

The shortest intermolecular contacts are reported. The structure consists of hydrogen-bonded rows of molecules, the hydrogen bonds being formed between molecules related by a glide plane. The  $O(3)\cdots O(1)$  distance between hydrogen-bonded atoms (see Figure 4) is 2.6 Å; the distance between  $O(1)$  and the least-squares plane containing the  $C-C(=O)-O$  group of atoms (see the end of the previous paragraph) is 0.16 Å. The  $O(2)$  atom not involved in hydrogen bonding is characterized by a large thermal motion, as might be expected (see Table II). As observed in most molecular

crystals, the values of the thermal parameters reflect a significant increase of the thermal motion of the more peripheral atoms (*cf.* thermal factors of  $C(10)$  and  $O(2)$ ).

**Acknowledgment.** We wish to thank Professor M. Goodman for his constant interest in this work. We also gratefully acknowledge the support of research grants from the National Science Foundation (GB 7558) and the National Institutes of Health (GM 08974).

## Symmetry Classification and Selection Rules for Some Electron Donor–Acceptor Complexes

George R. Anderson

*Contribution from the Laboratory of Physical Chemistry, Groningen University, The Netherlands, and the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. Received December 9, 1969*

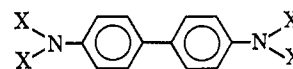
**Abstract:** The structure and electronic spectra of molecular complexes composed of  $\pi$ -electron donor (D) and acceptor (A) molecules are discussed. Based upon estimates of low-lying  $\pi$ -electron orbital symmetries, complex stabilization due to charge-transfer delocalization in the DA pair is allowed or can be ruled out for specific configurations of the complex. These results are tabulated for a number of D and A molecules possessing  $D_{2h}$  symmetry (Tables VI–IX). DA complexes for which structural data are known are all found to have correct symmetries for charge-transfer stabilization from the lowest lying  $D^+A^-$  electronic state. The spectra of DA complexes follow the selection rules given by group theory in the point group to which the complex belongs. There are seven different ways to arrange D and A molecules so that they share together at least one element of symmetry (Figure 1). From the representations of the charge-transfer states given in Tables VI–IX for the various D–A molecular configuration, one may easily predict which charge-transfer transitions are allowed and the axes of polarization. Previously known spectra are discussed. When polarization data are reported, assignments are discussed and some additional DA structural information is advanced for the solids. In the case of Amano, Kuroda, and Akamatu's recent findings, two (not one) charge-transfer bands are reported for several DA complex solids for which the axes of polarization are perpendicular relative to each other. Their interesting results can be explained on the basis of D and A molecular orbital symmetries and selection rules based on possible orientations of the complex.

The spectroscopic observations recently reported by Amano, Kuroda, and Akamatu<sup>1</sup> on the polarization of charge-transfer (CT) bands of some crystalline electron donor–acceptor complexes give cause for the following paper. Their spectra of a series of eight solids showed the presence of two low-lying CT bands in the frequency range below the first expected  $\pi \rightarrow \pi$  transition of either donor or acceptor molecules. Their account of the spectral positions and spacings of the two CT bands was sound and in line with previous observations made in solution.

The polarization axes of the first and second CT bands, however, were not always parallel relative to one another, and in four of the eight solids studied the first and second CT bands were perpendicular relative to one another. This result was discussed in the paper but not adequately resolved. In contrast to the analysis of Amano, Kuroda, and Akamatu, an alternative explanation of their spectra is presented here with a more general discussion of the symmetry of DA complexes and the possible selection rules that result from group theoretical considerations.

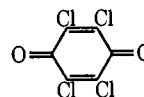
(1) T. Amano, H. Kuroda, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **42**, 671 (1969).

The anomalous polarization results were reported for the four DA complex solids composed of benzidine and  $N,N,N',N'$ -tetramethylbenzidine

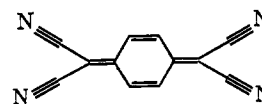


(X = Me or H)

and the two acceptor molecules, chloranil



and 7,7,8,8-tetracyanoquinodimethane (TCNQ).



All four molecules belong to the  $D_{2h}$  point group; the coordinate axis applied to each molecule has the  $z$  axis normal to the paper,  $y$  and  $x$  axes vertical and horizontal, respectively. Thin platelets of the complex were

grown from solution as small parallelograms, and the authors assign  $X$ - $Y$  axes to the crystals (not to be confused with the axes above) so as to be consistent with the spectroscopic results; the  $X$  axis was always chosen to be parallel to the first (lowest lying) CT band and the  $Y$  axis perpendicular to it. In three of the four crystals the  $X$  axis was also the "needle" axis or dimension of greatest elongation of the crystals. By noting the infrared band shifts for the neutral and ionic molecular D and A components, the authors further concluded from the infrared spectra of the DA complexes that the ground state was predominately nonionic; *i.e.*, DA rather than  $D^+A^-$ .

### Theory

The theory of charge-transfer spectra and the stabilization of DA complexes is based upon the general picture put forward by Mulliken in 1952.<sup>2</sup> Let the base states of the complex be given by

$|D \cdots A\rangle$  = no-bond wave function  
 $|D^+A^- \rangle$  = lowest lying dative bond wave function  
 $|D^*A^- \rangle$  = a dative bond wave function originating from an excited molecular state of the donor ion radical,  $D^{*+}$

The description of the stationary states of the complex, therefore, is given by a linear combination of the base states

$$|\psi_i\rangle = a_i|D \cdots A\rangle + b_i|D^+A^- \rangle + c_i|D^*A^- \rangle + \dots \quad (1)$$

The mixing coefficients  $a_i$ ,  $b_i$ ,  $c_i$ , ... are matrix elements which tell how much of one base state is mixed into the ground and various excited states of the complex. The absolute value of the coefficients are chosen so that the stationary states are normalized, approximately.

$$|a_i|^2 + |b_i|^2 + |c_i|^2 + \dots = 1$$

The symmetry of the DA complex can now be used to simplify the problem as the Hamiltonian mixes only states of the same representation. Thus, certain of the  $a$ 's,  $b$ 's,  $c$ 's, ... are identically zero when one or more elements of symmetry are present in the DA complex. Spectroscopic selection rules for transitions between various states of the complex are taken directly from the character tables.

The usual notation for the ground stationary state of the complex is  $|\psi_N\rangle$ , and the first (observed) electronically excited state is  $|\psi_E\rangle$ . For the most part, both states may be expected to belong to the totally symmetric representation,  $\Gamma_1$ , of the point group to which the complex belongs. This follows from the fact that the no-bond base state,  $|D \cdots A\rangle$ , is almost always a  $\Gamma_1$  representation.

