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## Multiple Charge-Transfer Bands in Complexes Involving Aromatic Donors

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RECEIVED DECEMBER 3, 1963

The charge-transfer spectra of substituted benzene donors with tetracyanoethylene as acceptor were investigated. Sometimes single, and other times double charge-transfer bands were observed. These were examined on the basis of Orgel's theory which assumes that the two bands derive from a splitting of the degeneracy of the ground state of the benzene cation on substitution. Thus, the charge-transfer energies are expected to be proportional to the first two ionization potentials of the donor component of the complex. The results obtained in this work quite generally confirm this. However, a simple approximation using an equation of the type  $h\nu = aID$  was found inadequate: evaluation of the experimental data with this equation gave variable perturbation parameters, instead of the constants predicted by Orgel's theory.

## Introduction

Early observations<sup>2a,b</sup> of two charge-transfer (c.-t.) absorption bands in  $\pi$ -complexes having substituted benzenes as the donor component were attributed by Orgel<sup>3</sup> to the fact that the transferred electron might come from either of the two levels arising when the degeneracy of the  $E_1$  level of benzene is removed by substitution. Orgel used a simple first-order perturbation calculation to evaluate both the shifts in position of the c.-t. absorption from that found in the complex of benzene with a given acceptor and the splitting resulting from substitution of the benzenoid donor in various possible ways. Although Orgel showed his results to be in general agreement with the experimental data available at that time, few additional data have been reported<sup>4-8</sup> and no attempt has been made to test the rather crude approximations of the Orgel theory. In this paper some of the deviations are considered and accounted for satisfactorily in a qualitative manner.

## Theory

In benzene the highest occupied level is doubly degenerate. On ring substitution, the degeneracy is removed; the two orbitals now split to an extent depending on the number of substituents, their nature, and relative positions on the ring. The resultant two electronic states have two different ionization energies. Orgel<sup>3</sup> has treated this problem theoretically by a first-order perturbation calculation and obtains the following expression for the energy difference between the ionization potential,  $I_B$ , of benzene itself and the two ionization potentials,  $I_1$  and  $I_{11}$ , of the substituted molecule.

$$I_{1,11} = I_B - n\gamma_S - p_{1,11}\epsilon_S \quad (1)$$

Here  $n$  = the number of substituents  $S$  on the ring;  $\epsilon_S$  and  $\gamma_S$  are parameters arising from perturbation by  $S$  and depend on the nature of the substituent;  $\epsilon_S$  relates to the total interaction of  $S$  with the  $\pi$ -electron system of the ring, while  $\gamma_S$  describes the interaction of  $S$  with the  $\sigma$ -system of the ring;  $p_{1,11}$  are constants depending on both  $n$  and the relative positions of the

substituents; their values were calculated by Orgel.<sup>3</sup> It is well known that the energy of a charge-transfer absorption process may be expressed as<sup>9</sup>

$$h\nu_{CT} = I_D^\nu - (E_A^\nu + G_1 + G_0) + X_1 - X_0 \quad (2)$$

where  $I_D^\nu$  is the vertical donor ionization potential;  $E_A^\nu$  is the vertical electron affinity of the acceptor;  $G_0$  is the sum of several no-bond ground-state terms, such as polarization interactions, dispersion forces, etc.;  $G_1$  is the sum of several dative-state terms, including the large Coulomb interaction,  $e^2/r_{AD}$ , at the equilibrium distance  $r_{AD}$  of the complex in the excited state, the small valence term of the dative bond between  $D^+A^-$  and various correction terms;  $X_0$ ,  $X_1$  are the resonance energies between no-bond and dative structures in the ground and excited states of the complex, respectively. For most  $\pi$ - $\pi$  complexes the donor ionization potential  $I_D$  is by far the largest quantity in eq. 2. Therefore, making the very simplest assumption, that  $I_D$  is the only variable in c.-t. complexes formed from different donors but the same acceptor, eq. 1 and 2 may be combined to give (for substituted benzenes as donors)

$$h\nu_{1,11} \simeq I_{1,11} = I_B - n\gamma_S - p_{1,11}\epsilon_S \quad (3)$$

This equation together with the calculated values of  $p_1$  and  $p_{11}$  lead to the following expectations: (i) Two charge-transfer bands will result for all substitutions where  $p_1 \neq p_{11}$ ; for  $p_1 = p_{11}$ , only one band should be observed. (ii) When  $p_{1,11} = 0$ , the charge-transfer energy should be fairly close to that of the benzene complex, since usually  $\gamma_S$  turns out to be rather small compared to  $\epsilon_S$ . (iii) The band separation

$$h\nu_{1,11} \simeq I_{11} - I_1 = \Delta p_{1,11}\epsilon_S$$

should be largest for *para*-disubstituted and symmetrically tetrasubstituted donors. (iv) The amount of splitting relative to the benzene level

$$h\nu_{1,11} - h\nu_{\text{benzene}} \simeq I_{1,11} - I_B = -n\gamma_S - p_{1,11}\epsilon_S$$

since it depends on the magnitude of the interaction parameter,  $\epsilon_S$ , should increase with increasing donor property of substituent:  $H < CH_3 < OH < OCH_3 < NH_2 < NHCH_3 < N(CH_3)_2$ . The value of  $p_{1,11}$  is independent of the nature of the substituents but reflects their number and relative positions. The parameter  $\gamma_S$  relates to substituent-ring-carbon interaction *via* the  $\sigma$ -electron system and relative magnitudes

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- (2) (a) N. Smith, Ph.D. Dissertation, The University of Chicago, 1954;
- (b) A. Bier, Ph.D. Dissertation, Amsterdam, Holland, 1954.
- (3) L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955).
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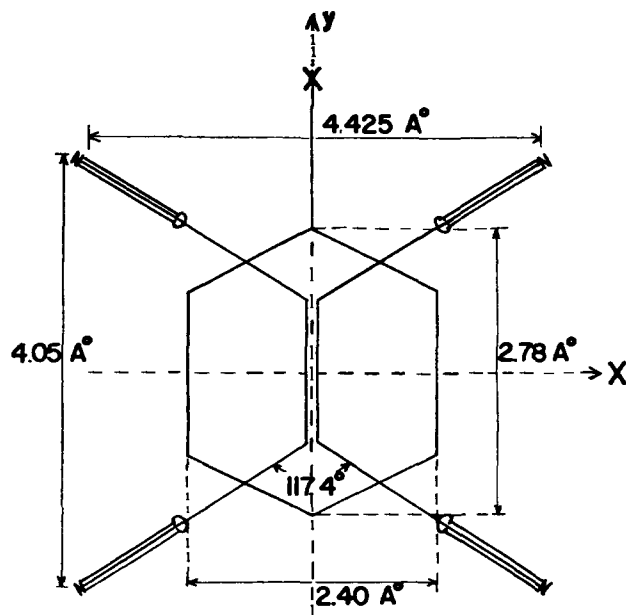


Fig. 1.—Model  $R_y$  of a TCNE-monomonstituted (X) benzene c.-t. complex.

for it may be estimated roughly by comparison of the "inductive strengths" of substituent groups, e.g.,  $F > Cl > Br > I$ .

