Charge-transfer Complexes of Iodine with Diphenyl Sulphides [1]

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Charge transfer complexes of iodine (a σ acceptor) with mono- and di-substituted diphenyl sulphides have been studied in cyclohexane at 25°. Spectral data, stability constants, and thermal parameters are reported. The data fit the Hammett equation with ρ values of $-0{\cdot}64$ and $-0{\cdot}43$ for mono- and di-substitution, respectively. The stability–structure correlation is discussed in terms of electronic and steric factors and gives information on the conjugative contribution from the π system to the interaction of the sulphur lone pair with iodine.

THE charge transfer (c.t.) association constants of iodine with thiophenols and related sulphur compounds were reported previously.[2] Evidence was given for the formation of a 1 : 1 complex in which the sulphur atom is the donor site with a conjugative contribution from the π system of the aromatic derivatives. This paper extends the previous study to the c.t. complexes of iodine with a series of substituted diphenyl sulphides. The aim is to obtain further information on the nature of these complexes and to study the effect of both symmetrical and unsymmetrical ring substitution on the c.t. equilibrium constants through the usual free energy relationships. A similar study has been performed by McCullough *et al.*[3] on the association between halogens and diphenyl selenides; while this shows good additivity of substituent effects for the formation of dibromides, the data for the few iodine complexes investigated do not allow firm conclusions.

EXPERIMENTAL

Materials.—Twice sublimed iodine (Carlo Erba RP) was purified by sublimation from potassium iodide and stored in a desiccator. Cyclohexane (Carlo Erba RP) was purified following Vogel,[4] dried, and stored under nitrogen.

Aromatic sulphides, except diphenyl sulphide, which is a commercial product, were prepared by the Ziegler method [5] from the diazonium salt of the appropriate amines and substituted benzenethiolates in aqueous solution. Thiophenols were commercial products or prepared by standard methods.[6] Sulphides were purified by distillation under vacuum of crude products and further by chromatography on silica gel with light petroleum as eluant. Physical properties and u.v. spectra were in agreement with those previously reported.[7]

*Bis-*2,6-*dimethylphenyl sulphide* crystallized from absolute ethyl alcohol as plates, m.p. 78°, $\lambda_{\text{max.}}$ (C_6H_{12}) 245 (log ε 4·0) and 272 nm (3·6) (Found: C, 77·8; H, 7·2. $C_{16}H_{18}S$ requires C, 79·5; H, 7·0%).

Diphenyl ether (Fluka AG purum grade) was purified by distillation under vacuum.

Analytical Methods.—Stability constants were determined from spectrophotometric measurements on the assumption of a 1 : 1 complex being formed; arguments in favour of this were presented previously.[2] A single beam Saitron Monospec B spectrophotometer (with 1 cm path quartz cells and a thermostatted jacket) was used. Preliminary spectra were run with a double beam Optica CF4-DR spectrophotometer. As the c.t. band does not overlap the absorptions of the donors and iodine, the Benesi–Hildebrand equation [8] was used in the form (1)

$$1/\varepsilon_a = 1/K_{\text{c.t.}}[\text{D}]\varepsilon_c + 1/\varepsilon_c \qquad (1)$$

where ε_a is the apparent molar extinction coefficient, ε_c is the molar extinction coefficient of the complex, and [D] is the donor concentration. The range of concentrations was 1—8 × 10^{-2} or 0·5—2 × 10^{-2}M, depending on the donor. Iodine concentration was always 5 × 10^{-4}M. Equilibrium constants and molar extinction coefficients were determined at different wavelengths, in the range 350—400 nm at both the peak and tail of the c.t. band. Good linearity of the experimental plots was found in every case (correlation coefficients r 0·9910—0·9999). In one case (bis-4-methylphenyl sulphide) the linearity of the Benesi–Hildebrand plot was further checked by a Scatchard plot,[9] using equation (2). A good correlation coefficient (r

$$\varepsilon_a/[\text{D}] = K_{\text{c.t.}}\varepsilon_c(1 - s) \qquad (2)$$

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0·9985) for measurements over a wide range of saturation fraction (s 0·06—0·76) [10] was obtained (Figure 1).

The reported $K_{c.t.}$ values are averages of 4—5 values obtained at different λ (mean deviation *ca.* 4%). The measurements were not performed at the perturbed iodine band, as it was not sufficiently shifted relative to that of free iodine.

The temperature effect was investigated in the range 17—35° and the thermal parameters were obtained from plots with r 0·9960—0·9999.