Experimentally, the states  $|\psi_N\rangle$  and  $|\psi_E\rangle$  are both found to contain the  $|D \cdots A\rangle$  base state so that their respective symmetries are fixed and the same. A CT transition  $\Gamma_1 \leftrightarrow \Gamma_1$  is always allowed by selection rules in the point groups available to D-A complexes. However, the transition dipole orientation may or may not be uniquely specified, depending upon the DA symmetry point group. Not until higher lying CT states are considered is group theory of significant value to spectroscopy.

(2) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

Selection rules are usually overlooked for DA complexes because structural information on the relative orientation of the molecular components generally has not been available. In the crystalline phase, however, accurate crystal structure determinations in the recent years have added valuable information to this area but much more is needed. The crystal structure of the four DA complexes of concern in this paper are all unknown. Thus conjecture must be used to fill in the gaps where data are missing.

### Crystal Structure and Symmetry of DA Complexes

From surveys of crystal structure determinations<sup>3</sup> and from recent published structural data of DA complexes (some of which contain the species benzidine, tetramethylbenzidine, chloranil, or TCNQ) given in Table I, one may derive several general rules to which most DA solids of this type are subject.<sup>4-12</sup>

**Table I.** Symmetry Characteristics of Certain Crystalline 1:1 DA Complexes

DA complex <sup>a</sup>	Space group	Site D	Group A	DA complex	Ref
TMPD-chloranil	C2/m	C <sub>2h</sub>	C <sub>2h</sub>	C <sub>2</sub> (C <sub>2v</sub> )	4
HMB-chloranil	P2 <sub>1</sub> /c	C <sub>i</sub>	C <sub>i</sub>	None	5
Anthracene-TCNQ	C2/m	C <sub>2h</sub>	C <sub>2h</sub>	C <sub>s</sub> (y) (C <sub>2v</sub> )	6
TMPD-TCNQ	C2/m	C <sub>2h</sub>	C <sub>2h</sub>	C <sub>s</sub> (y)	7
Bis(8-hydroxyquinolinato)copper(II)-TCNQ	P1	C <sub>i</sub>	C <sub>i</sub>	None	8
Benzidine-TNB				None (C <sub>2</sub> )	3
Naphthalene-TCNB	C2/m	C <sub>2h</sub> <sup>b</sup>	C <sub>2h</sub>	(C <sub>2</sub> )	9
Perylene-fluoranil	P2 <sub>1</sub> /n	C <sub>i</sub>	C <sub>i</sub>	(C <sub>s</sub> (x))	10
TMPD-TCNB	P1	C <sub>i</sub>	C <sub>i</sub>	None	11
Pyrene-TCNE	P2 <sub>1</sub> /a	C <sub>i</sub>	C <sub>i</sub>	None	12

<sup>a</sup>TMPD = N,N,N',N'-tetramethyl-*p*-phenylenediamine, HMB = hexamethylbenzene, TCNQ (see text), TNB = trinitrobenzene, TCNB = 1,2,4,5-tetracyanobenzene, TCNE = tetracyanoethylene.  
<sup>b</sup> Naphthalene orientation in the lattice is disordered.

(1) The D and A molecules are arranged in linear arrays or columns exhibiting large  $\pi$ -orbital overlap. The molecules alternate DADADA... along the columns with the "interplanar" separation between the D and A species often significantly less than the van der Waals contact distance (of 3.4 Å in graphite).

(2) The minimum contact distances between molecules of different columns is always large and never less than the sum of the van der Waals radii. There is no apparent  $\pi$  overlap between the columns.

(3) The majority of DA solids reported crystallize in a monoclinic system. Molecules of high symmetry (*i.e.*, D<sub>2h</sub>) often retain part of their molecular symmetry at their site in the lattice (such as C<sub>2h</sub> or C<sub>i</sub>, as shown in Table I). The general theory that centrosymmetric

- (3) (a) S. C. Wallwork, *J. Chem. Soc.*, 494 (1961); (b) J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem.*, **69**, 2153 (1965).  
 (4) J. L. de Boer and A. Vos, *Acta Crystallogr., Sect. B*, **24**, 720 (1968).  
 (5) T. T. Harding and S. C. Wallwork, *ibid.*, **8**, 787 (1955).  
 (6) R. M. Williams and S. C. Wallwork, *ibid.*, **24**, 168 (1968).  
 (7) A. W. Hanson, *ibid.*, **19**, 610 (1965).  
 (8) R. M. Williams and S. C. Wallwork, *ibid.*, **23**, 448 (1967).  
 (9) S. Kumakura, F. F. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Jap.*, **40**, 1826 (1967).  
 (10) A. W. Hanson, *Acta Crystallogr.*, **16**, 1147 (1963).  
 (11) Y. Ohaski, H. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Jap.*, **40**, 1789 (1967).  
 (12) I. Ikemoto and H. Kuroda, *Acta Crystallogr., Sect. B*, **24**, 383 (1968).

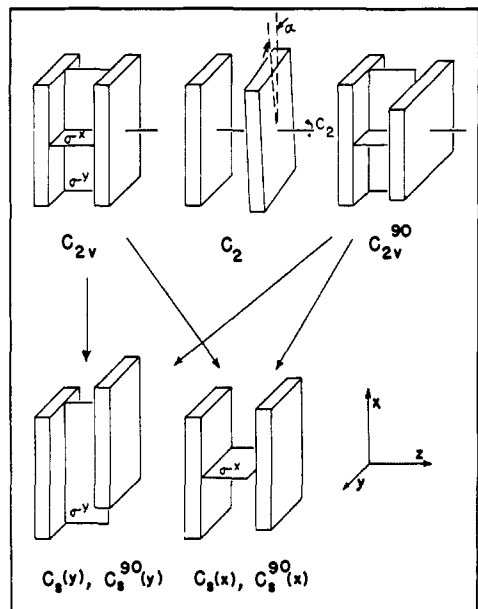


Figure 1. The seven DA complex structural configurations with one or more nontrivial symmetry elements ( $C_2$  or  $\sigma$ ). The D and A component molecules are assumed to have molecular symmetry of benzidine, chloranil, etc. ( $D_{2h}$ ). The notations,  $C_{2v}^{90}$  and  $C_s^{90}$ , are merely to denote the cases when the A molecule is rotated  $90^\circ$  about the  $z$  axis from its usual (or defined) coordinate axis; this notation does not imply a new point group.

molecules form centrosymmetric solids also holds for DA solids.

(4) Interactions between D and A molecules along the column are usually identical both "up" and "down" the DADADA... column; there is no preferential DA...DA...DA... alternation. This is usually a consequence of the symmetry of the lattice and the site symmetry of the molecule (e.g.,  $C_i$ ).