If there are several, mutually independent substituents on the ring, Orgel's expression (2) may be expanded to give

$$I_{1,11} = I_B - \sum_i n_i \gamma_{Si} - p_{1,11} \epsilon_S \quad (4)$$

where the second term sums over the  $i$  substituents and  $\bar{\epsilon}_S$  in the last term is a weighted average of the  $\epsilon_S$  for the different substituents. For the charge-transfer energies arising from benzene donors with mixed substituents, the ionization potentials of eq. 4 give an expression analogous to that found for  $n$  equal substituents in eq. 3.

$$h\nu \approx I_{1,11} = I_B - \sum_i n_i \gamma_{Si} - p_{1,11} \epsilon_S \quad (5)$$

Furthermore, the two charge-transfer bands deriving thus from ionization of the transferred electron from the two uppermost levels of a substituted benzene donor are associated with two isomeric complex configurations, according to theory.<sup>3,10</sup>

The two donor orbitals differ in the position of their nodal planes. While both these planes pass through the center of the ring and lie perpendicular to the molecular plane, the symmetric orbital has a transverse nodal plane (*i.e.*, cutting across two opposite C-C bonds of the ring) and the antisymmetric orbital has a longitudinal nodal plane which passes through the 1,4-C atoms. In donors with electron-releasing substituents the symmetric orbital which encompasses the substituent(s) is expected to have the lower ionization potential.

As regards the acceptor, it is assumed here that the transferred electron will always go into the same lowest empty acceptor orbital, *i.e.*, excited anion acceptor states are neglected. This appears a reasonable assumption for tetracyanoethylene (TCNE), where Pen-

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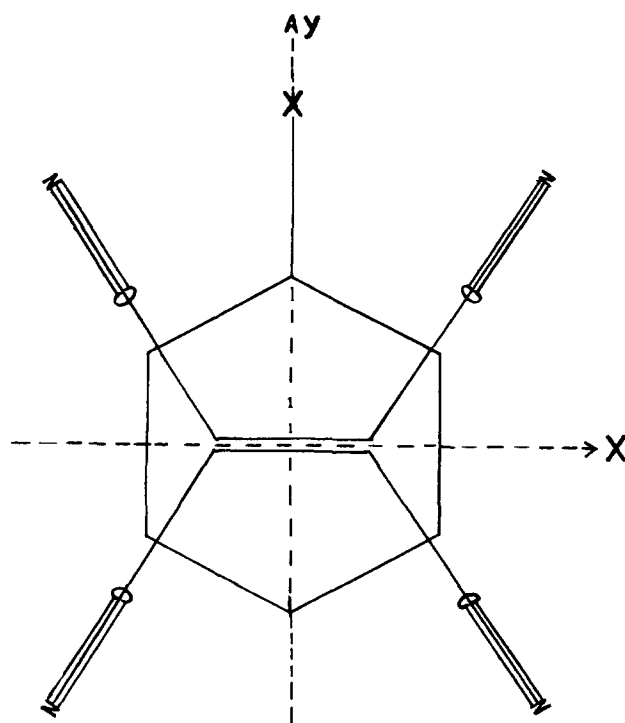


Fig. 2.—Model  $R_x$  of a TCNE-monomonstituted (X) benzene c.-t. complex.

fold and Lipscomb<sup>11</sup> calculated an energy difference of 2.07 e.v. between the lowest and second lowest empty MO's. Also, they found that the first unoccupied orbital is but slightly antibonding and has  $b_{2g}$  symmetry (in  $D_{2h}$ ).

For stable  $\pi$ - $\pi$  complexes the most stable configurations have been shown to be those where donor and acceptor lie above each other with their molecular planes more or less parallel.<sup>10,12-14</sup> Thus we expect at most an over-all  $C_n$ -type complex symmetry. Considering then the symmetries of donor and acceptor orbitals in  $C_n$  for TCNE-substituted benzene complexes and applying Mulliken's maximum overlap condition,<sup>10</sup> two most favorable complex configurations are obtained. They are depicted to scale in Fig. 1 and 2, in which the molecular dimensions of TCNE were taken from Bekoe and Trueblood,<sup>15</sup> those for benzene from Mulliken<sup>16</sup> (except for X, since the distance C-X varies with X). Model  $R_y$  (Fig. 1) involves the symmetric donor orbital and model  $R_x$  (Fig. 2) the antisymmetric orbital.

Although Fig. 1 and 2 show two definite molecular configurations, we must emphasize that these are not the only configurations allowed, nor will they be expected as sole contributors to the c.-t. bands, especially at room temperature and in solution. Mutual rotation of the two components and displacements from the center of the complex either along the  $x$  or  $y$  axis or obliquely may contribute substantially to the c.-t. absorptions.<sup>17</sup> For particularly large and/or strongly polar substituents a tilting away of the two planes from each other will also be expected.

