

Charge Transfer Complexes of Aryl Diphenylmethyl Sulphides with Iodine and with Tetracyanoethylene¹

By Sergio Santini,* Gustavo Reichenbach, and Salvatore Sorriso, Istituto di Chimica Fisica, Università di Perugia, 06100 Perugia, Italy
Alberto Cecon, Istituto di Chimica Fisica ed Elettrochimica, Università di Padova, 35100 Padova, Italy

Charge transfer complexes of iodine (σ acceptor) and tetracyanoethylene (π acceptor) with aryl diphenylmethyl sulphides, $X^1C_6H_4(X^2C_6H_4)CH_2S \cdot C_6H_4Y$, have been studied in cyclohexane and carbon tetrachloride at 25°. The effect of substituents X and Y on the charge transfer constant, K_{ct} , is notably different. Y Substituents modify this constant much more than do X substituents. The presence in the donor molecule of two electron-donating sites could produce the formation of multiple equilibria. If the sulphide is regarded as a combination of diphenylmethyl and thiyl radicals, spectral and equilibrium data show that iodine interacts exclusively with the thiyl portion. On the other hand, tetracyanoethylene interacts competitively with both halves of diphenylmethyl phenyl sulphide to give two isomeric, stable 1:1 charge transfer complexes. The absence of multiple equilibria involving the formation of 2:1 and 1:2 stable complexes is discussed.

Our earlier investigations have dealt with charge transfer (c.t.) complexes of σ (iodine) and π [tetracyanoethylene (TCNE), chloranil, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone] acceptors with benzenethiol² and diphenyl sulphide donors.^{3,4} From our data and those of other workers on the complexes between iodine and thioanisole⁵ it appears that the reactivity of the phenylthio-system is influenced to some extent by the possibility of the 3*p* orbitals of the sulphur atom conjugating with the π electrons of the phenyl ring, *i.e.* the donor orbital, which is to a great extent localized on the sulphur atom, is no longer a pure *n* orbital, but the unshared electrons are partially conjugated with the π orbitals of the ring.⁶

It is of interest to extend the study of charge transfer complexes to substrates which have another electron donating source besides the phenylthio-system. In this case π and σ acceptors can, in principle, interact competitively with the two different centres. The nature of the complexes formed could depend on the type of acceptor and on the relative concentrations of the two partners.⁷

In this work we have investigated the charge transfer complexes of benzyl, diphenylmethyl, and triphenylmethyl phenyl sulphides, where the two donor centres are the phenyl ring(s) and the phenylthio-system, with iodine and tetracyanoethylene. Steric and substituent effects have been used in order to elucidate the nature of the complexes.

EXPERIMENTAL

Materials.—Aryl diphenylmethyl sulphides were prepared from appropriately substituted diphenylmethanols

¹ S. Santini, G. Reichenbach, and S. Sorriso, presented in part at the VI Convegno Nazionale di Chimica Inorganica, Firenze, 1973.

² G. Reichenbach, S. Santini, and U. Mazzucato, *J.C.S. Faraday I*, 1973, 143.

³ S. Santini, G. Reichenbach, and U. Mazzucato, *J.C.S. Perkin II*, 1974, 494.

⁴ G. G. Aloisi, S. Santini, and S. Sorriso, *J.C.S. Faraday I*, in the press.

⁵ J. Van der Veen and W. Stevens, *Rec. Trav. chim.*, 1963, **82**, 287.

and benzenethiols in acetic acid.⁸ Phenyl triphenylmethyl sulphide was obtained by the same method. Physical characteristics and elemental analyses have been reported elsewhere.⁹ Benzyl phenyl sulphide was obtained from benzyl bromide and benzenethiol by the usual procedure. Diphenylmethane (Fluka AG) was purified by distillation. Twice sublimed iodine (Carlo Erba RP) was resublimed from potassium iodide and stored in a desiccator. TCNE (Fluka AG) was recrystallized from chlorobenzene. Cyclohexane and carbon tetrachloride (Carlo Erba RP) were purified following Vogel,¹⁰ dried, and distilled.

Measurements.—Absorption spectra were determined using both single beam Unicam SP 500/2 and double beam Optica CF4-DR spectrophotometers with thermostatted cell compartments.

The stability constants, K_{ct} , of the complexes with iodine in cyclohexane at 25° were determined using the Benesi-Hildebrand¹¹ and the Scatchard¹² equations assuming 1:1 complexation (see Discussion section). Donor and acceptor concentrations ranged from 0.004 to 0.15M and from 4.5×10^{-4} to 5.2×10^{-4} M respectively. Spectra and stability constants of the complexes Ph_2CH_2 -TCNE and $Ph_2CH_2S \cdot Ph$ -TCNE were determined in carbon tetrachloride at 25°. The K_{ct} values were obtained using the Benesi-Hildebrand equation. The acceptor concentration was 3.4×10^{-4} M, while that of the donors ranged from 0.056 to 0.29M for Ph_2CH_2 and from 0.02 to 0.4M for $Ph_2CH_2S \cdot Ph$.

