

gratefully acknowledge the use of the facilities of the Indiana University Research Computing Center. Thanks are also due Mr. Ralph Christofferson for read-

ing some of the microphotometer traces and Mrs. Joanne Knight for her help in preparing the manuscript.

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

## Molecular Complexes and Their Spectra. XVII. The Iodine and the Chloranil Complexes with Thianthrene Analogs

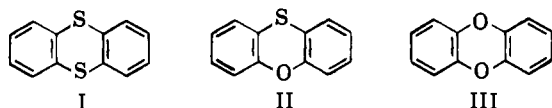
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RECEIVED FEBRUARY 25, 1963

The thermodynamic properties of the iodine complexes with the thianthrene analogs I, II, and III in solution were spectroscopically studied. Their charge transfer bands were also studied in comparison with the ones of the chloranil complexes with the thianthrene analogs. From the obtained results, it is concluded that the thianthrene analogs are essentially *n*-donors for iodine. Furthermore, referring to the energies of the charge transfer bands of the chloranil complexes, the appropriate integral values for the thianthrene analogs in the Hückel MO method were studied.

### Introduction

Many studies have hitherto been carried out with various charge-transfer type molecular complexes. But there have been only few works in which unsaturated heterocyclic compounds except for azines were used as donors. Recently, Lang<sup>2</sup> studied spectroscopically the iodine complexes with five-membered unsaturated heterocyclic compounds. Since thianthrene analogs have two heteroatoms, it is particularly interesting to study the charge transfer interaction between iodine and these molecules, the principal reason for undertaking the present study. In the present study, thianthrene (I), phenoxathiin (II), and diphenylene dioxide (III) were used as donors.



### Experimental

**Materials.**—Fisher certified iodine was resublimed under reduced pressure. Fisher spectrograde dichloromethane and carbon tetrachloride were dried with Drierite and distilled with a Podbielniak column. Phillips 66 "pure" grade *n*-heptane was washed twice with concentrated sulfuric acid, then several times with water, dried with Drierite, and distilled with a Podbielniak column. Eastman Pure Chemicals of thianthrene, phenoxathiin, and chloranil were purified by recrystallization from *n*-heptane-ethanol (1:1) mixture, *n*-heptane, and toluene, respectively (m.p. 158.5–159.5° for thianthrene, 57–57.5° for phenoxathiin). Commercially available diphenylene dioxide was washed twice by dilute aqueous sodium hydroxide solution and, after drying, recrystallized repeatedly from *n*-heptane (m.p. 119–120°).

**Method.**—Absorption spectra were measured with a Beckman spectrophotometer Model DK-2 attached with a thermostated cell jacket. Square silica cells of 1-cm. path length were used. The molar extinction coefficients near the peaks of the charge transfer absorption bands<sup>3</sup> and the equilibrium constants were obtained by the formula of Ketelaar, *et al.*<sup>4</sup> In the cases of thianthrene and phenoxathiin, the concentrations of iodine were  $4.6 \sim 5.3 \times 10^{-4} M$  and those of the donors  $0.05 \sim 0.20 M$ . In the case of diphenylene dioxide the concentration of iodine was  $3.7 \times 10^{-3} M$  and those of the donors were  $0.21 \sim 0.36 M$ . Since the tail of the long wave length absorption band of thianthrene and the CT band of its iodine complex considerably overlap with each other, especially in carbon tetrachloride,  $E_T$  in the formulas of Ketelaar, *et al.*,<sup>4</sup> was obtained by dividing the difference between the absorption of thianthrene and that of the complex solution by the iodine concentration. The absorption

intensities of thianthrene were always less than 7.5% those of the complex solutions. The CT bands of the complexes between chloranil and the thianthrene analogs were measured with equal volume mixtures of the chloranil and the thianthrene analogs solutions, both nearly saturated. The CT band shapes of the iodine and the chloranil complexes were obtained by subtracting the absorptions corresponding to the added quantities of both components of the complexes from the absorptions of the complex solutions. The oscillator strengths of the CT bands were calculated by the approximate formula given by Tsubomura and Lang.<sup>5,6</sup>