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TABLE I  
 CHARGE-TRANSFER SPECTRA OF METHOXYBENZENE-TCNE COMPLEXES<sup>a</sup>

Donor	Acceptor: TCNE							
	Transition I <sup>c</sup>		Transition II <sup>c</sup>		$q_1^d$	Separation from benzene		Separation II-I $\Delta\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>
	$\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}_{1/2}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}_{1/2}$ , 10 <sup>3</sup> cm. <sup>-1</sup>		$\Delta\bar{\nu}(\text{Benz-I})$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}(\text{Benz-II})$ , 10 <sup>3</sup> cm. <sup>-1</sup>	
Benzene (reference)	25.8 ± 0.1	5.8	...	...	...	...	...	...
Anisole, obsd.	19.6 ± 0.1	...	25.8 ± 0.1	...	0.83	...	...	...
Analyzed	19.6 ± 0.1	5.0	26.1 ± 0.15	5.5	0.77	6.2 ± 0.2	-0.3 ± 0.25	6.5 ± 0.25
<i>o</i> -Dimethoxybenzene, obsd.	16.9 ± 0.1	...	23.2	...	0.58	...	...	...
Analyzed	16.9 ± 0.1	5.3	23.3 ± 0.2	5.8	0.5	8.9 ± 0.2	2.5 ± 0.3	6.4 ± 0.3
<i>m</i> -Dimethoxybenzene, obsd.	18.35	...	20.8	...	0.86	...	...	...
Analyzed	17.9 ± 0.4	5.2	22.7 ± 0.5	5.8	0.51	7.9 ± 0.5	3.1 ± 0.6	4.8 ± 1.1
<i>p</i> -Dimethoxybenzene	15.7 ± 0.05	5.9	26.3 ± 0.1	6.0	0.56	10.1 ± 0.15	0.5 ± 0.2	10.6 ± 0.15
1,2,3-Trimethoxybenzene	19.4 ± 0.15	6.3	...	...	...	6.4 ± 0.25	...	...
1,3,5-Trimethoxybenzene <sup>b</sup>	18.1	...	...	...	...	7.7	...	...
1,2,4-Trimethoxybenzene, obsd.	14.6	...	22.7	...	0.33	...	...	...
Analyzed	14.6 ± 0.1	6.1	23.4 ± 0.4	5.7	0.27	11.2 ± 0.2	2.4 ± 0.5	8.8 ± 0.5
1,2,4,5-Tetramethoxybenzene <sup>b</sup>	12.5	...	22.7	...	...	13.3	3.1	10.2

<sup>a</sup> Solvent: CH<sub>2</sub>Cl<sub>2</sub>; 22°. <sup>b</sup> C-t. energies from ref. 8. <sup>c</sup>  $\Delta\bar{\nu}_{1/2}$  = width at half-maximum intensity of the absorption band. <sup>d</sup>  $q_1$  = ratio of optical densities of transition II to I: OD<sub>max II</sub>/OD<sub>max I</sub>.

Nevertheless, for charge-transfer complexes as strong as the TCNE-substituted benzenes,<sup>6</sup> and in which donor and acceptor have such favorable relative molecular sizes, as well as favorable symmetries of the two interacting MO's, such complex orientations will be preferred where  $\pi$ -overlap between the two components can occur over large molecular regions of like sign and if symmetry rules are obeyed.

Experimentally there is some evidence that such two isomeric complexes exist in solution.<sup>5,18</sup>

### Experimental

**Reagents.**—Tetracyanoethylene (Eastman Kodak, White Label) was recrystallized twice from chlorobenzene and twice sublimed. All donors used were obtained commercially and of best available grade. Solid donors were all recrystallized several times from either ether or 95% ethanol and subsequently dried under vacuum. Liquid donors, when available as spectrograde or B.D.H. Analar, were used directly; otherwise they were fractionated or redistilled under reduced pressure.

**Special Data.**—Thioanisole (K & K Lab., Inc.) was purified by vapor phase chromatography; 1,2,3-trimethoxybenzene (K & K Lab., Inc.), after four recrystallizations from 95% ethanol and subsequent drying under vacuum, gave a m.p. 47–48° (lit.<sup>19</sup> m.p. 47°); 1,2,4-trimethoxybenzene (Columbia Chemicals) was found quite impure; after repeated distillations at reduced pressure, a fraction of b.p. 129–130° (6 mm.) and  $n_D^{20}$  1.5339 was used (lit.<sup>20</sup> b.p. 242.5° and  $n_D^{20}$  1.5309); hexafluorobenzene (Pierce Chemical Co.) was found quite pure by vapor phase chromatography, b.p. 80.5–81°. The solvent used was dichloromethane (Eastman Spectrograde) for all measurements.

**Spectra.**—All spectra were taken on a Cary Model 14 spectrophotometer. A pair of tared, stoppered quartz cells of 1-cm. path length were used and the measurements made with the cell compartments thermostated at 22°. The complex component concentrations ( $\sim 10^{-4}$  to  $10^{-3}$  M TCNE and  $\sim 10^{-2}$  to  $10^{-1}$  M for the donors) were adjusted to give c.-t. bands of optical density  $\sim 0.4$ – $0.5$ . As a reference we used a donor-dichloromethane solution of the same concentration as that used for complex preparation. Under above conditions 1:1 molecular complexes are formed.<sup>6</sup>

The generally broad, overlapping charge-transfer bands were decomposed in the manner described in detail elsewhere.<sup>22</sup>

Complexes having single transitions only, quite generally belong to either of two classes: (a) proper, single c.-t. absorptions or (b) they represent the sum of two strongly overlapping

bands. TCNE complexes of the former class were always found to be asymmetric and they followed Briegleb's empirical half-widths relationship.<sup>23</sup> Complexes belonging to the second class, however, did not only have exceptionally large half-widths, they also deviated in their band shapes from those of class a.<sup>22</sup>

### Results and Discussion

Tables I, II, and III give the observed and analyzed c.-t. spectra of a number of substituted benzene complexes with TCNE.

That Orgel's general predictions are borne out is shown by the following observations (see points i to iv under Theory above).

(i) Without exception, a maximum of two c.-t. bands was observed in the region under study as expected if the multiplicity arises from the splitting of the doubly degenerate benzene level. Single bands were observed only if the substituents were of the kind expected to interact only weakly with the ring, or in cases where Orgel's parameters  $p_I$  and  $p_{II}$  were identical.

(ii) The second c.-t. band of some substituted benzene-TCNE complexes occurred at a position close to that of the benzene-TCNE complex itself. Such complexes had the following donor components—monosubstituted: anisole, thioanisole, styrene; disubstituted: *p*-dimethoxybenzene, *p*-methylanisole, *o*-chloroanisole, *o*-bromoanisole.

The two *o*-complexes in the above list are exceptional in that their second c.-t. bands lie close to that of the benzene complex only by accident, *i.e.*, due to the particular values of  $\epsilon_S$  and  $\gamma_S$  in these cases. Apart from these, the list contains only donors for which  $p_{II} = 0$ , the very condition that benzene orbital "II" is perturbed only by the small term involving  $\gamma_S$  (eq. 3).