RESULTS AND DISCUSSION

The values of K_{ct} for the charge transfer complexes of iodine with *meta*- and *para*-substituted diphenylmethyl phenyl sulphides are listed in Table 1. A Hammett plot for the same substrates is shown in Figure 1. De-

⁶ D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *J. Phys. Chem.*, 1972, **76**, 1030.

⁷ B. Dodson, R. Foster, A. A. S. Bright, M. I. Foreman, and G. Gorton, *J. Chem. Soc. (B)*, 1971, 1291.

⁸ C. Finzi and V. Bellavita, *Gazzetta*, 1932, **62**, 699.

⁹ G. Farnia, A. Cecon, and P. Cesselli, *J.C.S. Perkin II*, 1972, 1016.

¹⁰ A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 3rd edn., 1957, p. 173.

¹¹ H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

¹² G. Scatchard, *Ann. New York Acad. Sci.*, 1949, **51**, 660.

pending on substituents X or Y, two distinct linear correlations are obtained. The substituents on the diphenylmethyl skeleton give a line the slope of which, $\rho_X -0.23$ (correlation coefficient $r 0.984$), is notably

TABLE 1

Substituent effect on charge transfer equilibria of substituted diphenylmethyl phenyl sulphides $X^1C_6H_4-(X^2C_6H_4)CHSC_6H_4Y$ with iodine in cyclohexane at 25°

Compound	X ¹	X ²	Y	$K_{ct}/$ l mol ⁻¹
(I)	H	H	H	5.2
(II)	H	H	4-OMe	12.0
(III)	H	H	4-Me	9.7
(IV)	H	H	4-Cl	3.2
(V)	H	H	3-Cl	2.6
(VI)	H	H	4-F	4.5
(VII)	4-Me	H	H	6.4
(VIII)	4-Cl	H	H	4.8
(IX)	4-Ph	H	H	5.5
(X)	4-Me	4-Me	H	6.9
(XI)	4-Cl	4-Cl	H	4.6
(XII)	4-OMe	4-OMe	H	7.5

lower than that obtained for substituents on the benzenethiol ring, $\rho_Y -1.04$ ($r 0.997$). The much greater influence of Y substituents on the reaction centre indicates that electrophilic attack by iodine must occur at

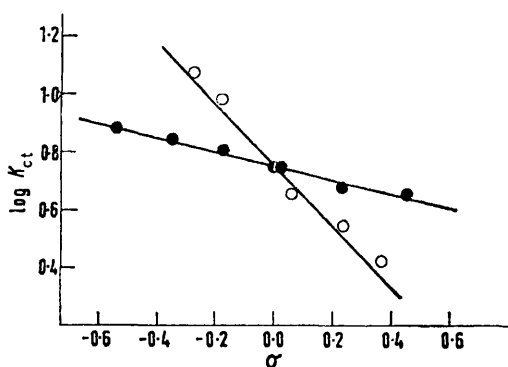


FIGURE 1 Hammett plot for the stability constants of c.t. complexes between iodine and diphenylmethyl phenyl sulphides in cyclohexane at 25° : O, compounds (I)–(VI) (see Table 1 for key) (Y varies); ●, compounds (VII)–(XII) (X^1, X^2 vary)

the sulphur atom rather than at the diphenylmethyl system.* X Substituents transmit their effect only by an inductive mechanism and the sensitivity of the reaction is rather low because of the relatively large distance between the sulphur atom and the substituent. Y Substituents influence the sulphur atom by both inductive and resonance mechanisms,⁶ and the resulting effect is about four-fold greater. Moreover, the values of the Hammett reaction constants indicate that a non-classical conjugative interaction¹³ be-

* It is worth noting that a similar, though smaller, influence of the substituent was found⁹ in the polarographic reduction of the same series of sulphides in *NN*-dimethylformamide ($\rho_X = 0.203$ V, $\rho_Y = 0.386$ V). In this case the sulphur atom suffers nucleophilic attack by the cathode.

tween the SPh and Ph_2CH systems is rather unlikely; $\rho_Y, -1.04$, is not much different from the ρ value, -1.3 ,⁵ found for thioanisoles. Through-space conjugation between the two halves of the molecule is also excluded on the basis that this would cause a levelling effect on the ρ values. Results obtained from u.v. measurements on benzyl phenyl sulphides¹⁴ confirm the view that no conjugative mechanism is operating in these systems.