### Results

Since the formula of Ketelaar, *et al.*,<sup>4</sup> was satisfied in all cases, it is clear that the one-to-one charge transfer complexes were formed in the concentration ranges used in this work. Table I shows the equilibrium constants and the molar extinction coefficients obtained. In the calculation of the equilibrium constants, the molarity was used as the units of the concentrations of iodine and the donors. As shown in Table I, the obtained molar extinction coefficients of the complexes somewhat fluctuated over the temperature range adopted in the present study, but it is likely that in all cases the molar extinction coefficients are independent of temperature. Therefore, the equilibrium constants shown in Table I were evaluated using the average values of the molar extinction coefficients obtained at various temperatures. As shown in Fig. 1, good linearities between the logarithms of the equilibrium constants and the reciprocals of temperatures were obtained in all cases. The binding energies ( $\Delta H$ ) and the entropies of formation ( $\Delta S$ ) of the complexes are obtained from the slope and the intercept of the straight lines shown in Fig. 1. The thermodynamic constants and the features of the CT bands obtained are shown in Tables II and III, respectively. The features of the CT bands of the chloranil complexes with the thianthrene analogs at 20° are also shown in Table III for the purpose of comparison;  $\Delta\nu^-$  and  $\Delta\nu^+$  in the sixth and the seventh columns of Table III are the differences in wave number between the peak positions of the CT bands and their half-height positions of the CT bands at the longer and the shorter wave length sides, respectively, and the sums of these two values are the half-widths ( $\Delta\nu_{1/2}$ ) of the CT bands which are shown in the eighth column. The peak positions of the CT bands and the CT band shapes of the iodine complexes with the thianthrene analogs are almost independent of temperature. In the last column the oscillator strengths of the CT bands, *f*-values, are

(1) On leave of absence from the Government Chemical Industrial Research Institute, Tokyo, Shibuya-ku, Tokyo, Japan.

(2) R. P. Lang, *J. Am. Chem. Soc.*, **84**, 4438 (1962).

(3) In the following, the term "the charge transfer absorption band" is abbreviated as "the CT band."

(4) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzeubas, *Rec. trav. chim.*, **71**, 1104 (1952).

(5) H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961).

(6) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

shown. In the iodine-thianthrene complex,  $\Delta\nu^+$  could not be obtained owing to the overlap of the CT band with the absorption band of thianthrene. As in the chloranil-thianthrene complex the first and the second CT bands considerably overlap each other; both the apparent and the true peak positions of the CT bands are shown. Therefore, the peak positions of the CT band of the iodine-thianthrene complex in Table III are thought to be the apparent ones. Thermodynamic and spectroscopic data on the iodine complexes with the aliphatic thioethers and ethers by other authors are shown in Table IV for the purpose of comparison. The ionization potentials of electron donors can be evaluated from the energies of the CT bands of the chloranil complexes in carbon tetrachloride by the aid of the Briegleb-Czekalla formula.<sup>7</sup> The actual evaluated values are 7.9, 7.6, and 7.7 e.v. for thianthrene, phenoxathiin, and diphenylene dioxide, respectively.

TABLE I

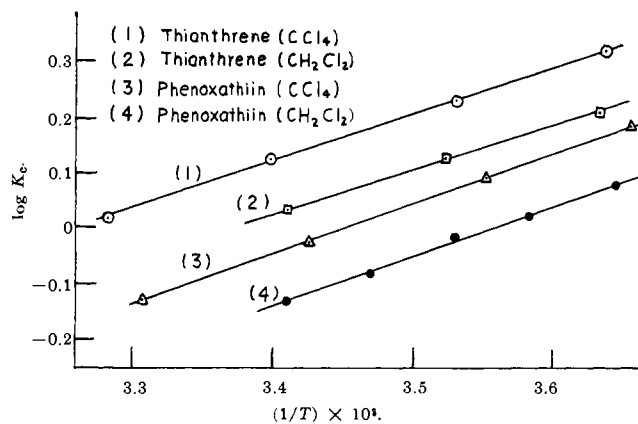
EQUILIBRIUM CONSTANTS AND MOLAR EXTINCTION COEFFICIENTS OF THE IODINE COMPLEXES WITH THE THIANTHRENE ANALOGS