(iii) The band separations,  $\Delta\bar{\nu}_{\max}(\text{II-I})$ , observed on varying the number and position of donor substituent groups (OMe, Cl, and Br, respectively) were: *para*-disubstituted donor  $>$  *ortho*- and *meta*-disubstituted donor  $\approx$  monosubstituted donor. Again, this agreed with what was predicted from the difference  $\Delta p(\text{II-I})$ : *para*-disubstituted  $>$  *ortho*- and *meta*-disubstituted = monosubstituted donor.

(iv) Charge-transfer shifts and band separations in complexes with mixed substituent donors were found

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TABLE II  
 CHARGE-TRANSFER SPECTRA OF HALOBENZENE-TCNE COMPLEXES<sup>a</sup>

Donor	Acceptor: TCNE					Separation from benzene		Separation 11-1 $\Delta\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>
	Transition I		Transition II		$\Delta\bar{\nu}$ (Benz-1), 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}$ (Benz-11), 10 <sup>3</sup> cm. <sup>-1</sup>		
	$\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}^{1/2}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}^{1/2}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$q_1$			
Benzene (reference)	25.8 ± 0.1	5.8	...	...	...	...	...	...
Chlorobenzene, obsd.	26.4 ± 0.1	7.9	...	...	...	...	...	...
Analyzed	24.9 ± 0.3	4.6	28.3 ± 0.4	5.4	0.9	0.9 ± 0.4	-2.5 ± 0.5	3.4 ± 0.7
Bromobenzene, obsd.	25.4 ± 0.2	8.2	...	...	...	...	...	...
Analyzed	24.6 ± 0.2	4.8	28.2 ± 0.3	5.9	0.8	1.2 ± 0.3	-2.4 ± 0.4	3.6 ± 0.5
<i>p</i> -Dibromobenzene, obsd.	23.8 ± 0.1	...	29.7 ± 0.2	...	0.99	...	...	...
Analyzed	23.8 ± 0.1	5.4	29.5 ± 0.2	6.0	0.93	2.1 ± 0.2	3.7 ± 0.3	5.8 ± 0.3
<i>o</i> -Dichlorobenzene, obsd.	26.8 ± 0.1	7.9	...	...	...	...	...	...
Analyzed	25.0 ± 0.3	4.7	28.7 ± 0.4	5.4	0.8	0.8 ± 0.3	-2.9 ± 0.5	3.7 ± 0.7
<i>m</i> -Dichlorobenzene, obsd.	27.6 ± 0.1	7.8	...	...	...	...	...	...
Analyzed	25.4 ± 0.4	4.6	28.6 ± 0.6	5.4	0.9	0.4 ± 0.4	-2.8 ± 0.7	3.2 ± 1.0
<i>p</i> -Dichlorobenzene, obsd.	24.9 ± 0.1	...	29.8 ± 0.2	...	0.9	...	...	...
Analyzed	24.5 ± 0.1	5.4	29.7 ± 0.2	6.0	0.87	1.4 ± 0.2	-3.9 ± 0.3	5.3 ± 0.3
1,3,5-Trichlorobenzene	28.1 ± 0.1	6.5	...	...	...	-2.3 ± 0.2	...	...
<i>p</i> -Difluorobenzene, obsd.	25.6	...	28.9	...	1.1	...	...	...
Analyzed	25.4 ± 0.3	4.8	29.8 ± 0.4	4.5	0.85	0.4 ± 0.4	-4.0 ± 0.5	4.4 ± 0.7
Hexafluorobenzene	30.6 ± 0.2	4.5	...	...	...	-4.8 ± 0.3	...	...
Iodobenzene, obsd.	22.4 ± 0.1	...	28.1 ± 0.2	...	1.0	...	...	...
Analyzed	22.3 ± 0.1	4.6	27.8 ± 0.3	5.9	1.0	3.5 ± 0.2	-2.0 ± 0.4	5.5 ± 0.4
<i>p</i> -Diiodobenzene, obsd.	21.7 ± 0.2	...	28.2 ± 0.3	...	0.95	...	...	...
Analyzed	21.7 ± 0.2	5.5	29.0 ± 0.5	6.0	0.9	4.1 ± 0.3	-3.2 ± 0.6	7.3 ± 0.7

<sup>a</sup> Solvent: CH<sub>2</sub>Cl<sub>2</sub>; 22°.