(5) Any particular DA pair along a DADADA... column may or may not share planes of symmetry or rotation axes; in Table I, five examples do possess DA symmetry elements in common and five examples do not. The highest possible symmetry a DA pair may exhibit is  $C_{2v}$  (when composed of  $D_{2h}$  molecular species). This situation is approximately, though not rigorously, realized for the two systems, TMPD-chloranil and anthracene-TCNQ. In Table I these entries are noted in parentheses.

(6) The factors which appear to effect the relative orientation of DA molecules in the lattice are not well understood, and CT stabilization appears to be a moderately weak force.<sup>13</sup> Packing considerations of the D and A molecules in the solid, accommodation of polar groups of the D and A molecules, London dispersion forces, and higher lying CT states are all thought to play a role in deciding how the molecules fit together in the lattice or in DA pairs in solution.

Thus CT interaction is only one of many types of interactions between DA molecules, but perhaps it is the most "visible" experimentally. The spectroscopy (including esr<sup>14</sup> and vibrational<sup>15</sup>) of the complex is affected, if not dominated, by the CT interaction.

(13) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron, Suppl.*, No. 7, 97 (1966).

(14) H. Hayashi, S. Iwata, and S. Nagakura, *J. Chem. Phys.*, 50, 993 (1969).

(15) H. B. Friedrich and W. B. Person, *ibid.*, 44, 2161 (1966).

Wave functions based upon known or plausible symmetry relations should be useful to the spectroscopist for band assignments and as a tool to uncover new data and offer new predictions.

For the present, we are going to overlook the translational lattice effect and the symmetric interaction of the D and A components in the DADADA... lattice. The correct description of the solid is based upon a set of crystalline wave functions, a matter which must be taken up separately. Instead, the solid is treated as one DA pair (or rather as a collection of isolated DA pairs) based upon established theory as developed by Mulliken,<sup>1</sup> Briegleb,<sup>16</sup> McGlynn and Boggus,<sup>17</sup> and others. The refinements from consideration of the entire lattice will not significantly alter predictions of polarizations of the CT bands in weak complexes.

### Symmetry-Based Wave Function

Next we would like to establish a method and nomenclature for estimating the symmetry representation of DA wave functions.

Serious attempts have been made in recent years to predict the structure of DA complexes by extended MO calculation which include configuration interaction (CI) of numerous CT states of the complex.<sup>17,18</sup> Within a chosen range of positions and relative orientations of the D and A molecules, DA complex structures were predicted from a minimum in the energy eigenvalue for the ground state. For reasons of economy, a finite number of structural choices was made over a rather wide latitude of variables of position and angles. The use of symmetry or symmetry-based wave functions does not appear from the literature to be applied in the discussion of the structure nor in the choice of structural variable. This may be a matter of preference on the part of the authors rather than oversight, since the computation should give the correct answer whether symmetry is invoked or not.

For symmetry considerations, we shall use the point group notations outlined in Figure 1 as it applies to relative orientations of D and A molecules. The D molecule we shall say is on the left with the coordinate frame fixed to it. The A molecule is on the right and is moved about in a plane mutually parallel to their molecular planes. We can assume the molecules both have  $D_{2h}$  symmetry, separately. The important fact is, however, that a general DA representation,  $\Gamma_i$ , correlates smoothly through all distortions of the complex and correlates with the representations of the  $D^*$  and  $A^*$  components in excited mutually charged states separated to infinity,  $\Gamma(D^*)$  and  $\Gamma(A^*)$ . That is

$$\Gamma_i(DA^*) = \Gamma(D^*)\Gamma(A^*) \quad (2)$$

where the direct product is taken in the point group of the DA complex (and not  $D_{2h}$ ). Since the point group of the complex is a subgroup of  $D_{2h}$  molecular symmetry, it is not difficult to determine the  $\Gamma(D^*)$  and  $\Gamma(A^*)$  if the molecular representations are known. In Figures 2 and 3, the specific correlation diagrams are

(16) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(17) S. P. McGlynn and J. D. Boggus, *J. Amer. Chem. Soc.*, 80, 5096 (1958).

(18) H. Kuroda, I. Ikemoto, and H. Akamatu, *Bull. Chem. Soc. Jap.*, 39, 1842 (1966).

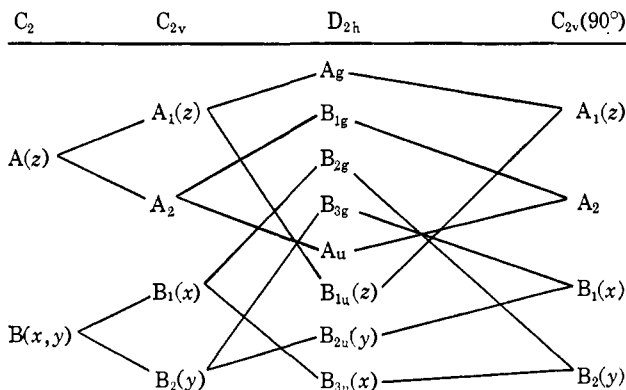


Figure 2. Correlation diagram for the molecular components of a DA complex with axial ( $C_2$  or  $C_{2v}$ ) symmetry; the donor and acceptor molecules are assumed to have  $D_{2h}$  symmetry. To find the representation under  $C_{2v}^{90^\circ}$  symmetry of an acceptor molecule, for instance, rotated  $90^\circ$  about the  $z$  axis, the  $C_{2v}(90^\circ)$  column is added on the right. See Figure 1.

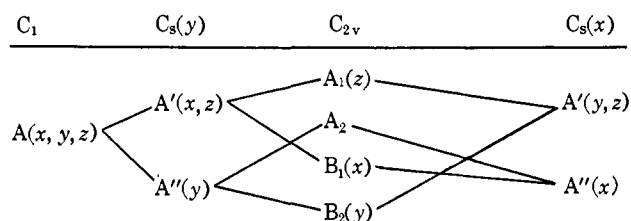


Figure 3. Correlation diagram for a DA complex with  $x/y$  shear-axis distortion from  $C_{2v}$  symmetry as shown in Figure 1. A shear displacement of  $A$  with respect to the  $D$  molecule along the  $x$  axis leaves the  $\sigma_y$  plane of symmetry operative and is denoted  $C_s(y)$ . Shear along the  $y$  axis similarly gives  $C_s(x)$ . Shear along an arbitrary axis in the  $xy$  plane produces the trivial point group,  $C_1$ , and leaves no symmetry restrictions on the wave functions nor transitions between them. This is the case for half (5) of the DA solids given in Table I.

given for the two types of distortions of the complex. The character tables for point groups  $D_{2h}$  and  $C_{2v}$  are given in Tables II and III.

