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SULPHUR SUBSTITUTED ORGANOTIN COMPOUNDS

VII *. CHARGE TRANSFER INTERACTIONS OF ARYLTHIOMETHYL(TRIPHENYL)TIN COMPOUNDS WITH TETRACYANOETHYLENE

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Summary

Charge-transfer interactions of $Ph_3SnCH_2SC_6H_4X$-*p* (X = MeO, Me, H, Cl or Br) with tetracyanoethylene are reported. Values of λ_{max}, the absorption maxima, have been obtained and compared with the values for $CH_3SC_6H_4X$-*p*—$(CN)_2C{=}C(CN)_2$ interactions. The effect of the Ph_3Sn substituent is to shift λ_{max} by 15—26 nm to longer wavelengths.

Introduction

The reaction of $Ph_3SnCH_2SC_6H_4Me$-*p* with iodine was reported a few years ago [2]. Complexation between these reagents was suggested from the new intense visible absorption generated on mixing the solutions. Unfortunately the fairly rapid reaction between I_2 and $Ph_3SnCH_2SC_6H_4Me$-*p* made it impossible to study such complexes. As we wished to investigate the donor properties of the sulphides, $R_3SnCH_2SC_6H_4X$-*p*, we turned to acceptors other than iodine and found that the π-acceptor, tetracyanoethylene, was most suitable.

Charge-transfer complexes of $(CN)_2C{=}C(CN)_2$ with totally organic sulphides have been variously studied [3—11]. In the main, these studies have simply provided the maxima of the charge-transfer absorptions of the complexes [3—8]; on a few occasions, formation constants have also been obtained [9—11]. These constants invariably are small and indicate the weakness of the complexes.

Tetracyanoethylene has been a popular reagent for use with organotin systems. For example, interactions with Sn—N bonds [12], Sn—Sn bonds [13,14],

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[*] For Part VI see ref. 1.

Sn—S bonds [15] and Sn—C bonds [16—18] have all been reported. These lead either to fairly stable charge-transfer complexes or to insertion products (as with Sn—N, Sn—S, Sn—Sn and some Sn—C systems).

The results of the interaction of $Ph_3SnCH_2SC_6H_4X$-*p* with TCNE are now reported.

Experimental

Materials. Tetracyanoethylene was sublimed at 0.1 mmHg pressure, prior to use. Dichloromethane was a dry redistilled commercial sample. Arenethiols were also commercial samples.

Iodomethyltriphenyltin. This was prepared from a zinc/copper couple, CH_2I_2 and Ph_3SnCl according to published procedures [2].

Arylthiomethyl(triphenyl)tin compounds. To a solution of sodium ethoxide in ethanol were added sequentially the arenethiol and Ph_3SnCH_2I (all equimolar). The resulting solution was refluxed for a few hours. On cooling, arylthiomethyl(triphenyl)tin precipitated and was recrystallized from ethanol. Melting points, analytical and NMR data are listed in Table 1. The ^{119}Sn chemical shifts previously reported [19] are also included.

Organic sulphides. The methyl aryl sulphides were produced by methylating the appropriate arenethiol in alkaline medium. Physical properties are in good agreement with those published [20].

Analytical data

$CH_3SC_6H_4OMe$-*p*. Found: C, 62.3; H, 6.6; S, 20.8. $C_8H_{10}OS$ calcd.: C, 62.4; H, 6.5; S, 20.8%.

$CH_3SC_6H_4Me$-*p*. Found: C, 69.4; H, 7.1; S, 23.3. $C_8H_{10}S$ calcd.: C, 69.6; H, 7.2; S, 23.2%.

$CH_3SC_6H_5$. Found: C, 67.9; H, 6.6; S, 25.7. C_7H_8S calcd.: C, 67.8; H, 6.5; S, 25.8%.

$CH_3SC_6H_4Cl$-*p*. Found: C, 52.9; H, 4.4; S, 20.4; Cl, 22.5. C_7H_7SCl calcd.: S, 53.0; H, 4.4; S, 20.2; Cl, 22.4%.

UV spectra

Solutions of $Ph_3SnCH_2SC_6H_4X$-*p* (or $CH_3SC_6H_4X$-*p*) and $(CN)_2C{=}C(CN)_2$ were made up in dry, oxygen-free dichloromethane and the UV-visible spectra recorded on a Unicam SP 800 spectrophotometer. The solutions were thermostatted at 30.0 ± 0.1°C. As wide a range as possible of concentrations of each sulphide was taken with a constant concentration of $(CN)_2C{=}C(CN)_2$. The λ_{max} values are quoted in Table 2. No attempt was made to decompose the lower charge-transfer absorption (λ_2). However overlap of the lower charge-transfer band with other bands, probably occurs.