Temp., °C.	$K_c, \text{l. mole}^{-1}$				Av.	$\epsilon, \text{l. mole}^{-1} \text{ cm.}^{-1}$		
	375 m $\mu$	380 m $\mu$	385 m $\mu$	385 m $\mu$		375 m $\mu$	380 m $\mu$	385 m $\mu$
(a) Donor, thianthrene; solvent, carbon tetrachloride								
1.6	2.11	2.12		2.115	13100	12400		
10.0	1.72	1.73	1.72	1.72	12750	12200	11100	
20.0	1.34	1.35	1.33	1.34	14400	13700	13450	
31.4	1.05	1.06	1.05	1.05	13200	13000	12400	
				Av.	13350	12800	12300	
(b) Donor, thianthrene; solvent, dichloromethane								
1.9	1.56	1.69	1.68	1.64	12200	10050	10200	
10.5	1.30	1.37	1.38	1.35	12200	12200	11400	
20.0	1.05	1.11	1.11	1.09	12400	12400	12150	
				Av.	12300	11550	11250	
(c) Donor, phenoxathiin; solvent, carbon tetrachloride								
	390 m $\mu$	395 m $\mu$	400 m $\mu$	Av.	390 m $\mu$	395 m $\mu$	400 m $\mu$	
1.8	1.565	1.50	1.55	1.54	13400	14950	13850	
10.0	1.26	1.225	1.245	1.24	14250	14900	15100	
20.5	0.96	0.93	0.95	0.95	14100	14600	13950	
31.0	0.76	0.73	0.74	0.74	12200	13400	13700	
				Av.	13900	14500	14150	
(d) Donor phenoxathiin; solvent, dichloromethane								
	395 m $\mu$	400 m $\mu$	405 m $\mu$	Av.	395 m $\mu$	400 m $\mu$	405 m $\mu$	
1.1	1.225	1.22	1.16	1.205	14000	14500	15500	
5.7	1.07	1.075	1.02	1.055	14200	13800	15300	
10.0	0.98	0.975	0.935	0.965	13800	14700	15000	
15.0	.84	.84	.81	.83	15200	14250	14250	
20.0	.75	.75	.72	.74	15500	16000	16000	
				Av.	14550	14650	15200	
(e) Donor, diphenylene dioxide; solvent, carbon tetrachloride								
20.1	0.30	0.25	0.275	0.275	3030	3580	3230	

TABLE II

THERMODYNAMIC CONSTANTS OF THE IODINE COMPLEXES WITH THE THIANTHRENE ANALOGS

Donors	Solvents	$K_c, 20^\circ,$ l./mole	$-\Delta H_c$	$-\Delta S_c$
			kcal./ mole	$\pm 0.5,$ e.u.
Thianthrene	CCl <sub>4</sub>	1.34	3.82	12.4
Thianthrene	CH <sub>2</sub> Cl <sub>2</sub>	1.09	3.71	12.5
Phenoxathiin	CCl <sub>4</sub>	0.95	4.12	14.3
Phenoxathiin	CH <sub>2</sub> Cl <sub>2</sub>	.74	4.12	14.6
Diphenylene dioxide	CCl <sub>4</sub>	.27		

(7) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).Fig. 1.—The plot of  $\log K_c$  vs.  $1/T$  for the iodine complexes with the thianthrene analogs.