Table II. The  $D_{2h}$  Character Table. The Three Reflection Planes ( $\sigma$ 's) Are Designated According to Their Respective Normal Axes

$D_{2h}$	E	$C_2^z$	$C_2^y$	$C_2^x$	$i$	$\sigma^z$	$\sigma^y$	$\sigma^x$
$A_g$	1	1	1	1	1	1	1	1
$B_{1g}$	1	-1	-1	1	1	-1	-1	1
$B_{2g}$	1	-1	1	-1	1	-1	1	-1
$B_{3g}$	1	1	-1	-1	1	1	-1	-1
$A_u$	1	1	1	1	-1	-1	-1	-1
$B_{1u}(z)$	1	-1	-1	1	-1	1	1	-1
$B_{2u}(y)$	1	-1	1	-1	-1	1	-1	1
$B_{3u}(x)$	1	1	-1	-1	-1	-1	1	1

Table III. The  $C_{2v}$  Character Table

$C_{2v}$	E	$C_2^z$	$\sigma^z$	$\sigma^y$
$A_1(z)$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1(x)$	1	-1	-1	1
$B_2(y)$	1	-1	1	-1

The representations of the various states of the  $D$  and  $A$  molecule (ions),  $\Gamma(D^*)$  and  $\Gamma(A^*)$ , may be estimated from MO theory and extended calculations

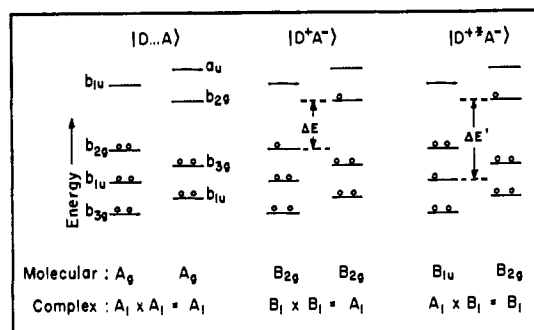


Figure 4. A molecular orbital picture of the nonbonding and two low-lying CT states of a DA complex possessing  $C_{2v}$  symmetry. The component  $D$  and  $A$  molecules are assumed to have  $D_{2h}$  symmetry. One-electron energy level diagrams (the vertical dimension) are usually very crude and the ordering of states according to symmetry of various ionic and molecular excited states cannot be relied upon.

on the individual species, or in a few cases can be learned (or verified) through indirect spectroscopic studies. The simplest answers are had from one-electron molecular orbital calculations of the individual molecules, but the simple MO approach can be often misleading. Even approximate energies of ionic and excited molecular states (such as  $D^+$ ,  $D^{*+}$ ,  $A^-$ ,  $A^{*-}$ , etc.) are often far off in energy. The ordering of the various excited electronic states is important if the problem is to converge and is more important if the basis set of available excited states is to be terminated after the first few. Nevertheless, it is instructive to see how far the simple-minded picture can be carried.

Figure 4 illustrates a type of Hückel MO approach<sup>19</sup> to the problem of specifying symmetry wave functions of the DA complex. Two hypothetical molecules form the complex of the type we have been discussing. Four MO's of the donor and four of the acceptor are shown in three simulated energy level diagrams. Ten electrons occupy the levels one or two at a time, and their configuration specifies the energy of the complex and symmetry of the wave function as shown. The no-bond state at the left is taken as the zero of energy. The two other diagrams to the right illustrate two different CT states of the complex higher in energy ( $\Delta E$ ) than the no-bond state. The symmetry representations of the ( $D_{2h}$ ) component molecules and the  $C_{2v}$  DA complex are derived as shown from the one-electron orbital symmetries (printed in lower case).

If one limits the basis set to the three wave functions listed in Figure 4, one may describe (perhaps) qualitatively the low-lying stationary states of the complex and predict its spectroscopic behavior. The functions  $|D...A\rangle$  and  $|D^+A^-\rangle$  mix as given in eq 1 as they are of the same symmetry,  $A_1$ .  $|D^+A^*\rangle$  corresponds to a  $B_1$  representation and is not mixed (in the simple picture) into any other states of the complex. Dipole transitions among all three states are allowed and have axis of polarization given by

$$A_1 \leftrightarrow A_1 \quad z \text{ axis}$$

$$A_1 \leftrightarrow B_1 \quad x \text{ axis}$$

In other words, the first and second CT bonds have axes of polarization perpendicular to one another.

(19) M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, **83**, 4560 (1961).

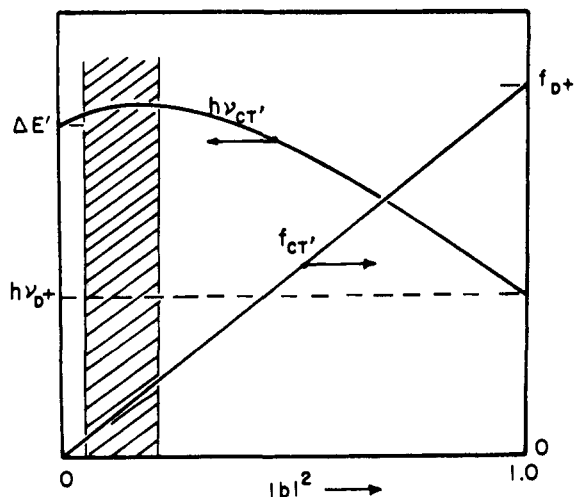


Figure 5. The frequency and oscillator strength of the second CT band of a DA complex,  $B_1 \leftarrow A_1$ , as a function of ionic character of the ground electronic state. The value of  $\Delta E'$  is given in Table IV;  $h\nu_{D^+}$  is the frequency of the donor ion radical,  $D^+$ ; and  $f_{D^+}$  is the oscillator strength of  $D^+$ , typically in the range  $f_{D^+} \approx 0.1$ – $1.0$ . The hatch marks indicate the range of ionic character for many weak DA complexes, benzidine–chloranil, etc., included.