For comparison purposes the absorption spectrum and stability constant of the complex iodine + diphenyl ether were also determined. The $K_{c.t.}$ value was obtained by the equation of Van de Stolpe.[11]

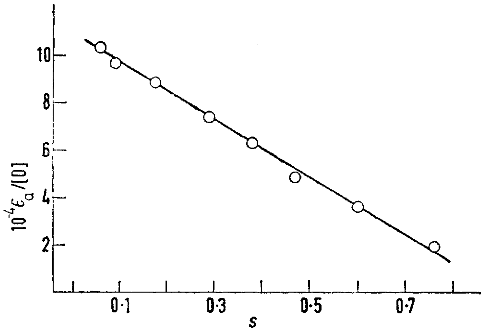

FIGURE 1 Scatchard plot for the c.t. equilibrium of bis-4-methylphenyl sulphide with iodine in cyclohexane (linearity confirms 1 : 1 stoicheiometry)

All measurements were taken in air-saturated solutions. The systems were stable over a period of several hours at the experimental temperatures, as shown by the constancy of their absorption spectrum.

RESULTS AND DISCUSSION

Iodine Complexes with R_2O, R_2S, *and* R_2Se.—The $K_{c.t.}$ values for the complexes between iodine and diaryl ethers, sulphides, and selenides are collected in Table 1 together with the corresponding values for the dialkyl derivatives for comparison purposes. The association constants of the latter complexes ($n \longrightarrow \sigma^*$) increase in the order O < S < Se, as expected from the increase in basicity and the size of the heteroatom on going from oxygen to selenium.

TABLE 1

Charge transfer equilibria of iodine with alkyl and aryl ethers, sulphides, and selenides in inert solvents at 25°

Donor	$K_{c.t.}$/l mol^{-1}	$\lambda_{c.t.}$/nm	Solvent
Et_2O [12]	0·84	249	CCl_4
Et_2S [13]	170·0	302	n-Heptane
Me_2S [3a]	71·0		CCl_4
Me_2Se [3a]	471·0	433	CCl_4
Ph_2O	0·39	345	Cyclohexane
Ph_2S [2]	3·90	350	Cyclohexane
Ph_2Se [3c]	27·8	355	CCl_4

The large difference in $K_{c.t.}$ between dialkyl and diaryl derivatives, particularly large for the sulphur and selenium compounds, has been already pointed out for Et_2S and Ph_2S and explained in terms of both electronic and steric effects.[2]

The large increase in stability of the selenium complexes compared with the sulphur complexes may be due not only to increased basicity of the heteroatom but also to a decrease in steric hindrance in the selenides by the *ortho*-hydrogen atoms due to the increased size of the selenium atom. Reduced conjugation of the p electrons of selenium with the π electrons of the ring should also be taken into account.

Consistent comparisons in the diaryl series should be limited to sulphur and selenium compounds where the heteroatom should act as the donor site, as indicated by the results of structural and equilibrium studies on these and related compounds.[2,3] In the case of diphenyl ether, a comparison would have less significance since the nature of the interaction seems to change into $\pi \longrightarrow \sigma^*$. This conclusion is based on comparison of alkyl and aryl ethers. While $K_{c.t.}$ decreases *ca.* 18 times on changing from dimethyl to diphenyl sulphides and selenides, it remains practically the same for the corresponding ethers. Comparison with the iodine + anisole complex confirms the different nature of the diphenyl ether complex.[12]

Substituent Effects.—Table 2 collects the $K_{c.t.}$ and $\lambda_{c.t.}$ values, and Figure 2 shows a plot of log $K_{c.t.}$ *vs.* σ for a series of substituted sulphides. There is a rough correlation between $K_{c.t.}$ and the frequency of the c.t. absorption, related to the donor ionization potential. The frequency increases when the stability of the complex decreases.

TABLE 2

Substituent effects on charge transfer absorptions and equilibria of some substituted diphenyl sulphides with iodine in cyclohexane at 25°

Substituents	$K_{c.t.}$/l mol^{-1}	$\lambda_{c.t.}$/nm(±2)
None	3·9	350 (4·08) *
p-Me	5·5	355 (4·08)
p-OMe	6·3	360 (3·94)
p-Cl	3·1	348 (3·90)
m-Me	4·7	354 (3·90)
m-OMe	3·6	353 (3·80)
m-Cl	2·4	346 (3·86)
o-Me	5·4	354 (3·93)
p,p'-Me_2	6·1	362 (4·24)
p,p'-$(OMe)_2$	7·2	365 (4·08)
p,p'-Cl_2	2·8	350 (3·78)
o,o'–Me_2	5·8	357 (3·62)
p-Cl,*p'*-OMe	4·0	355 (3·70)
o,o,o',o'-Me_4	3·7	~360 (3·62)

* log $\varepsilon_{c.t.}$ in parentheses obtained from the intercept of the Benesi–Hildebrand plot.