Attempts to calculate the formation constants, K, were made using the

$$\underset{(D)}{Ph_3SnCH_2SC_5H_4X\text{-}p} + \underset{(A)}{(CN)_2C{=}C(CN)_2} \overset{K}{\rightleftharpoons} \underset{(DA)}{[Ph_3SnCH_2SC_6H_4Me\text{-}p : (CN)_2C{=}C(CN)_2]}$$

$$K = \frac{[DA]}{[A][D]}$$

(continued on p. 33)

TABLE 1

ANALYTICAL DATA, MELTING POINTS AND NMR DATA FOR $Ph_3SnCH_2SC_6H_4X$-*p*

$Ph_3SnCH_2SC_6H_4X$-*p*	M.p. (°C)	Chemical shifts (ppm)			Analysis, Found (calcd. (%))			
		$\delta(^{119}Sn)$ [a]	$\delta(^{1}H)$ (CH_2) [b]	$\delta(^{13}C)$ (CH_2) [b]	C	H	S	X
X = H	106—108	−118.0 ± 0.5	2.90 *J*(49)	11.21	63.1 (63.4)	4.4 (4.6)	6.9 (6.8)	— —
X = Me	112—113		2.90 *J*(49)	12.01	64.0 (63.9)	4.8 (4.9)	6.5 (6.5)	— —
X = Bu-t	115—116.5	−119.0 ± 0.5	2.91 *J* (49)	11.63	65.9 (65.9)	5.3 (5.7)	6.2 (6.1)	— —
X = Cl	99—101	−118.5 ± 0.5	2.86 *J*(49)	11.51	59.9 (59.4)	4.5 (4.2)		
X = Br	94.5—96	−118.5 ± 1.0	2.85 *J*(48)	11.21	54.7 (54.4)	4.1 (3.8)	5.8 (5.8)	14.2 Br (14.5) Br
X = MeO	76.5—77.5	−119.5 ± 1.5	2.90 *J*(48)	13.65	62.4 (62.1)	4.5 (4.8)	6.7 6.4	— —
X = NO_2	143—145	−118.2 ± 0.5	2.80 *J*(49)	10.18	58.4 (58.0)	5.5 (5.4)	6.3 (6.2)	3.1 N (2.7) N
X = NH_2	118—120	−120.7 ± 0.5	2.88 *J*(48)	14.54	61.2 (61.4)	4.7 (4.7)	6.6 (6.5)	2.9 N (2.9) N

[a] Ref. 19; to low field of Me_4Sn. [b] In $CDCl_3$ solution; relative to TMS; *J* values are av. $J(^{117,119}Sn-^{1}H)$ values in Hz.

TABLE 2

CHARGE-TRANSFER MAXIMA FOR $(CN)_2C{=}C(CN)_2$—ALKYL ARYL SULPHIDES IN CH_2Cl_2 SOLUTION

X	$Ph_3SnCH_2SC_6H_4X$				$CH_3SC_6H_4X$			
	λ^1_{max}(nm)	λ^2_{max}(nm)	ϵ_2/ϵ_1	$\epsilon_1 \times K \times 10^{-2}$	λ^1_{max}	λ^2_{max}	ϵ_2/ϵ_1	$\epsilon_1 \times K \times 10^{-2}$
MeO	664	374	0,93	22,4	649 [a] [650] [b]	358 [a] [355] [c]	0.70 [a] [0.53] [c]	22,5
Me	634	384	0,71	22,5	610 [a] [610] [c]	386 [a] [390] [c]	0.36 [a] [0.36] [c]	24,6
H	598	389	0,90	14	572 [a] [573] [c,d]	379 [a] [380] [c,d]	0.32 [a] [0.30] [c,d]	15,8
Cl	598	373	1,25	6	572 [575] [e]	370sh	0.3	6,5
Br	599	402sh	1,4					
Bu_3Sn					600	397	0.53	

[a] This study. [b] Ref. 5. [c] Ref. 4. [d] Ref. 6. [e] Ref. 7.

Benesi-Hildebrand or related procedures [21]. The acceptor concentrations were in the region of 10^{-3} *M*, with the $Ph_3SnCH_2SC_6H_4S$-*p* concentrations in the range 3×10^{-2} to 0.25 *M*. However the charge-transfer complexes were too weak and with the concentrations used, it was not possible to obtain accurate values of *K*. Composite terms, $\epsilon_1 \times K$ however could be obtained. These are quoted in Table 2.