### Discussion

As seen in Tables III and IV, the energies of the CT bands of the iodine complexes with the thianthrene analogs are nearly equal to each other and far smaller than the ones of the iodine complexes with the aliphatic thioethers and ethers. These facts show that in the thianthrene analogs the  $\pi$ -electronic conjugation occurs to a considerable extent. In Tables II and III, it is noticeable that the binding energies and the intensities of the CT bands of the iodine complexes with thianthrene and phenoxathiin are nearly equal to each other, whereas the equilibrium constant and the intensity of the CT band of the iodine-diphenylene dioxide complex are considerably smaller than the ones of the iodine complexes with thianthrene and phenoxathiin. These marked facts are unambiguously related to the absence of a sulfur atom in diphenylene dioxide. On the other hand, as seen in Table IV, the equilibrium constants, the binding energies, and the intensities of the CT bands of the iodine complexes with the aliphatic thioethers (diethyl sulfide, 1,4-dithiane, and 1,4-thiodioxane) are far larger than the iodine complexes with the corresponding aliphatic ethers (diethyl ether and 1,4-dioxane), respectively. It is known that aliphatic thioethers and ethers are n-donors for iodine and in the iodine complexes with 1,4-dithiane analogs in solution the iodine molecule coordinates one of two heteroatoms of 1,4-dithiane analogs. From these facts, it is concluded that the thianthrene analogs are essentially n-donors for iodine like aliphatic thioethers and ethers, and the iodine molecule coordinates one of the two heteroatoms of the thianthrene analogs.

The equilibrium constants and the binding energies of the iodine complexes with thianthrene and phenoxathiin are smaller than those of the iodine complexes with the aliphatic thioethers, and the equilibrium constant of the iodine-diphenylene dioxide complex is smaller than those of the iodine complexes with the aliphatic ethers. In the iodine complexes with n-donors, the strength of the charge transfer interaction may be sensitive to the lone-pair orbital hybridization of the heteroatoms in the donors, which depends upon the bond angles of the heteroatoms. The bond angles of the sulfur atoms of thianthrene, phenoxathiin, and 1,4-dithiane are  $100^\circ$ ,<sup>8</sup>  $92-94^\circ$ ,<sup>9</sup> and  $99^\circ$ ,<sup>10</sup> respectively. Therefore, it is thought that the lone-pair orbital hybridizations<sup>11</sup> of the sulfur atoms in thianthrene and 1,4-dithiane are

(8) H. Lynton and E. G. Cox, *J. Chem. Soc.*, 488 (1956); I. Rowe and B. Post, *Acta Cryst.*, **11**, 372 (1958).(9) S. Hosoya, Dissertation, University of Wales, 1958; *Acta Cryst.*, **16**, 310 (1963).(10) R. E. Marsh, *ibid.*, **8**, 91 (1955).(11) R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 887 (1955).

TABLE III  
 THE FEATURES OF THE CT BANDS OF THE IODINE AND THE CHLORANIL COMPLEXES WITH THE THIANTHRENE ANALOGS

Acceptors	Donors	Solvents <sup>a</sup>	$\lambda_{\max}$ , m $\mu$	$\epsilon_{\max}$	$\Delta\nu^-$ , cm. <sup>-1</sup>	$\Delta\nu^+$ , cm. <sup>-1</sup>	$\Delta\nu^{1/2}$ , cm. <sup>-1</sup>	<i>f</i>
Iodine	Thianthrene	CCl <sub>4</sub>	371	13350	2800			
	Thianthrene	CH <sub>2</sub> Cl <sub>2</sub>	375	12300	3510			
	Phenoxathiin	CCl <sub>4</sub>	396	14200	3320	~2720	~6040	0.370
	Phenoxathiin	CH <sub>2</sub> Cl <sub>2</sub>	400	14800	3620	~2920	~6540	0.418
	Phenoxathiin	C <sub>7</sub> H <sub>16</sub>	390		2000	~1910	~3910	
	Diphenylene dioxide	CCl <sub>4</sub>	399.5	3280	2860	~3060	~5920	0.0840
	Diphenylene dioxide	CH <sub>2</sub> Cl <sub>2</sub>	~394					
Chloranil	Thianthrene	CCl <sub>4</sub>	~520(515) <sup>b</sup> ~418(420) <sup>b</sup>					
	Thianthrene	CH <sub>2</sub> Cl <sub>2</sub>	~525					
	Phenoxathiin	CCl <sub>4</sub>	580		2580	~2880	~5460	
			<400					
	Phenoxathiin	CH <sub>2</sub> Cl <sub>2</sub>	587		2770	~3040	~5810	
	Phenoxathiin	C <sub>7</sub> H <sub>16</sub>	558		2600	~2960	~5560	
	Diphenylene dioxide	CCl <sub>4</sub>	556		2240	~2760	~5000	
			<400					
	Diphenylene dioxide	CH <sub>2</sub> Cl <sub>2</sub>	560					

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub> and C<sub>7</sub>H<sub>16</sub> denote dichloromethane, and *n*-heptane, respectively. <sup>b</sup> The values in parentheses denote the apparent peak positions.

