CH_2$ shifts (10). These observations suggest that the positions of the benzene-solute interaction are somewhat different in these two compounds.

The proton magnetic resonance spectra were measured at room temperature using a Japan Electron Optics JNM-3H-60 spectrometer operating at 60 Mc/sec and tetramethylsilane was used as an internal standard. The solvents used in the spectral measurements were dried and distilled.

REFERENCES

1. T.Schaefer and W.G.Schneider, J.Chem.Phys. 32, 1218 (1960)
2. J.V.Hatton and R.E.Richards, Mol.Phys. 3, 253 (1962)
3. W.G.Schneider, J.Phys.Chem. 66, 2653 (1962)
4. J.V.Hatton and W.G.Schneider, Can.J.Chem. 40, 1258 (1962)
5. R.E.Klinck and J.B.Stothers, Can.J.Chem. 40, 2329 (1962)
6. J.Ronayne and D.H.Williams, Chem.Comm. 712 (1966)
7. Y.Kawasaki, Mol.Phys. 12, (1967) in press
8. G.Matsubayashi, Y.Kawasaki, T.Tanaka and R.Okawara, Bull.Chem.Soc.Japan (1967) in press
9. M.Honda and R.Okawara, to be published
10. J.V.Hatton and R.E.Richards, Mol.Phys. 5, 139 (1962)