 TABLE III  
 CHARGE-TRANSFER SPECTRA OF TCNE WITH BENZENE DONORS WITH MIXED SUBSTITUENTS<sup>a</sup>

Donor	Acceptor: TCNE					Separation from benzene		Separation 11-1 $\Delta\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>
	Transition I		Transition II		$\Delta\bar{\nu}$ (Benz-1), 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}$ (Benz-11), 10 <sup>3</sup> cm. <sup>-1</sup>		
	$\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}^{1/2}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\bar{\nu}_{\max}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$\Delta\bar{\nu}^{1/2}$ , 10 <sup>3</sup> cm. <sup>-1</sup>	$q_1$			
Benzene (reference)	25.8 ± 0.1	5.8	...	...	...	...	...	...
<i>p</i> -Methylanisole	17.8 ± 0.1	4.8	25.3 ± 0.1	5.5	0.7	8.0 ± 0.2	0.5 ± 0.2	7.5 ± 0.2
<i>m</i> -Methylanisole, obsd.	18.8 ± 0.1	...	23.4 ± 0.1	...	0.8	...	...	...
Analyzed	18.8 ± 0.1	4.6	24.0 ± 0.3	5.5	0.8	7.0 ± 0.2	1.8 ± 0.4	5.2 ± 0.4
<i>o</i> -Methylanisole, obsd.	18.3 ± 0.1	...	23.8 ± 0.1	...	0.8	...	...	...
Analyzed	18.3 ± 0.1	4.7	23.9 ± 0.2	5.4	0.8	7.5 ± 0.2	1.9 ± 0.3	5.6 ± 0.3
<i>p</i> -Chloroanisole	19.5 ± 0.1	5.7	28.1 ± 0.15	5.9	0.65	6.3 ± 0.2	-2.3 ± 0.25	8.6 ± 0.25
<i>o</i> -Chloroanisole, obsd.	20.3 ± 0.1	...	25.4 ± 0.1	...	0.96	...	...	...
Analyzed	20.1 ± 0.2	4.8	25.7 ± 0.3	5.7	0.9	5.7 ± 0.3	0.1 ± 0.4	5.6 ± 0.5
<i>p</i> -Bromoanisole	19.3 ± 0.1	5.7	27.9 ± 0.15	6.0	0.65	6.5 ± 0.2	-2.1 ± 0.25	8.6 ± 0.25
<i>o</i> -Bromoanisole, obsd.	20.1 ± 0.1	...	24.0 ± 0.1	...	1.0	...	...	...
Analyzed	19.7 ± 0.2	4.8	25.4 ± 0.2	5.6	0.9	6.1 ± 0.3	0.4 ± 0.3	5.7 ± 0.4
<i>p</i> -Fluoroanisole	19.9 ± 0.1	5.8	28.4 ± 0.2	6.0	0.7	6.1 ± 0.2	-2.6 ± 0.3	8.5 ± 0.3
<i>p</i> -Phenylnisole, analyzed	16.6 ± 0.2	5.3	26.8 ± 0.3	6.7	1.8	9.2 ± 0.3	-1.0 ± 0.4	10.2 ± 0.5
<i>o</i> -Phenylnisole, analyzed	18.2 ± 0.2	4.8	24.2 ± 0.4	6.0	1.0	7.2 ± 0.3	1.2 ± 0.5	6.0 ± 0.6
Phenetole, obsd.	19.3 ± 0.1	...	25.6 ± 0.1	...	0.8	...	...	...
Analyzed	19.3 ± 0.1	5.4	26.0 ± 0.15	5.7	0.76	6.5 ± 0.2	-0.2 ± 0.25	6.7 ± 0.25
Thioanisole, obsd.	17.5 ± 0.1	...	26.5 ± 0.1	...	0.3	...	...	...
Analyzed	17.5 ± 0.1	4.6	26.0 ± 0.2	5.1	0.26	8.3 ± 0.2	0.2 ± 0.3	8.5 ± 0.3
Styrene, obsd.	20.7 ± 0.1	...	25.2 ± 0.1	...	0.8	...	...	...
Analyzed	20.8 ± 0.2	4.9	25.9 ± 0.4	5.0	0.8	5.0 ± 0.3	-0.1 ± 0.5	5.1 ± 0.6
<i>p</i> -Chlorotoluene, analyzed	22.3 ± 0.4	4.7	27.1 ± 0.4	5.4	0.8	3.5 ± 0.5	-1.3 ± 0.5	4.8 ± 0.8
<i>o</i> -Chlorotoluene, obsd.	24.7 ± 0.2	7.1	...	...	...	...	...	...
<i>p</i> -Bromotoluene, analyzed	21.8 ± 0.3	4.6	26.6 ± 0.4	5.4	0.8	4.0 ± 0.4	-0.8 ± 0.5	4.8 ± 0.7
<i>o</i> -Bromotoluene, obsd.	24.3 ± 0.2	7.9	...	...	...	...	...	...
1,2,3-Trimethylbenzene	21.4 ± 0.1	5.3	...	...	...	4.4 ± 0.2	...	...
1,3,5-Trimethylbenzene	...	...	...	...	...	...	...	...
<i>p</i> -Iodoanisole	18.5 ± 0.1	5.2	27.7 ± 0.5	6.0	1.0	7.3 ± 0.2	-1.9 ± 0.6	9.2 ± 0.6
<i>p</i> -Iodotoluene	20.6 ± 0.1	4.6	27.0 ± 0.2	5.6	0.88	5.2 ± 0.2	-1.2 ± 0.3	6.4 ± 0.3

<sup>a</sup> Solvent: CH<sub>2</sub>Cl<sub>2</sub>; 22°.

to be additive in the manner described by eq. 5, with certain limitations.

The data leave no doubt that Orgel's theoretical treatment reproduces most of the essential features of the charge-transfer spectra of substituted benzenes with TCNE. It remains to be determined to what ex-

tent they do so in detail and whether the results obtained with TCNE are in agreement with data for other acceptors, insofar as such data exist.

The Parameters  $\epsilon_S$  and  $\gamma_S$ .—Table IV gives the substituent parameters  $\epsilon_S$  and  $\gamma_S$  calculated with eq. 3 from the data in Tables I, II, and III. It is seen

TABLE IV  
 PARAMETERS  $\epsilon_S$  AND  $\gamma_S$  FROM THE CHARGE-TRANSFER SPECTRA OF SUBSTITUTED BENZENE DONORS WITH TCNE

Complexes	$n$	$\Delta p$	$\epsilon_S$ , $10^4 \text{ cm.}^{-1}$	$\gamma_S$ , $10^4 \text{ cm.}^{-1}$	$\epsilon_S^*$ , $10^4 \text{ cm.}^{-1}$	$\gamma_S^*$ , $10^4 \text{ cm.}^{-1}$
(a) Methoxybenzene-TCNE						
Anisole	1	1	$6.5 \pm 0.25$	$-0.3 \pm 0.2$	$7.8 \pm 0.3$	$-0.35 \pm 0.25$
<i>o</i> -Dimethoxybenzene	2	1	$6.4 \pm 0.3$	$-0.4 \pm 0.2$	$7.7 \pm 0.35$	$-0.5 \pm 0.25$
<i>m</i> -Dimethoxybenzene	2	1	$4.8 \pm 1.1$	$-0.4 \pm 0.3$	$5.8 \pm 1.3$	$-0.5 \pm 0.3$
<i>p</i> -Dimethoxybenzene	2	2	$5.3 \pm 0.1$	$-0.25 \pm 0.1$	$6.4 \pm 0.1$	$-0.3 \pm 0.15$
1,2,4-Trimethoxybenzene	3	1.74	$5.1 \pm 0.3$	$-0.3 \pm 0.2$	$6.1 \pm 0.35$	$-0.35 \pm 0.25$
1,3,5-Trimethoxybenzene <sup>a</sup>	3	0	5.9	-0.4	7.1	-0.5
1,2,4,5-Tetramethoxybenzene <sup>a</sup>	4	2	5.1	-0.5	6.1	-0.6
(b) Halogenbenzene-TCNE						
Chlorobenzene	1	1	$3.4 \pm 0.7$	$-2.5 \pm 0.5$	$4.2 \pm 0.85$	$-3.0 \pm 0.6$
<i>o</i> -Dichlorobenzene	2	1	$3.7 \pm 0.7$	$-2.4 \pm 0.6$	$4.4 \pm 0.85$	$-2.9 \pm 0.7$
<i>m</i> -Dichlorobenzene	2	1	$3.2 \pm 1.0$	$-2.2 \pm 0.9$	$3.9 \pm 1.2$	$-2.6 \pm 1.0$
<i>p</i> -Dichlorobenzene	2	2	$2.7 \pm 0.15$	$-1.9 \pm 0.25$	$3.3 \pm 0.2$	$-2.3 \pm 0.3$
Bromobenzene	1	1	$3.6 \pm 0.5$	$-2.4 \pm 0.4$	$4.5 \pm 0.6$	$-2.9 \pm 0.5$
<i>p</i> -Dibromobenzene	2	2	$2.9 \pm 0.15$	$-1.8 \pm 0.15$	$3.5 \pm 0.2$	$-2.1 \pm 0.2$
Iodobenzene	1	1	$5.6 \pm 0.4$	$-2.1 \pm 0.4$	$6.7 \pm 0.5$	$-2.8 \pm 0.5$
<i>p</i> -Diiodobenzene	2	2	$3.7 \pm 0.35$	$-1.6 \pm 0.3$	$4.5 \pm 0.4$	$-1.9 \pm 0.4$
<i>p</i> -Difluorobenzene	2	2	$2.2 \pm 0.35$	$-2.0 \pm 0.25$	$2.7 \pm 0.4$	$-2.4 \pm 0.3$
Hexafluorobenzene	6	0	3.1	-2.7	3.7	-3.2
(c) Methylbenzene-TCNE <sup>b</sup>						
Toluene	1	1	$1.9 \pm 0.4$	$+0.6 \pm 0.4$	$2.3 \pm 0.5$	$+0.75 \pm 0.5$
<i>p</i> -Xylene	2	2	$1.7 \pm 0.3$	$+0.4 \pm 0.3$	$2.0 \pm 0.35$	$+0.5 \pm 0.35$
1,2,3-Trimethylbenzene } 1,3,5-Trimethylbenzene }	3	0	1.9	+0.5	2.3	+0.6
Hexamethylbenzene	6	0	1.5	+0.5	1.8	+0.6