The effect of progressive substitution of the hydrogens of the methyl group in MeSPh by phenyl rings on the stability constant is shown in Table 2. Substitution of a

TABLE 2

Effect of substitution of methyl hydrogen atoms with phenyl groups on charge transfer equilibria of thioanisole and dimethyl sulphide with iodine at 25°

Donor	$K_{ct}/$ l mol ⁻¹	Solvent
MeSPh ^a	12.1	Cyclohexane
PhCH ₂ SPh	9.7	Cyclohexane
Ph ₂ CHSPh	5.2	Cyclohexane
Ph ₃ CSPh	3.2	Cyclohexane
MeSMe ^b	72.0	CCl ₄
Ph ₂ CHSMe	52.0	Cyclohexane

^a Data from ref. 5. ^b Data from N. W. Tidswell and J. D. McCullough, *J. Amer. Chem. Soc.*, 1957, **79**, 1031.

single hydrogen by a phenyl group causes a relatively small decrease of K_{ct} , but the effect is greater when a second phenyl group is introduced, K_{ct} decreasing to about one-half its value. An analogous decrease is observed on substitution of the third hydrogen. This irregular trend cannot be explained by invoking only intervention of the electronic effects of the phenyl groups ($\sigma_I = 0.1$),¹⁵ but the possibly more important steric effects on the reaction centre must also be taken into account. If this view is correct, from the K_{ct} values it appears that the first phenyl group should not interfere appreciably with the attacking molecule, while, when two phenyl groups are present, the conformation of the molecule is such that only one interferes sterically. In triphenylmethyl phenyl sulphide two of the three rings should give rise to steric hindrance. Dipole moment measurements in apolar solvents on the same compounds¹⁶ agree with the suggested conformation. Steric effects have previously been invoked to explain the decrease in reactivity observed when the alkyl portion becomes more crowded in the closely related reaction of oxidation of alkyl aryl sulphides to sulphoxides, which implies an attack by bromine on sulphur.¹⁷

Table 2 also reports the values of K_{ct} for the complexes between iodine and dimethyl sulphide, and between iodine and methyl diphenylmethyl sulphide for

¹³ S. Winstein, *Quart. Rev.*, 1969, **23**, 141.

¹⁴ V. Mancini, O. Piovesana, and S. Santini, submitted for publication in *Z. Naturforsch.*

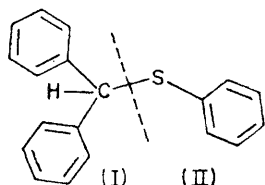
¹⁵ E. M. Kosower, 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968, p. 49.

¹⁶ S. Sorriso, G. Reichenbach, S. Santini, and A. Ceccon, *J.C.S. Perkin II*, in the press.

¹⁷ U. Miotti, G. Modena, and L. Sedeà, *J. Chem. Soc. (B)*, 1970, 802.

comparison. It appears that for these cases the substitution of two hydrogens by two phenyl groups reduces the K_{ct} value less than is the case for thioanisole. This is due to the fact that in dimethyl sulphide the reaction centre is less hindered and so the two phenyl groups exert smaller steric effects.^{17,18}

For a better understanding of the nature of the interaction between σ and π acceptors and diphenylmethyl phenyl sulphide, let us imagine that the skeleton of the molecule is the sum of two independent parts with no conjugative interaction between them. The two halves,



the diphenylmethyl (I) and thiyl (II) radicals, are both able to act as electron donors. One can consider the sulphide as a derivative of diphenylmethane with one hydrogen replaced by the thiyl radical, SPh. This should affect the diphenylmethyl system only by an inductive mechanism. On the other hand, the molecule may be regarded as a derivative of the thioanisole where two phenyl groups replace two hydrogens. While in part (I) the donor is represented by the π electron system of the two phenyl groups, in part (II) the donor centre is the orbital of the sulphur which is conjugated with the adjacent π system. With this scheme in mind, we have studied the charge transfer complexes of diphenylmethane with both iodine and TCNE, and those of thioanisole with the same acceptors. Table 3 shows the

TABLE 3

Comparison of wavelengths and association constants for c.t. complexes of diphenylmethane, thioanisole, and diphenylmethyl phenyl sulphide with I_2 and TCNE at 25°