This simple Hückel MO picture of the complex also was chosen to correspond to the findings of Amano, Kuroda, and Akamatu.<sup>1</sup> The origin of the second CT band was shown by spectroscopic comparisons to involve the promotion of an electron from the second highest lying donor orbital to the lowest lying acceptor orbital. Similar donor orbital promotion explanations have been offered for other DA complexes in solution exhibiting second CT transitions.<sup>16</sup>

The band intensity calculations of CT transitions are treated in reference texts for the type  $A_1 \leftrightarrow A_1$  transitions.<sup>16</sup> Such calculations are in rough agreement with measured values of oscillator strengths, typically

$$f_{CT} \approx 10^{-1} - 10^{-2}$$

For  $A_1 \leftrightarrow B_1$  or other transitions of a DA complex, the intensity arises from the following dipole moment terms.

$$\langle D^{+*}A^- | er | \Psi_N \rangle = \langle a_N D^{+*}A^- | er | D \cdots A \rangle + b_N \langle D^{+*}A^- | er | D^+A \rangle$$

The first term on the right is small due to intermolecular overlap. The second term includes the transition dipole term of an isolated donor molecule ion,  $D^+$ . In the one-electron approximation it is given by

$$\langle D^{+*}A^- | er | D^+A^- \rangle = \langle D^{+*} | er | D^+ \rangle = \mu_{D^+}$$

which typically is of appreciable magnitude and always  $x$ - or  $y$ -axis polarized. The oscillator strength of the second CT transition then turns out to be

$$f_{CT'} = |b_N|^2 f_{D^+}$$

where  $|b_N|^2$  is nominally the fraction of ionic character of the ground-state complex (2–20%) and  $f_{D^+}$  is the oscillator strength ( $\approx 1$ – $0.1$ ) of the donor cation. The crude calculation, therefore, is in rough agreement with observations. The intensity of the second CT band found in the laboratory, generally, is of the same order of magnitude as the first in cases reported and assigned.

The degree of ionic character in the ground state is found in some DA complexes to be virtually zero and increases to nearly a whole electron charge,  $D^+A^-$ , in other cases

$$0 < |b_N|^2 < 1$$

In a hypothetical DA complex in which we vary  $|b_N|^2$  as we choose, it is of interest to see what happens to the frequency and intensity of the second CT band of the type  $A_1 \leftrightarrow B_1$ . The polarization we know is fixed. The other observables must vary smoothly over this range and terminate (where  $|b_N|^2 = 1$ ) at the band frequency and intensity of the donor ion radical. This behavior is shown graphically in Figure 5.

In a very weak complex,  $|b_N|^2 \approx 0$  and a perpendicular second CT band is correspondingly very weak as indicated on the extreme left of the figure. On the right where  $|b_N|^2 \approx 1$ , the transition is no longer identified as a CT band and has the correct frequency and intensity for the transition of donor ion radical,  $D^{+*} \leftarrow D^+$ .

## Discussion

Two important facts are known. (1) The benzidine–chloranil type DA complexes exhibit perpendicularly polarized first and second CT bands in the solid.<sup>1</sup> (2) Symmetry-based selection rules for DA complexes provide theoretical grounds for perpendicularly polarized first and second CT bands. Can these two facts be related? And if so, what additional implications come from a symmetry-based approach to DA complexes?

To answer these questions, Tables IV and V have

Table IV. Orbital Symmetries of the First and Second Donor  $\pi$  Orbitals as Determined by Various Investigators<sup>a</sup>

Ref	Donor molecule	Donor $\pi$ orbitals	
		First	Second
20	Benzene ( $D_{6h}$ )	$b_{2g}$ (degenerate)	$b_{3g}$
17, 20	Naphthalene	$a_u$	$b_{1u}$
17, 20	Anthracene	$b_{2g}$	$b_{3g}$
18	Pyrene	$b_{3g}$	$b_{2g}$
21	Perylene	$a_u$	$b_{1u}, b_{2g}$
22	TMPD	$b_{2g}$	$b_{3g}$
1	Benzidine	$b_{2g}$	$b_{1u}$

<sup>a</sup> The first symmetry is that of the first accessible orbital for CT participation. The second donor orbital symmetry is the symmetry of the first (doublet) excited state of the donor ion radical,  $D^{+*}$ . The coordinate system is chosen so that the  $x$  axis is the longer of the two planar molecular axes; the  $z$  axis is the normal axis.

Table V. Orbital Symmetries of the First and Second Acceptor  $\pi$  MO's as Determined by Various Investigators<sup>a</sup>

Ref	Electron acceptor molecule	Acceptor $\pi$ orbitals	
		First	Second
23	<i>p</i> -Benzoquinone	$b_{2g}$	
23	Chloranil, fluoranil, etc.	$b_{2g}$	
24	TCNQ	$b_{2g}$	
18	TCNE	$b_{2g}$	$a_u$
25	TCNB	$a_u$	$b_{1u}$
20	HFB	$a_u$ (degenerate)	$b_{1u}$
17	<i>s</i> -Trinitrobenzene ( $D_{3h}$ )	$e''$	

<sup>a</sup> The second acceptor orbitals are not usually found to contribute to the low-energy CT spectra except in few instances (e.g., TCNB complexes).

Table VI.  $B_{2g}$  Acceptor in DA Complexes of Various Geometric Configurations

Donor	$C_{2v}$	$C_{2v}^{90}$	$C_2$	$C_s(y)$	$C_s^{90}(y)$	$C_s(x)$	$C_s^{90}(x)$
Benzene	$A_1A_2$	$A_2A_1$	A A	$A'A''$	$A'A'$	$A'A''$	$A'A'$
Naphthalene	$B_2(B_1)$	$B_1(B_2)$	B(B)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Anthracene	$A_1(A_2)$	$A_2(A_1)$	A(A)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Pyrene	$A_2(A_1)$	$A_1(A_2)$	A(A)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Perylene	$B_2(B_1, A_1)$	$B_1(B_2, A_2)$	B(B,A)	$A''(A', A')$	$A''(A', A')$	$A''(A', A')$	$A''(A', A')$
TMPD	$A_1(A_2)$	$A_2(A_1)$	A(A)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Benzidine	$A_1(B_1)$	$A_2(B_2)$	A(B)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$

Table VII.  $B_{3g}$  Acceptor in DA Complexes of Various Geometric Configurations

Donor	$C_{2v}$	$C_{2v}^{90}$	$C_2$	$C_s(y)$	$C_s^{90}(y)$	$C_s(x)$	$C_s^{90}(x)$
Benzene	$A_2A_1$	$A_1A_2$	AA	$A''A'$	$A''A''$	$A''A'$	$A''A''$
Naphthalene	$B_1(B_2)$	$B_2(B_1)$	B(B)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Anthracene	$A_2(A_1)$	$A_1(A_2)$	A(A)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Pyrene	$A_1(A_2)$	$A_2(A_1)$	A(A)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Perylene	$B_1(B_2, A_2)$	$B_2(B_1, A_1)$	B(B,A)	$A''(A', A')$	$A''(A', A')$	$A''(A', A')$	$A''(A', A')$
TMPD	$A_2(A_1)$	$A_1(A_2)$	A(A)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$
Benzidine	$A_2(B_2)$	$A_1(B_1)$	A(B)	$A''(A')$	$A''(A')$	$A''(A')$	$A''(A')$