The reaction constant for monosubstitution (ρ −0·64, r 0·9986) has the same sign but is smaller than that found for thiophenols (ρ −1·11),[2] probably because of conjugative intramolecular transmission of electronic effects between the two phenyl groups through the sulphur bridge, which could reduce the change in

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electron density at the S atom induced by the substituent. It is known that this effect depends on the nature of the bridging atom (the order S > Se > O is deduced on the basis of spectroscopic and kinetic studies) and on the nature of the ring substituent, being particularly important when the bridge links powerful electron-donating and electron-accepting systems of delocalized π bonds.[14] Besides this speculative assumption, the small ρ value found for diphenyl sulphide can also be accounted for by a greater steric hindrance by the phenyl groups around the reaction centre.* The close approach of the donor–acceptor partners is in fact prevented, leading not only to lower stability with respect to thiophenol but also to less sensitivity to substituent effects.

Table 2 and Figure 2 also report the stability constants for some disubstituted derivatives. They show a slight but clear deviation from additivity ($K_{c.t.}$ values are smaller than they should be on the basis of σ additivity for electron-donating substituents, while they are higher for chloro-derivatives), as found, *e.g.*, for some electrophilic side chain reactions, like the solvolysis of benzhydryl chlorides[19] and bromination of 1,1-diarylethylenes.[20] The lack of additivity is usually explained by assuming that a substituent modifies the reaction constant for a second substituent, especially when polarizable groups are conjugated with a common reaction centre, regardless of whether the multiple substitution is in the same ring or in different rings. Consequently, two different reaction constants can be obtained for mono- and di-substituted substrates.

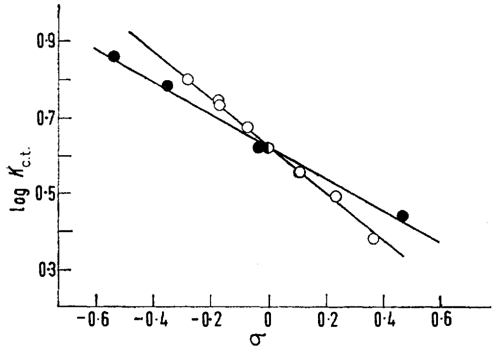

FIGURE 2 Hammett plot for the stability constants of c.t. complexes between diphenyl sulphides and iodine in cyclohexane at 25°. Open circles represent monosubstituted derivatives; filled circles disubstituted derivatives

In the linear free energy correlation plot the points for the diphenyl sulphide complexes fit two straight lines, the disubstituted derivatives falling on that with the smaller slope (−**0·43**). The lack of additivity in this case can also be related to the conjugative transmission of electronic effects between the phenyl rings through the sulphur bridge. This assumption could also explain why McCullough *et al.* found additivity in halogen + selenide complexes because of the low ability of the selenium bridge to transmit electronic effects and the consequently smaller interaction between the two substituents. It should be noted that McCullough *et al.* found good additivity only with diphenyl selenium–dibromides which show high sensitivity to changes in electron density on the Se atom (ρ −2·1, *r* 0·9835).[3b] However, they are not c.t. complexes as they have a Br–Se–Br bond structure.[21] The Hammett plot for diphenyl selenium–di-iodides (c.t. complexes [21]) has ρ −0·7 similar to that of the sulphur compounds, but the few derivatives investigated and the poor correlation make the additivity at least questionable.[3c]

Table 2 also reports the equilibrium constants for some *ortho*-methyl substituted sulphides. Only the tetramethyl derivative shows a marked decrease in the association constant, while the mono- and di-substituted compounds have stabilities similar to those of the corresponding *para*-derivatives. A base-weakening steric effect, which can also affect the resonance interaction between the substituent and the reaction centre, is expected in the tetra-substituted compound, since the conformational study cited above indicates a crowded situation (rigid structure) even for the tri-substituted compound. Loss of conjugation is also shown from the c.t. spectra of its complex with π acceptors.[22]