TABLE IV

THERMODYNAMIC AND SPECTROSCOPIC DATA OF THE IODINE COMPLEXES WITH ALIPHATIC THIOETHERS AND ETHERS BY OTHER AUTHORS

Donors	Solvents	$K_o$ , 25°, l./mole	$-\Delta H_o$ , $\pm 0.1$ , kcal./mole	$-\Delta S_o$ , $\pm 0.5$ , e.u.	$\lambda_{\max}$ , m $\mu$	$\epsilon_{\max}$	$\Delta\nu^{1/2}$ , <sup>g</sup> cm. <sup>-1</sup>	<i>f</i> <sup>h</sup>
1,4-Dithiane <sup>a</sup>	CCl <sub>4</sub>	76.9	6.2	12.1	305	~17200		
1,4-Thiodioxane <sup>a</sup>	CCl <sub>4</sub>	58.1	5.2	9.5	~310	10500		
1,4-Dioxane <sup>4, a</sup>	CCl <sub>4</sub>	1.00	3.3	11.0	264	4360		
Diethyl sulfide	<i>n</i> -Heptane <sup>d</sup>	210 <sup>b</sup>	7.82	15.9	302	29800	5400	0.695
Diethyl sulfide	CCl <sub>4</sub> <sup>c</sup>	233 <sup>b</sup>	7.85	15.9	305	29400		
Diethyl ether	<i>n</i> -Heptane <sup>d</sup>	0.87	4.0	13.7	252	5650		
Diethyl ether	CCl <sub>4</sub> <sup>e</sup>	0.98 <sup>b</sup>	4.10	14.0	249	5700	6900	0.170

<sup>a</sup> J. D. McCollough and I. C. Zimmermann, *J. Phys. Chem.*, **65**, 888 (1961). <sup>b</sup> The values at 20°. <sup>c</sup> M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *J. Am. Chem. Soc.*, **83**, 4329 (1961). <sup>d</sup> Sr. M. Brandon, M. Tamres, and S. Searles, Jr., *ibid.*, **82**, 2129 (1960); M. Tamres and Sr. M. Brandon, *ibid.*, **82**, 2134 (1960). <sup>e</sup> P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

nearly equal to each other and different from that in phenoxathiin to some extent. From this, the charge transfer interaction seems not sensitive to the lone-pair orbital hybridization of the sulfur atoms in these cases. The relatively weak charge transfer interaction in the iodine complexes with the thianthrene analogs is, probably, mainly due to the lone pairs of the heteroatoms of the thianthrene analogs participating in the  $\pi$ -electronic conjugation.

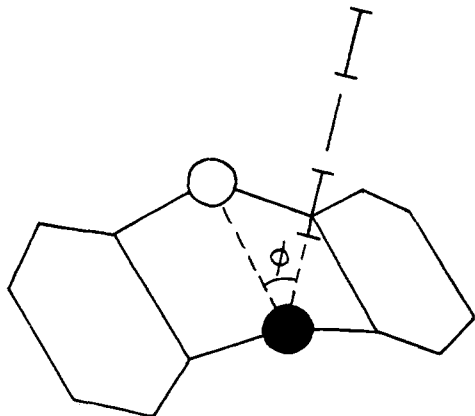


Fig. 2.—The assumed structure of the iodine complexes with the thianthrene analogs.