<sup>a</sup> Data calculated from ref. 8. The 1,2,3-trimethoxy donor (Table I) was omitted from this list, since its high c.-t. energy is very likely due to steric interaction between the methoxy groups in the donor.<sup>8</sup> <sup>b</sup> The  $\epsilon_S$  and  $\gamma_S$  values for the methyl substituent were obtained by an approximate analysis of their composite bands.<sup>22</sup>

directly that neither parameter is constant within a series of related donors. As  $n$  and  $p_{11} - p_1$  increase,  $\epsilon_S$  and  $\gamma_S$  show a tendency to decrease, the decrease being dependent upon the nature of the substituent. One finds empirically that the parameters  $\epsilon_S$  and  $\gamma_S$  for *para*-disubstitution are reduced from the value for the monosubstituted compounds by the factors shown in Table V.

 TABLE V  
 VARIATION OF  $\epsilon_S$  AND  $\gamma_S$  ON COMPARISON OF MONO- AND  
*para*-DISUBSTITUTED DONORS

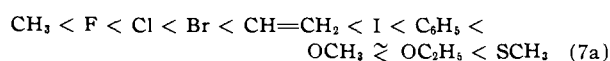
Substituent	$\frac{(\epsilon_S)_{p-d}}{(\epsilon_S)_{mono}}$	$\frac{(\gamma_S)_{p-d}}{(\gamma_S)_{mono}}$
Methoxy	0.8	0.7
Chloro	0.8	0.8
Bromo	0.8	0.75
Iodo	0.66	0.76
Methyl	0.85	0.7

Generally, one may write

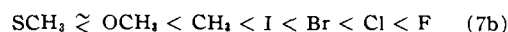
$$\epsilon_S, \gamma_S = f_S(p, n) \quad (6)$$

However, there are insufficient data to decide how  $\epsilon_S$  and  $\gamma_S$  behave for values of  $n > 3$ .  $p_{11} - p_1$  does not increase beyond the value 2 for the *para* case. The factors in Table V were found useful for the prediction of charge-transfer energies of mixed substituted benzene donors from  $\epsilon_S$  and  $\gamma_S$  values obtained for the "pure" series in Table IV. Alternatively, approximate values of  $\epsilon_S$  and  $\gamma_S$  for any substituent may be obtained by measuring the c.-t. energy and band separation of a suitable *para* isomer selected from the series listed in Table IV and calculating the  $\epsilon_S$  and  $\gamma_S$  from eq. 4 together with the factors of Table V. When the magnitude and sign of the parameters for the various substituent groups are considered, the follow-

ing trends are established: (i)  $\epsilon_S > \gamma_S$  in all cases; (ii)  $\epsilon_S$  was always found positive for all substituent groups studied and increased in the order



(iii)  $\gamma_S$  was found positive or negative; positive only for  $\text{CH}_3$  as substituent; negative for all the other substituent groups studied here.  $\gamma_S$  increases in magnitude as



Perturbation theory as applied by Orgel in the derivation of eq. 1<sup>3</sup> provides the following interpretations for the above observations:

(i) The perturbation *via* the  $\sigma$ -electron system of the benzene ring by the substituent is in all cases greater than the perturbation *via* the  $\pi$ -electron system.

(ii) The energy separation of c.-t. bands I and II for varying substituents occupying the same positions on the ring can be related to the perturbation of the  $\pi$ -electron system of the benzene cation by substituent groups. The order of substituent interaction in sequence 7a derives from the fact that  $\epsilon_S$  is a "mixed" parameter, including electrostatic and resonance interaction of substituent with the  $\pi$ -electron system.

It is evident that the substituent interaction described by  $\epsilon_S$  follows largely the ionization potential order of the substituted donor (excepting  $\text{CH}_3$  and  $\text{CH}=\text{CH}_2$ ). In particular, the halogens show an order of interaction reversed to that observed from reactivities of substituted aromatics,<sup>24</sup> or from equilibrium constants of c.-t. complexes between iodine and halogen substituted thioanisoles.<sup>25</sup> This is probably due to the

(24) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(25) J. Van Der Veen and W. Stevens, *Rec. trav. chim.*, **82**, 287 (1963).

fact that donor interactions as obtained from c.-t. energies relate predominantly to the donor radical cations. In that case one expects that (a) any electron-releasing mechanism is enhanced over that in the corresponding neutral donor molecule and (b) the d-acceptor orbital interaction of the halogens<sup>26</sup> is strongly suppressed in the cations. Consequently, the parameters  $\epsilon_S$  reflect the net electron release to the  $\pi$ -system of the donor cation as the sum of halogen-carbon ( $p$ - $p$ ) overlap and halogen inductive interaction. In contrast, the data on iodine-halogen-substituted thioanisole complexes cited above involve  $n$   $\sigma$ -complexes.<sup>25</sup> In this case electron transfer is from the nonbonding sulfur orbital rather than the benzene  $\pi$ -orbital. Therefore, the halogen substituents do not interact directly with the cation as they do in this study, so that their different order of interaction is not surprising.