Table VIII.  $A_u$  Acceptor in DA Complexes of Various Geometric Configurations

Donor	$C_{2v}$	$C_{2v}^{90}$	$C_2$	$C_s(y)$	$C_s^{90}(y)$	$C_s(x)$	$C_s^{90}(x)$
Benzene	$B_2B_1$		BB	$A''A'$		$A''A''$	
Naphthalene	$A_1(A_2)$		A(A)	$A''(A')$		$A''(A')$	
Anthracene	$B_2(B_1)$		B(B)	$A''(A')$		$A''(A')$	
Pyrene	$B_1(B_2)$	(Same)	B(B)	$A''(A')$	(Same)	$A''(A')$	(Same)
Perylene	$A_1(A_2, B_2)$		A(A,B)	$A''(A', A')$		$A''(A', A')$	
TMPD	$B_2(B_1)$		B(B)	$A''(A')$		$A''(A')$	
Benzidine	$B_2(A_2)$		B(A)	$A''(A')$		$A''(A')$	

Table IX.  $B_{1u}$  Acceptor in DA Complexes of Various Geometric Configurations

Donor	$C_{2v}$	$C_{2v}^{90}$	$C_2$	$C_s(y)$	$C_s^{90}(y)$	$C_s(x)$	$C_s^{90}(x)$
Benzene	$B_1B_2$		BB	$A'A''$		$A''(A')$	
Naphthalene	$A_2(A_1)$		A(A)	$A''(A')$		$A''(A')$	
Anthracene	$B_1(B_2)$		B(B)	$A''(A')$		$A''(A')$	
Pyrene	$B_2(B_1)$	(Same)	B(B)	$A''(A')$	(Same)	$A''(A')$	(Same)
Perylene	$A_2(A_1, B_1)$		A(A,B)	$A''(A', A')$		$A''(A', A')$	
TMPD	$B_1(B_2)$		B(B)	$A''(A')$		$A''(A')$	
Benzidine	$B_1(A_1)$		B(A)	$A''(A')$		$A''(A')$	

been assembled from literature data<sup>1,17,18,20-25</sup> and contain  $\pi$ -orbital symmetry representations of a number of common donor and acceptor molecules belonging to the  $D_{2h}$  point group. Most of the data come from MO calculations and have not been confirmed spectroscopically. For this and other reasons mentioned above, the assignments are considered tentative. In view of these limitations one may now discuss the (probable) point group representations of low-lying DA electronic states under the seven geometrical configurations illustrated in Figure 1.

To help assemble the data in useful form, Tables VI-IX were computed following the procedure outlined above and give the final state representation of the

DA complex in its first and (in parentheses) second CT states for all seven symmetric orientations. Knowing the geometry of a complex, one can anticipate its spectra. Knowing the CT spectra (and axis of polarization if possible), one is able to suggest a structure or structural alternatives of the DA complex.

In relation to Amano, Kuroda, and Akamatu's spectra,<sup>1</sup> one notes from Table V that chloranil and TCNQ both are  $b_{2g}$  acceptor molecules. This type of acceptor is treated in Table VI. Benzidine and its tetramethyl analog have similar  $\pi$  orbitals ( $b_{2g}$  and  $b_{1u}$  from Table IV) and appear on the last line of Table VI. Under the various symmetry point groups listed at the top, one notes the representations of the first and second CT states. The reported spectra<sup>1</sup> suggest the transitions are of the type  $A_1 \leftarrow A_1$  and  $B_1 \leftarrow A_1$ , respectively. This criterion eliminates DA symmetries  $C_{2v}^{90}$ ,  $C_s^{90}(y)$ , and  $C_s^{90}(x)$  from possible consideration. Four symmetric configurations remain and the one asymmetric,  $C_1$ , point group, not listed. Of these five, the DA complex of  $C_{2v}$ ,  $C_2$ , and  $C_s(x)$  configurations all have *allowed* and *perpendicular* second CT bands. The asymmetric case,  $C_1$ , also fits into this category in a

(20) T. E. Peacock, "Electronic Properties of Aromatic and Heterocyclic Molecules," Academic Press, Inc., New York, N. Y., 1965, p 138.

(21) T. H. Goodwin, *J. Chem. Soc.*, 4851 (1960).

(22) H. Kuroda, S. Hiroma, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **41**, 2855 (1968).

(23) K. Higasi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry," Interscience Publishers, New York, N. Y., 1965, p 243.

(24) D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967); E. Menefee and Y. H. Pao, *ibid.*, **36**, 3472 (1962).

(25) S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).

more or less accidental way; but noting the self-consistency of results from these four molecular species, the  $C_1$  symmetry seems less likely. This leaves the  $C_s(y)$  configuration excluded since the two CT states,  $A'(A')$ , give probable parallel effects. It is not rigorously excluded, however, since an  $A' \rightarrow A'$  transition dipole lies somewhere in the  $x,z$  plane and the first and second CT transitions may accidentally turn out to have perpendicular orientations. Once again, this is unlikely. In summary, therefore, the benzidine-chloranil type complex probably assumes one of three types of symmetric configurations in the solid where the D and A components share a plane of symmetry ( $C_s$ ), a twofold axis ( $C_2$ ), or both ( $C_{2v}$ ). Their long molecular ( $x$ ) axes are predicted to be parallel or at a small angle with one another.

Returning to Table I, one may note the symmetry of other DA complexes (in the lattice) and one may discuss the probable selection rules and spectra of the solid. The TMPD-chloranil lattice<sup>4</sup> exhibits approximate  $C_{2v}$  symmetry in the vicinity of the DA complex; and from Table VI, one predicts the first and second CT states to have representations  $A_1$  and  $A_2$ , respectively. This allows for CT stabilization of the ground state ( $A_1$ ) and a  $z$ -axis first CT band transition,  $A_1 \leftarrow A_1$ . The second CT band is forbidden to this approximation. The rigorous symmetry of the TMPD chloranil DA complex in the solid is  $C_2$ , and under this symmetry the second CT band is allowed and perpendicular to the first.

Single-crystal reflection<sup>26</sup> and polycrystalline absorption<sup>27</sup> spectra are reported for the TMPD-chloranil complex. These spectra indicate the presence of a broad first CT band located at  $10,000 \text{ cm}^{-1}$  ( $1 \mu$ ) which is polarized parallel to the  $z$  axis ( $b$  crystallographic axis). Two additional bands polarized perpendicular to the first appear in the visible spectral range and their origins seem to be in dispute as the amount of ionic character one assigns to the ground state (DA or  $D^+A^-$  or  $D^{2+}A^{2-}$ ) is not established. The recent low-temperature X-ray structural analysis of de Boer and Vos suggest the DA crystal is predominantly a molecular and is not an ionic solid.<sup>4</sup> From this point of view, the perpendicular visible bands at 520 and 420 nm *might* be assigned to perpendicular CT bands. The origin of the two visible bands should probably be left unspecified until more accurate wave functions are derived.