Results and discussion

Charge-transfer complexes of $Ph_3SnCH_2SC_6H_4X$-*p* and $CH_3SC_6H_4X$-*p* (X = MeO, Me, H, Cl or Br but not NO_2) were obtained with $(CN)_2C{=}C(CN)_2$. For each $(CN)_2C{=}C(CN)_2$—sulphide interaction, two charge-transfer absorption bands are observed in the UV-visible spectrum. These two bands arise from transitions from each of the two highest filled MO's of the aryl sulphide to the LUMO of the acceptor [4]. In PhH (only one charge-transfer band at 385 nm) the two highest filled MO's are the degenerate e_{ig} pair (LCAO approximation). Such a degeneracy is removed on substitution (e.g. at C(1) or disubstitution at

$$\psi_2 = \frac{1}{\sqrt{12}} (2\varphi_1 + \varphi_2 - \varphi_3 - 2\varphi_4 - \varphi_5 + \varphi_6)$$

$$\psi_3 = \tfrac{1}{2}(\varphi_2 + \varphi_3 - \varphi_5 - \varphi_6)$$

C(1) and C(4)) of benzene due to the greater interaction of the orbital(s) of the substituent(s) with ψ_2. The other orbital, ψ_3, should be essentially unaffected. This is borne out by the first two IP's of PhSMe being 8.07 and 9.28 eV, compared to that of PhH at 9.24 eV [3].

A relationship links the IP with the frequency of the charge transfer for π complexes, equation 1.

$$\delta_{\mathrm{cm}^{-1}} = 7331\ \mathrm{IP} - 41830 \qquad (1)$$

Using equation 1, the first ionization potentials of each organotin containing sulphide were calculated and are quoted in Table 3.

Literature values for $MeSC_6H_4X$-*p* are also given; these values were either obtained indirectly from λ_{max} or by direct measurement using photoelectron

TABLE 3

IONIZATION POTENTIALS (IP)

$Ph_3SnCH_2SC_6H_4X$-*p*		$CH_3SC_6H_4X$-*p*
X	IP (eV)	IP (eV)
MeO	7.76	7.82 [a]; 7.8 [b]
Me	7.86	7.95 [a]; 7.9 [b]
H	7.99	8.10 [a]; 8.07 [b]
Cl	7.99	8.09 [a]; 8.07 [b,c]
Br	7.98	8.17 [b]

[a] Ref. 7. [b] F. Bernardi, G. Distefano, A. Mangini, S. Pignataro and G. Spunta, J. Electron. Spectrosc. Relat. Phenom, 7 (1975) 457. [c] H. Bock, G. Wagner and J. Kroner, Chem. Ber., 105 (1972) 3850.

spectroscopy. The Ph_3Sn substitution only has a small impact on the ionization potential, with lower values of ca. 0.1 eV being obtained.

While the maxima of the longer wavelength absorptions can be readily assigned, those of the shorter wavelength bands are generally more difficult to precisely locate due to overlapping bonds. This is a general occurrence with arenes. To this general difficulty can be added specific complications for the $Ph_3Sn(CH_2)SC_6H_4X$ complexes. Additional charge-transfer absorptions may arise from the Ph_3Sn or phenyl groups also acting as donor sites and as the IP of Ph_3Sn should be about that of benzene *, the additional band would be about 380—400 nm. In Table 2 are presented ratios of the extinction coefficients for the two absorptions and it is apparent that additional intensity is indeed found for the organotin-containing sulphides at the lower wavelengths. A complete resolution of the lower wavelength bands was not achieved and the overall maxima are simply reported as obtained. The ratio of the extinction coefficients, ϵ_2/ϵ_1, for each sulphide complex was found to be constant throughout the concentration ranges employed.

The compounds, $Ph_3SnCH_2SC_6H_4NO_2$-*p* and $CH_3SC_6H_4NO_2$-*p*, did not give detectable charge-transfer adducts with TCNE.

The absorptions did not vary with time; no subsequent reactions occurred. Values of $\epsilon_1 \times K$ (ϵ_1 = extinction coefficient of long wavelength absorption; K = equilibrium constant) were calculated from the Hildebrand-Benesi plots. The individual values of ϵ_1 and K were not obtained, due to the low values of K and the concentration ranges of $Ph_3SnCH_2SC_6H_4X$-*p* which were available to us. Under these conditions, the errors in K would be so large that the values would be quite meaningless. Values of $\epsilon_1 \times K$ are unfortunately not too significant, unless it can be assumed that ϵ_1 values are similar for all the complexes. In that case the product $\epsilon_1 \times K$ could be taken to be a relative measure of the donor ability of the sulphides. However, there is sufficient evidence for complexes of simple arenes that ϵ_1 varies in a significant (but random) manner with a related series of compounds [21,22]. Hence we did not feel able to make the assumption of a constant ϵ_1 for our sulphide complexes and so are unable to expand on the $\epsilon_1 \times K$ values. Despite this, we wish to point out the similarity of the values of the product term, $\epsilon_1 \times K$, for each $Ph_3SnCH_2SC_6H_4X$-*p*/$CH_3SC_6H_4X$-*p* pairing.