It was determined by X-ray crystal analysis<sup>8,9,12</sup> that thianthrene analogs containing sulfur atoms, such as thianthrene and phenoxathiin, have folded structures about the axes combining the two hetero-

(12) R. G. Wood, C. H. McCale, and G. Williams, *Phil. Mag.*, **31**, 71 (1941).

atoms, and the dihedral angle of thianthrene<sup>8</sup> is 128°. As for diphenylene dioxide, from the isomorphous relationship<sup>13</sup> it was concluded to be planar, whereas from its dipole moment<sup>14</sup> its dihedral angle was estimated at 160°. From these results it is likely that diphenylene dioxide is nearly planar. Chao and McCollough<sup>15</sup> studied the structures of the iodine complexes with 1,4-dithiane and 1,4-diselenane by the X-ray crystal analysis techniques. Referring to the results obtained by them as the configuration of the iodine complexes with the thianthrene analogs, the one in Fig. 2 is thought to be highly probable. In this figure, the black and white circles represent X and Y heteroatoms, respectively, and the iodine molecule coordinates with the X atom. The line (I-I-X) is linear and lies in the symmetry plane containing the two heteroatoms. The angle  $\phi$  ( $\angle$ I-X-Y) cannot be determined from the results obtained in this study, but is, probably, formed in such a way that the overlap between the  $\sigma$ -antibonding orbital<sup>16</sup> of the iodine molecule and the lone-pair orbital of X atom is the largest.

In Table III, the CT bands of the iodine complexes with thianthrene and phenoxathiin, and the chloranil complexes with the thianthrene analogs in dichloromethane, are at longer wave lengths than the ones in carbon tetrachloride, whereas in the iodine-diphenylene dioxide complex the reverse fact is found. Since

(13) N. M. Cullinane and W. T. Rees, *Trans. Faraday Soc.*, **36**, 507 (1940).

(14) K. Higasi, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **38**, 331 (1941).

(15) G. Y. Chao and J. D. McCollough, *Acta Cryst.*, **13**, 727 (1960). The structure<sup>10</sup> of 1,4-dithiane is unaltered by complexing with iodine.

(16) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

in these molecular complexes the charge transfer excited states are far more polar than are the ground states, the energy of the CT band is thought to decrease as the polarity or the polarizability of a solvent, as a bulk effect, becomes larger. The orders of the magnitudes of the polarity and the polarizability of solvents, as a bulk effect, agree with the ones of the dielectric constants and the refractive indices of the solvents, respectively. The dielectric constants<sup>17</sup> of carbon tetrachloride, dichloromethane, and *n*-heptane at 20° are 2.238, 9.08, and 1.924, respectively, and the refractive indices<sup>17</sup> for sodium D line at 20° are 1.460, 1.425, and 1.388, respectively. Therefore, the fact mentioned above may show that in the iodine complexes with thianthrene and phenoxathiin and the chloranil complexes with the thianthrene analogs the polarity of a solvent, as a bulk effect, has a predominant effect on the energies of the CT bands, and in the iodine-diphenylene dioxide complex the polarizability of a solvent, as a bulk effect, has the predominant effect.

As seen in Table III, in the chloranil complexes the energy of the CT band for phenoxathiin is smaller than that for diphenylene dioxide, whereas in the iodine complexes the energies of the CT bands for both the donors are nearly equal. Since the charge transfer interaction in which  $\pi$ -acceptors participate is, usually, not strong, the charge transfer interaction between chloranil and the thianthrene analogs is also, probably, not strong. Therefore, the above unusual fact is thought to be due to the energy of the CT band of the iodine-phenoxathiin complex being relatively large owing to the relatively strong charge transfer interaction between iodine and phenoxathiin similar to that found in some strong iodine complexes.<sup>18</sup>

The asymmetries of the CT band shapes are represented by  $\Delta\nu^-$  and  $\Delta\nu^+$  in Table III. It is noticeable that in the iodine-diphenylene dioxide complex and the chloranil complexes with phenoxathiin and diphenylene dioxide  $\Delta\nu^+$  is larger than  $\Delta\nu^-$ , as in the chloranil complexes with aromatic hydrocarbons studied previously by the present author,<sup>19</sup> whereas in the iodine complex with phenoxathiin the reverse fact is found. It is also noticeable that the half-width of the CT band of the iodine-phenoxathiin complex in *n*-heptane is considerably smaller than those in the other solvents, whereas that of the chloranil-phenoxathiin complex in *n*-heptane is nearly equal to those in the other two solvents. The results obtained about the CT band shapes and the solvent effects upon the energies of the CT bands are interesting, but it seems difficult to explain them theoretically at this stage.