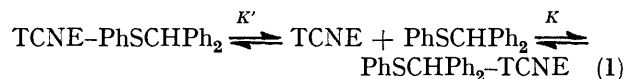
Donor	I_2 (In cyclohexane)		TCNE (In CCl_4)	
	$K_{ct}/l \text{ mol}^{-1}$	λ_{ct}/nm	$K_{ct}/l \text{ mol}^{-1}$	λ_{ct}/nm
MeSPh	12.1 ^a	333	4.2 ^b	400, 562
Ph_2CH_2	0.25		3.6	420
Ph_2CHSPh	5.2		8.3	400, 420, 560

^a Data from ref. 5. ^b Data from ref. 4.

values of the K_{ct} obtained for these molecules and for Ph_2CHSPh . K_{ct} for the diphenylmethane-iodine complex is *ca.* 1/20 than K_{ct} for diphenylmethyl phenyl sulphide, which, in turn, is less than half that of thioanisole. Of the two possible donor centres of the sulphide molecule, iodine should interact almost exclusively with the phenylthio-system rather than with the π electrons of the diphenylmethyl portion. These observations agree with the effect of substituents discussed above. We assume that the stoichiometry is 1 : 1, by

analogy with similar sulphur compounds previously studied.^{2,3,5} In addition, some evidence is given by the good linearity (r 0.990) of the Scatchard plots.¹⁹ Unfortunately they were limited to a saturation fraction from 0.06 to 0.61, owing to the low solubility of sulphides in cyclohexane.

With TCNE, diphenylmethane and thioanisole give charge transfer complexes of similar stability, $K_{ct} = 3.6$ and $4.2 l \text{ mol}^{-1}$ respectively. From these data we can assume that in phenyl diphenylmethyl sulphide both portions interact competitively with TCNE to give c.t. complexes as in equation (1). The presence of two 1 : 1



isomeric equilibria has been confirmed by comparison of spectral and equilibrium data for the interaction of TCNE with the whole molecule and its parts. The diphenylmethane complex has a maximum at 420 nm, while thioanisole shows two maxima at 400 and 562 nm.

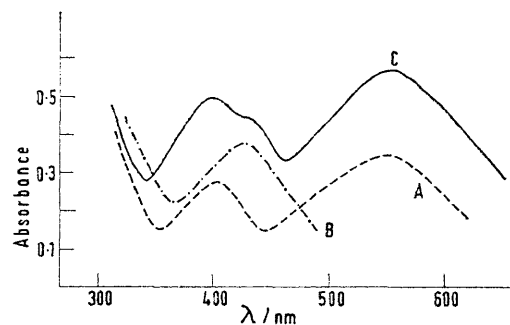


FIGURE 2 Absorption spectra of c.t. complexes between TCNE and A, thioanisole; B, diphenylmethane; and C, diphenylmethyl phenyl sulphide in CCl_4 at 25°

Diphenylmethyl phenyl sulphide gives a complex with three principal bands, one with a maximum at 560 nm while the other two partially overlap with maxima at 420 and 400 nm (see Figure 2). We assign the two bands at 560 and 400 nm to the interaction between TCNE and the phenylthio-system, whereas the band at 420 nm can be attributed to the c.t. interaction of TCNE with the diphenylmethyl group. The assignment is supported by u.v. data on the complex of TCNE with bis-4-methoxyphenylmethyl phenyl sulphide. In this case, the band and the position of the maximum at 560 nm do not change appreciably, as one would expect if the band is caused by the interaction with phenylthio-system which is common to both the molecules. On the other hand, the band at 420 nm assigned to the c.t. interaction with the diphenylmethyl system, is shifted to lower frequencies and is better resolved.

It is possible to obtain the value of $(K + K')$ by plotting the experimental data using the Benesi-Hildebrand and Scatchard equations applied to equilibrium

¹⁸ E. T. Strom, W. L. Orr, B. S. Snowden, jun., and D. E. Woessner, *J. Phys. Chem.*, 1967, **71**, 4017.

¹⁹ D. A. Deranleau, *J. Amer. Chem. Soc.*, 1969, **91**, 4050.

(1). The value obtained is almost equal to the sum of the two constants for the separate parts of the molecule (see Table 3). This confirms the simultaneous presence of two isomeric complexes as in equilibrium (1). The linearity of the Scatchard plot obtained over a wide range of saturation fraction (s 0.14—0.77) is good evidence that a 2:1 (donor-acceptor) complex is not formed.¹⁹ Since the TCNE:sulphide ratio varies from

1:50 to 1:200, the possibility of the formation of a 1:2 (donor-acceptor) complex may also be ruled out.⁷

In conclusion, while iodine (σ acceptor) interacts with the thiyyl part of the molecule, and more specifically with the sulphur atom, TCNE (π acceptor) reacts with both halves of diphenylmethyl phenyl sulphide each of which competes for the electrophile.

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