The values of λ_{max} for $Ph_3SnCH_2SC_6H_4X$-*p*/$(CN)_2C{=}C(CN)_2$ complexes are always greater than for the corresponding $CH_3SC_6H_4X$-*p* adducts. This reflects the greater electron release of the Ph_3SnCH_2 group relative to the CH_3 group.

References

1 Part VI. J.L. Wardell and R.D. Taylor, Tetrahedron Lett., (1982) 1735.
2 R.D. Taylor and J.L. Wardell, J. Chem. Soc. Dalton Trans., (1976) 1345; J. Organometal. Chem., 77 (1974) 311.
3 H. Bock, G. Wagner and J. Kroner, Chem. Ber., 105 (1972) 3850; H. Bock and G. Wagner, Tetrahedron Lett., (1971) 3713.

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[*] The IP's of Ph_3SnH and Ph_3SnCl are 9.13 and 9.29 eV, compared to that of PhH = 9.24 eV. The tetracyanoethylene adduct with Ph_2CHSPh exhibits bands at 560 and 400 nm (due to SPh as donor) and at 420 nm (Ph_2CH as donor) [10].

4 A. Zweig, Tetrahedron Lett., (1964) 89; J. Phys. Chem., 67 (1963) 506.
5 A. Zweig and J.E. Lehnsen, J. Am. Chem. Soc., 87 (1965) 2647.
6 E.M. Voigt, J. Am. Chem. Soc., 86 (1964) 3611; E.M. Voigt and C. Reid, ibid., 86 (1974) 3930.
7 G.A. Chmutova and T.A. Podkovyrina, J. Gen. Chem. USSR (Engl. Trans.), 45 (1945) 145.
8 P.G. Sennikov, V.A. Kuznetsov, A.N. Egorochkin, S.M. Shostakovskii, N.S. Nikol'skii and S.V. Amosova, Izv. Akad. Nauk. SSSR, Ser. Khim., (1980) 2132.
9 W.M. Moreau and K. Weiss, J. Am. Chem. Soc., 38 (1966) 204.
10 S. Santani, G. Reichenbach, S. Sorriso and A. Cellon, J. Chem. Soc. Perkin Trans., 2 (1974) 1056.
11 G.G. Aloisi, S. Santani and S. Sorriso, J. Chem. Soc., Faraday Trans. 1, 70 (1974) 1908.
12 T.A. George and M. Lappert, J. Organometal. Chem., 14 (1968) 327.
13 P.J. Krusic, H. Stoklosa, L.E. Manzer and P. Meakin, J. Am. Chem. Soc., 97 (1975) 667; A.B. Cornwell, P.G. Harrison and J.A. Richards, J. Organometal. Chem., 67 (1974) C43; H. Sakurai, M. Kira and T. Uchida, J. Am. Chem. Soc., 95 (1973) 6826.
14 V.F. Traven and R. West, J. Am. Chem. Soc., 95 (1973) 6824.
15 O.A. Reutov, V.I. Rozenberg, G.V. Gavrilova and V.A. Nikanorov, Doklady Chem., 237 (1977) 356; G.V. Gavrilova, V.A. Nikanorov, O.E. Reutov and V.I. Rozenberg, J. Organometal. Chem., 177 (1979) 101.
16 W. Hanstein, H.J. Berwin and T.G. Traylor, J. Am. Chem. Soc., 92 (1970) 7476.
17 O.A. Reutov, V.I. Rozenberg, G.V. Gavrilova and V.A. Nikanorov, J. Organometal. Chem., 177 (1979) 101; S. Fukuzumi, C.L. Wong and J.K. Kochi, J. Am. Chem. Soc., 102 (1980) 2928; H.C. Gardner and J.K. Kochi, ibid., 98 (1976) 2460; D.F. Eaton, ibid., 102 (1980) 3278.
18 V.F. Traven, V.F. Donyagina, I.G. Makarov, S.P. Kotesnikor, V.M. Kazakova and B.I. Stepanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1042.
19 J.D. Kennedy, W. McFarlane, G.S. Pyne, P.L. Clarke and J.L. Wardell, J. Chem. Soc. Perkin Trans. 2, (1975) 1234.
20 E.E. Reid, Organic Chemistry of Bivalent Sulfur, Vol. II, Chemical Publishing Co., New York, 1960.
21 R.X. Ewall and A.J. Sonnessa, J. Am. Chem. Soc., 92 (1970) 2845.
22 R. Foster, Organic Charge-Transfer Complexes, Academic Press, 1969.