Anthracene-TCNQ also has approximate  $C_{2v}$  local symmetry<sup>6</sup> and has  $A_1$  and  $A_2$  CT states, as above.<sup>17</sup> The second CT band of the solid should be missing. The rigorous symmetry in this case is  $C_s(y)$ , however, which probably leads to a weakly allowed second CT band perpendicular to the first. The solid-state spectrum of anthracene-TCNQ has not been reported to date. Polarized spectra in this case would be of great interest for two reasons. The MO assignment of (anthracene)<sup>+</sup> ion ground state seems to be open to question.<sup>17,20</sup> And secondly, the DA spacing between the parallel molecular planes is reported to be anomalously large<sup>6</sup> ( $3.50 \text{ \AA}$  compared to spacing in other complexes  $\approx 3.3 \text{ \AA}$ ). Further study is warranted.

TMPD-TCNQ is predominantly ionic in the ground state ( $D^+A^-$ ).<sup>22</sup> The local symmetry of the DA complex in the solid is  $C_s(y)$  giving  $A'$  and  $A''$  as the first

and second CT states.<sup>7</sup> Transitions from the ground state are allowed to both states. The second CT band here is nearly the absorption spectrum of the TMPD<sup>+</sup> ion radical, however, so that one observes (correctly) the ion-radical spectra of TMPD<sup>+</sup>-TCNQ<sup>-</sup> and one low-lying CT band.<sup>22</sup>

Naphthalene-TCNB lattice has approximate  $C_2$  local symmetry in the solid phase complex.<sup>9</sup> Considering the first two donor and two acceptor states (Tables VIII and IX) as discussed in ref 25, four CT electron configurations result. These four *all* belong to the A representation which implies additional, CT stabilization in the ground state from four states instead of one. The four allowed CT transitions from the A ground state are  $z$ -axis polarized. Experimentally, two CT bands are found and are  $z$ -axis ( $c$  crystallographic axis) polarized.<sup>28</sup> The other two missing bands may be low in intensity, unresolved, or beyond the ranges of the spectrum.

A detailed analysis of the CT interaction in naphthalene-TCNB also was carried out and reported by Iwata, Tanaka, and Nagakura.<sup>28</sup> Their quantitative predictions from CI calculations go beyond the symmetry predictions here, but the results are compatible. They considered geometries  $C_{2v}$ ,  $C_{2v}^{90}$ ,  $C_2$ ,  $C_s(y)$ , and  $C_s(x)$  as represented in our notation and found maximum CT stabilization of the ground state (*ca.* 0.1 eV) under a  $C_2$  configuration. The angle of rotation,  $\alpha$ , was hardly effective in changing the energy; experimentally<sup>9</sup>  $\alpha = \pm 18^\circ$ . By comparison, Tables VIII and IX show that of all point groups listed, only the  $C_2$  geometry permits ground-state resonance with four (and not one or two) low-lying CT states.

The perylene-fluoranil crystal has a known crystal structure<sup>10</sup> and its polarized absorption spectra also are reported.<sup>29</sup> The DA complex in the crystalline lattice exhibits approximate  $C_s(x)$  symmetry. The first CT state from Table VI is labeled  $A'$  and correctly allows for a  $A' \leftarrow A'$  first CT band. In the crystal, this is reported to be  $c$ -axis polarized at  $14,200 \text{ cm}^{-1}$ . At  $28,700 \text{ cm}^{-1}$  a second intense peak appears in the  $c$ -axis spectrum which is attributed to a second CT band. This transition must also be of the type  $A' \leftarrow A'$  where the excited state is thought to arise predominantly from a state  $|D^+A^- \rangle$ . If one checks the molecular orbitals of perylene<sup>21</sup> in this case, there are two or perhaps three orbitals predicted to have about the same energy corresponding to the second highest lying filled orbital. Two of these orbitals are listed in Table IV ( $b_{1u}$  and  $b_{2g}$ ); the third one is  $b_{3g}$ . It is difficult to know which one to choose on the basis of MO energies alone. The symmetry of the complex, however, establishes uniquely which state of donor orbital is involved; and if one works backwards through the symmetry tables, one finds that only the  $b_{2g}$  state participates in an  $A' \leftarrow A'$  transition and that  $b_{1u}$  and  $b_{3g}$  states both give  $A''$  excited CT states. A transition  $A'' \leftarrow A'$  is  $x$ -axis polarized, which corresponds to the  $a$  crystallographic axis. The polarized spectra of perylene-fluoranil were measured on a single face of a crystal, the  $bc$  face. Thus if "perpendicular" CT transitions of the  $A'' \leftarrow A'$  type are important in this DA solid, they were not

(28) S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **89**, 2813 (1967).

(29) H. Kuroda, T. Kunii, S. Hiroma, and H. Akamatu, *J. Mol. Spectrosc.*, **22**, 60 (1967).

(26) B. G. Anex and E. B. Hill, Jr., *J. Amer. Chem. Soc.*, **88**, 3648 (1966).

(27) G. T. Pott and J. Kommandeur, *Mol. Phys.*, **13**, 373 (1967).

reported. (These symmetry arguments are all based upon the approximate symmetry of the complex,  $C_s(x)$ , which, for the overlapping aromatic rings, should be operative. The peripheral fluorine atoms of the fluoranil molecule deviate the most from eclipsed positions but they are not as important in the calculations.)

The complex mesitylene-TCNB does not fit the system of  $D_{2h}$  molecules (mesitylene is  $D_{3h}$ ) reviewed in this paper, but it is of interest since the complex was studied in some detail by Iwata, Tanaka, and Nagakura both spectroscopically and theoretically.<sup>25</sup> Its structure has not been reported but these authors suggest two structural alternatives. The molecular orbitals of mesitylene are benzene-like and only slightly perturbed from the degenerate levels listed in Table V. One can assume, therefore, that Tables VIII and IX can be examined for consistency with the predicted structure mentioned above. (Since TCNB is an acceptor shown to have two low-lying acceptor orbitals about  $6000\text{ cm}^{-1}$  apart, two tables need to be consulted.)