In a previous paper,<sup>20</sup> the present author found a linear relationship between the energies of the first

(17) A. Weissberger, *et al.*, "Organic Solvents," Interscience Publishers, Inc., New York, N. Y., 1955, pp. 59, 192, 194.

(18) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958); H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

(19) The unpublished data obtained in the work of A. Kuboyama (*J. Chem. Soc. Japan, Pure Chem. Sect.*, **81**, 558 (1960)). The ratios  $\Delta\nu^+/\Delta\nu^-$  are in the range from 1.2 to 1.4.

(20) A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **83**, 375 (1962). The linearity is expressed by the formula  $x = 0.430 \times 10^{-4}y - 0.269$ . In this formula,  $x$  is used in such a way that the highest filled Hückel molecular orbital energy of a donor is represented as  $\alpha + x\beta$  ( $\alpha$  and

CT bands and the highest filled Hückel molecular orbital<sup>21</sup> energies of the donors for the chloranil complexes with aromatic hydrocarbons in carbon tetrachloride. Using this linear relationship and the energies of the first CT bands of the chloranil complexes with the thianthrene analogs in carbon tetrachloride in Table III, the appropriate h.f.MO energies were determined as  $\alpha + 0.557\beta$ ,  $\alpha + 0.472\beta$ , and  $\alpha + 0.504\beta$ <sup>20</sup> for thianthrene, phenoxathiin, and diphenylene dioxide, respectively. Assuming that, in the thianthrene analogs, all the Coulomb integrals of the carbon atoms and the carbon-carbon exchange integrals are equal to those ( $\alpha$  and  $\beta$ <sup>20</sup>) in benzene, respectively, and the Coulomb integrals<sup>22</sup> of the oxygen and the sulfur atoms are  $\alpha + 2\beta$  and  $\alpha + \beta$ , respectively, the relation curves between h.f.MO energies and the carbon-heteroatom exchange integral values in thianthrene and diphenylene dioxide were obtained. From these relation curves the appropriate carbon-heteroatom exchange integral values were determined using the above h.f.MO energies obtained for thianthrene and diphenylene dioxide. The obtained values of the carbon-sulfur exchange integral for thianthrene is  $0.42\beta$  and that of the carbon-oxygen exchange integral for diphenylene dioxide is  $0.81\beta$ . Using Longuet-Higgins' model<sup>23</sup> for the sulfur atoms in thianthrene, the obtained value of the carbon-sulfur exchange integral is  $0.60\beta$ . These small values of the carbon-sulfur exchange integral suggest the small overlap between the lone-pair orbitals of the sulfur atoms and the 2p orbitals of the carbon atoms neighboring the sulfur atoms. The h.f.MO energies of phenoxathiin calculated with both methods, using the integral values for thianthrene and diphenylene dioxide, are  $\alpha + 0.54\beta$  and  $\alpha + 0.53\beta$ , respectively. These are too small in comparison with that obtained experimentally above for phenoxathiin. As mentioned before, the bond angle of the sulfur atom in phenoxathiin is smaller than that in thianthrene. Consequently, the calculated results for phenoxathiin may suggest that the modified integral values about the sulfur atom of phenoxathiin should be used instead of the ones for thianthrene.

**Acknowledgments.**—The author wishes to express his sincere thanks to Professor R. S. Mulliken for giving him the opportunity to work at the University of Chicago and for helpful suggestions. He also wishes to thank Professor S. Nagakura of the University of Tokyo for reading the manuscript and much helpful advice about it, Professor S. Hosoya of the University of Tokyo for helpful information about the molecular structures of the thianthrene analogs, and Dr. R. P. Lang for helpful advice in the experimental work. This research was supported in part by a grant from the National Science Foundation.

$\beta$  represent the Coulomb integral of the carbon atoms and the carbon-carbon exchange integral in benzene, respectively), and  $y$  represents the energies of the CT bands in wave number.

(21) In the following, the term "the highest filled Hückel molecular orbital" is abbreviated as "h.f.MO."

(22) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 117.

(23) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).