TABLE 3

Temperature dependence and related thermodynamic parameters of the c.t. equilibria of some diphenyl sulphides with iodine in cyclohexane

	$K_{c.t.}$/l mol⁻¹			−Δ*H*/	−Δ*S*/
Substituents	17°	25°	35°	kcal mol^{-1}	cal mol^{-1} K^{-1}
None	4·9	3·9	2·8	5·7	16·6
p-Me	7·9	5·5	4·0	6·8	19·3
p-OMe	9·1	6·3	4·0	8·1	23·6
p,p'-Me$_2$	9·3	6·1	3·9	8·7	25·0
o,o'-Me$_2$	8·7	5·8	3·6	8·8	26·2
o,o,o',o'-Me$_4$	5·9	3·7	2·1	10·2	32·2

That a steric effect is operative in the tetramethyl-*ortho*-substituted complex is also shown by the thermal

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* *X*-Ray analysis,[15] electrical refraction,[16] and theoretical studies[17] on diphenyl sulphide indicate a non-rigid 'butterfly' conformation, with a C–$\hat{S}$–C angle of 109°, partial double bond character of the C–S bond, and the twist angle (*ca.* 40°) of both rings in the opposite directions, out of coplanarity with the C–S–C plane. In *ortho*-trisubstituted compounds the different balance of steric and conjugative factors forces the rings to a wider twist angle.[18]

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parameters of some *ortho*- and *para*-substituted sulphides reported in Table 3 and Figure 3. The best straight line shown in the Figure for *para*-compounds has *r* 0·9979, which becomes slightly smaller (0·9948) for the *ortho*-dimethyl and even smaller (0·9894) for the *ortho*-tetramethyl derivative. Both the points for *ortho*-compounds deviate from the best straight line in the sense of an excessive entropy term. This behaviour, particularly evident for the tetramethyl derivative, reflects the rigidity of this complex wherein free rotation is hindered. The isoequilibrium temperature obtained from Figure 3 is 345 K, excluding the two deviating compounds. This value is significantly smaller than that obtained for the complexes of iodine with several alkyl sulphides, selenides, and ethers.[2] Even though comparisons with these aromatic sulphides should be treated with caution, the lower isoequilibrium temperature found in the present case may reflect the influence of entropy factors in the aromatic complexes.

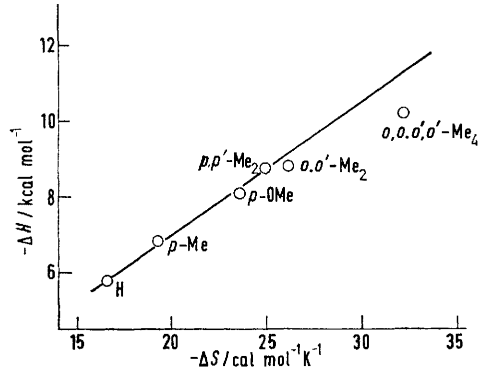

FIGURE 3 Relationship between enthalpies and entropies of c.t. complexes of some diphenyl sulphides with iodine in cyclohexane

Conclusions.—In diphenyl sulphides, as in related sulphur compounds,[2] the reaction with iodine occurs at the bridged heteroatom, leading to $n \longrightarrow \sigma^*$ complexes where, however, the 3*p* electrons of the donor atom interact with the π electrons of the phenyl rings. The stability is rather low compared with other sulphur complexes, mainly because of the participation of the sulphur *p* electrons in the aromatic system. This conclusion is in agreement with photoelectron spectroscopy data. The first I.P. for thiophenol (8·3 eV) has been ascribed to a lone pair electron with considerable π character.[23] Preliminary data on diphenyl sulphide (first I.P. 7·9 eV)[24] indicate that the last occupied orbital of this molecule has n–π character.

Essentially no additional steric effect is introduced by one *ortho*-methyl group in both rings. Only the introduction of four *ortho*-groups brings about a moderate base-weakening effect; further deviation from coplanarity, which reduces the leakage of charge due to conjugation through the bridge, matches in part the effect of an over-crowded reaction centre.

Leaking of electron density between the two rings justifies both the rather small sensitivity of complex equilibrium to ring substitution as well as the smaller reaction constant obtained for the disubstituted compounds.

The smaller $\rho_{c.t.}$, compared with that for the corresponding selenium compounds, and the deviation from additivity due to the conjugation of substituents with the common reaction centre, both indicate that transmission of substituent effects between the rings through the sulphur bridging atom is effective in diphenyl sulphides.

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