(iii) Perturbation of the  $\sigma$ -system by the substituent may be positive or negative. In agreement with all other experimental data on  $\sigma$ -interactions, only the methyl group among the substituents studied here shows a positive effect. Sequence 7b reflects the trend of  $\sigma$ -perturbation by substituents and is in the order that one might reasonably predict.

Thus far, c.-t. data are in surprisingly good qualitative agreement with theory. When the quantitative data are examined, however, the variations in  $\epsilon_S$  and  $\gamma_S$  throw doubt on the assumption that the interactions of the substituent with the ring are additive. A first-order perturbation treatment using Hückel MO's does not allow for the changes occurring in the parameters which describe substituent-ring interaction as the number of substituents on the ring is increased. It also neglects nonneighbor interactions and both these factors change the orbital ionization energies as calculated from eq. 3. Thus, it is not surprising to find that parameters  $\epsilon_S$  and  $\gamma_S$  vary with number, position, and nature of substituent.

However, it must also be remembered that both parameters were calculated using eq. 3 and 5 which carry the assumption that all c.-t. interactions are negligible as compared to the donor ionization potential differences. In order to see, therefore, whether the variations in the parameter derive predominantly from an inadequate approximation of the donor orbitals by theory or from neglect of c.-t. interactions in their calculation from the spectra, a comparison with data from other acceptors is desirable. The only such data reported and applicable to our study are those by Kuboyama<sup>7</sup> on some chloranil-methoxybenzene complexes.

Before a comparison between corresponding TCNE and chloranil complexes can be made, we must correct the  $\epsilon_S$  and  $\gamma_S$  values for c.-t. interactions, as far as such is possible. The author has shown elsewhere that the single, first c.-t. energies of the complexes of TCNE with substituted benzenes in the ionization potential range  $\sim 7.5$  to  $9.5$  e.v. are described fairly accurately by a linear relationship<sup>22</sup>

$$h\nu_{CT} = 0.83I_D - 4.42 \text{ e.v.} \quad (8)$$

where  $I_D$  is the ionization potential of the donor. Referring the ionization potentials now to that of benzene as in eq. 3, one obtains for TCNE

$$\Delta h\nu_{CT} = 0.83(I_D - I_{\text{benz}}) = -n\gamma_S - p\epsilon_S \quad (9)$$

Thus, dividing  $\Delta h\nu_{CT}$ , the c.-t. energy differences between the substituted benzene-TCNE and benzene-TCNE complexes, through by the factor 0.83 gives values of  $\epsilon_S$  and  $\gamma_S$  essentially independent of the c.-t. resonance interaction.<sup>27</sup> The parameters thus calculated are listed in Table IV as  $\epsilon_S^*$  and  $\gamma_S^*$ .

It should be noted that although eq. 9 relates to first ionization potentials, it was also used in calculating parameters from the second c.-t. bands. That is, we assumed that TCNE complexes involving ionization from the second highest filled orbitals in the substituted benzene donors have similar relative c.-t. resonance interactions as complexes involving the donor cation ground states. The implications of such an assumption will be commented on below.

To correct for the c.-t. resonance interactions in chloranil complexes we used

$$h\nu_{CT} = 0.87I_D - 4.27 \text{ e.v.} \quad (10)$$

Equation 10 was obtained in a manner analogous to (8), *i.e.*, by plotting single, first c.-t. energies of substituted benzene-chloranil complexes *vs.* donor photoionization potentials covering a range of  $\sim 7.8$  to  $9.3$  e.v. Together with eq. 3 we thus obtain for chloranil complexes

$$\Delta h\nu_{CT} = 0.87(I_D - I_{\text{ben}}) = -n\gamma_S - p\epsilon_S \quad (11)$$

The parameters  $\epsilon_S^*$  and  $\gamma_S^*$  as calculated from eq. 9 and 11 are shown in Table VI. It is seen that the parameter values thus obtained from the chloranil c.-t. spectra agree with those from TCNE spectra in magnitude within the limits of (our) experimental accuracy. This leads to the conclusion that the observed variability in the parameters is due mainly to an inadequate approximation of the donor orbital ionization energies by eq. 1.

On the other hand, Table VI also shows clearly that the sign of  $\gamma_{\text{methoxy}}$  as obtained from chloranil spectra is positive, but negative when derived from TCNE spectra.

Theoretically it is inconceivable that the parameter  $\gamma_S$  changes sign in different complexes. The  $\sigma$ -interaction of a substituent group with a given set of benzene orbitals will either be positive or negative, depending only on the nature of the substituent. The observation that  $\gamma_S$  as obtained from c.-t. energies of one donor with different acceptors and calculation by eq. 3 (or 9 and 11, respectively) may either be positive or negative means, therefore, that the quantity calculated from the c.-t. data does not correspond directly to the theoretical parameter  $\gamma_S$ .

The methoxy substituent group has a positive Taft  $\sigma_1$  parameter. By definition, its interaction with the benzene ring is then electron attracting relative to H as a substituent. Consequently, the  $\gamma_S$  term in eq. 3 is positive for methoxy-substituted benzenes. Specifically, for the case  $p_{11} = 0$ ,  $I_{11} - I_B > 0$ , and the second c.-t. band of a mono- or *para*-disubstituted methoxy complex is expected at higher frequency than the transition of the corresponding benzene complex.

This is not true for the anisole and *p*-dimethoxybenzene-chloranil complexes. Therefore, the approxima-

(26) J. R. Hoyland and L. Goodman, *J. Phys. Chem.*, **64**, 1816 (1960).

(27) The author wishes to thank a referee for raising this point.

TABLE VI  
COMPARISON OF CHLORANIL<sup>a</sup> AND TCNE-METHOXYBENZENE COMPLEXES

Donor	Acceptor					
	Chloranil			TCNE		
	$\Delta\nu$ (Benz-I), <sup>b</sup> 10 <sup>3</sup> cm. <sup>-1</sup>	Cor. by eq. 10	$\epsilon^*$ methoxy, 10 <sup>3</sup> cm. <sup>-1</sup>	$\gamma^*$ methoxy, 10 <sup>3</sup> cm. <sup>-1</sup>	$\epsilon^*$ methoxy, 10 <sup>3</sup> cm. <sup>-1</sup>	$\gamma^*$ methoxy, 10 <sup>3</sup> cm. <sup>-1</sup>
Anisole	7.3	8.4	7.9	0.5	7.8 ± 0.3	-0.35 ± 0.25
<i>o</i> -Dimethoxybenzene <sup>c</sup>	10.3	11.8	7.6	0.2	7.7 ± 0.35	-0.5 ± 0.25
<i>m</i> -Dimethoxybenzene <sup>d</sup>	10.2	11.7	5.0	0.7	5.8 ± 1.3	-0.5 ± 0.3
<i>p</i> -Dimethoxybenzene	11.3	13.0	6.3	0.25	6.1 ± 0.35	-0.3 ± 0.15
1,3,5-Trimethoxybenzene	9.1	10.5	6.0	(Value 0.5 used)	7.1	0.5

<sup>a</sup> See ref. 7. <sup>b</sup>  $\Delta\nu$  (Benz-I): separation of first c.-t. energy in methoxybenzene-chloranil complexes from the c.-t. energy of the benzene-chloranil complex. <sup>c</sup> Measured in this work: two c.-t. bands at 518 and  $\sim$ 386 m $\mu$  overlapping. <sup>d</sup> Two very strongly overlapping transitions and only approximate values used.

tions  $h\nu_{CT}(I,II) = aI_D(I,II)$  which were made in our calculation of  $\gamma_S^*$  are inaccurate, particularly for the one involving the second c.-t. band, and a more exact expression is required. The most complete description of  $h\nu_{CT}$  is given by eq. 2. Unfortunately, not enough data are available as yet to make use of this equation for a more precise, quantitative evaluation of our results.

Qualitatively, however, it is important to realize that simple approximations which described first c.-t. transitions quite accurately are insufficient for the description of second transitions. This is also evident from Hückel calculations on the molecular orbital energies of methoxybenzenes and subsequent comparison of their c.-t. energies with a number of acceptors.<sup>28</sup> A good linear correlation was found between the energies of the highest filled methoxybenzene orbitals with the first c.-t. energies of their complexes with all acceptors considered. With TCNE, they also compared the energies of the second highest filled donor MO's with the energies of the corresponding second c.-t. absorptions. In this case, no good linear correlation was obtained. Even though this correlation is improved when our analyzed c.-t. values (Table I) are used, the second c.-t. energies still do not fall on the same line with the first. Whether or not this is largely

(28) A. Zweig, J. E. Lehnson, and M. A. Murray, *J. Am. Chem. Soc.*, **85**, 3933 (1963).

the result of poor second MO energies, there can be little doubt that some of the irregularities derive from the c.-t. process.

If the complexes have structures similar to those shown in Fig. 1 and 2, then the configurations contributing primarily to the first c.-t. transitions are orthogonal to those contributing primarily to the second transitions. For benzene donor cations with electron-releasing substituents the ground state is expected to be antisymmetric for mono- and disubstituted isomers, while for tetra- and pentasubstituted isomers the symmetric orbital should be the lowest. Therefore, the first c.-t. band of the former derives principally from structures  $R_y$  (Fig. 1), that of the latter from structures  $R_x$  (Fig. 2). The opposite applies to configurations contributing to the second charge-transfer absorptions. Thus, a change in complex structure with increasing donor substitution is expected for each c.-t. band.

Apparently, this theoretically expected changeover in complex geometry does not show up in the experimental first c.-t. energies (at least of the methoxybenzenes). The second c.-t. energies cannot be correlated at present.

**Acknowledgments.**—This research was supported by the National Research Council of Canada. The writer also acknowledges with pleasure helpful discussions with Professor C. Reid.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

## The Mass and Microwave Spectra, Structures, and Dipole Moments of the Isomers of Sulfur Monofluoride<sup>1</sup>

BY ROBERT L. KUCZKOWSKI<sup>2</sup>

RECEIVED MARCH 17, 1964

Two isomers of  $S_2F_2$  were prepared by heating  $AgF$  and  $S$ . The relative mass spectral cracking patterns of both isomers are reported. For one isomer, microwave transitions for the  $S^{32}=S^{32}F_2$ ,  $S^{32}=S^{34}F_2$ , and  $S^{34}=S^{32}F_2$  species were obtained. The structure was determined to be pyramidal  $S=SF_2$  with  $d(SS) = 1.860 \pm 0.015$  Å.,  $d(SF) = 1.598 \pm 0.012$  Å.,  $\angle SSF = 107.5 \pm 1^\circ$ , and  $\angle FSF = 92.5 \pm 1^\circ$ . The dipole moment was  $1.03 \pm 0.03$  D. For the second isomer, microwave transitions for the  $FS^{32}S^{32}F$  and  $FS^{32}S^{34}F$  species were obtained. The structure was determined to be nonplanar chain  $FSSF$  with  $d(SS) = 1.888 \pm 0.01$  Å.,  $d(SF) = 1.635 \pm 0.01$  Å.,  $\angle FSS = 108.3 \pm 0.5^\circ$ , and the dihedral angle =  $87.9 \pm 1.5^\circ$ . The dipole moment was  $1.45 \pm 0.02$  D. A discussion of the observed structural parameters for both isomers is given.

### Introduction

The earlier reports in the literature concerning  $S_2F_2$  presented some conflicting data and gave rise to general

(1) This work was supported by a grant extended to Harvard University by the Office of Naval Research. Reproduction in whole or part is permitted for the U. S. Government.

(2) (a) Standard Oil of California Predoctoral Fellow 1963-1964; (b) National Bureau of Standards, Washington, D. C.

skepticism concerning this compound.<sup>3</sup> Because of an interest in this laboratory in the structure of some similar molecules, notably  $F_2O_2$ ,<sup>4</sup> we were prompted to re-investigate  $S_2F_2$  with the hope of unambiguously characterizing it as well as determining its structural param-

(3) See footnotes 2-9 in ref. 5 of this paper.

(4) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).