Under the three axial configurations,  $C_{2v}$ ,  $C_{2v}^{90}$ , and  $C_2$ , the complex is unstable to CT interaction since no totally symmetric A representation appears in any of the three columns in either Table VIII or IX. The mesitylene-TCNB complex cannot be oriented centrosymmetrically! Instead, any one of four  $C_s$  configurations noted leads to CT states of  $A'$  and  $A''$  representations which of course offers some possibility for CT stabilization of the ground ( $A'$ ) state. Since the degenerate  $b_{2g}$  and  $b_{3g}$  states of  $D_{2h}$  benzene are only slightly perturbed in mesitylene, an *a priori* prediction of the most stable CT configuration is not possible from symmetry alone. The prediction made by Iwata, Tanaka, and Nagakura was based upon a seven-excited-state CI calculation (including four CT states). They made no use of symmetry-based wave functions nor selection rules, but the two approaches give compatible answers with regard to structure of the complex. Shear displacement along the  $y$  axis,  $C_s(x)$  (our notation), maximized ground-state stabilization at about  $1.2\text{-}\text{Å}$  displacement from center.<sup>3</sup> Further displacement along the  $x$  axis ( $C_1$  symmetry) decreases the ground-state energy still further, but by an amount which may not be significant. CI computations were not reported for symmetries  $C_s^{90}(y)$  or  $C_s^{90}(x)$ , both of which lead to stabilization theoretically.

The polarized absorption uv spectra of mesitylene-TCNB reported by Iwata, Tanaka, and Nagakura are composed of broad bands and vague features not easily separated or assigned. The dichroic separation between parallel and perpendicular bands (relative to an elongated crystallographic axis) was never shown to be large or small compared with unity. Even below the frequency of the first  $\pi-\pi^*$  transition of TCNB, the observed CT dichroic ratio ( $\parallel:\perp$ ) is only 2.8. As suggested by the authors, this can be explained by mixing of CT states with  $\pi^*$  excited states of TCNB. On the other hand,  $C_s(y)$  symmetry of the DA complex limits the amount of  $\pi^*$  CT mixing and suggests the possibility of clear-cut separation of at least some transitions (since the  $y$  axis is unique). It seems reasonable to assume, therefore, that the mesitylene-TCNB complex has no symmetry at all,  $C_1$ , and that all states are able to mix with all other states, no holds barred.

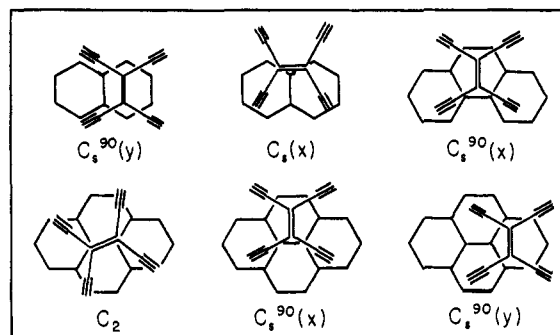


Figure 6. The structural alternatives discussed in the text for DA complexes between TCNE and the four donor molecules, naphthalene, phenanthrene, pyrene, and acenaphthene (similar to naphthalene).

Spectra of TCNE complexes were studied by Kuroda, *et al.*,<sup>30</sup> in which they reported first and second CT bands for four crystalline solids. The relative polarizations of the first and second CT bands are unknown since the spectra were measured on polycrystalline samples in a KBr matrix. Thus, one may overlay the structural possibilities of the donor-TCNE complex with prediction of spectroscopic polarization directions. The results may be summarized as follows, again disregarding a discussion of trivial symmetry,  $C_1$ .

**Naphthalene-TCNE.**  $C_s^{90}(y)$  and  $C_s(x)$  are the only structural assignments consistent with CT stabilization of the ground state by the first CT state (Table VI shows the same representation for both geometrics,  $A'(A'')$ ). Thus, either arrangement predicts perpendicular polarization of the first and second CT bands, relative to one another.

**Acenaphthene-TCNE** is similar to naphthalene-TCNE.

**Pyrene-TCNE.**  $C_2$  symmetry gives A ( $A$ ) representations for the first and second CT states which allows (but does not predict) the two transitions to be parallel.  $C_s^{90}(y)$  and  $C_s^{90}(x)$  both give  $A'(A'')$ , which requires that the two transitions be perpendicular.  $C_{2v}^{90}$  is ruled out,  $A_1(A_2)$ , since the second CT band is predicted to be missing (by selection rules  $A_1 \leftrightarrow A_2$ ) but experimentally the band is observed. Thus, there are only three structural alternatives possessing symmetry. The X-ray crystallographic results of Ikemoto and Kuroda<sup>12</sup> shows the pyrene-TCNE complex to have no symmetry,  $C_1$  (see Table I).

**Phenanthrene-TCNE.** The phenanthrene molecule possesses  $C_{2v}$  symmetry which is reduced to no more than  $C_s(y)$  symmetry in the complex. Its first and second donor orbitals are predicted to form  $b_1$  and  $a_2$  representations, respectively, under  $C_{2v}$  and  $a'$  and  $a''$  representations under  $C_s(y)$  symmetry.<sup>31</sup> In a DA complex with TCNE,  $C_s(y)$  symmetry leads to  $A'(A'')$  CT states, while  $C_s^{90}(y)$  leads to  $A''(A')$  states. The latter is ruled out by the CT stabilization argument leaving the former,  $C_s(y)$ , as the only alternative. The relative polarizations of the first and second CT bands are again perpendicular. Figure 6 presents all of the structural alternatives discussed above.

(30) H. Kuroda, M. Kobayashi, M. Kinoshita, and S. Takemoto, *J. Chem. Phys.*, **36**, 457 (1962).

(31) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of  $\pi$ -Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965.



## Conclusions

An attempt is made to explain the anomalous behavior of recently published polarized spectra of crystalline DA solids by considering the consequences of symmetry in DA complexes and the selection rules for electronic transitions which follow. Discussion is restricted to systems of the benzidine-chloranil types, where the component molecules (D and A separately) possess high symmetry (e.g.,  $D_{2h}$ ). The DA complex is stabilized in a "sandwich" configuration of relatively large intermolecular  $\pi$ - $\pi$  overlap. CT transitions of the DA complex are thus predicted to exhibit unique polarization effects. The first and second CT bands for benzidine-chloranil have, as the reported spectra indicate, axes of polarization perpendicular to one another under specific configurations (i.e.,  $C_{2v}$ ,  $C_2$ , or  $C_s(x)$ ). The crystal structures of this and related complexes have not been reported so that no direct comparisons are possible at present.

Symmetry-based wave functions provide a means to predict stable configurations of a large family of DA complexes once the respective molecular orbital representations of  $D^+$  and  $A^-$  ion radicals are known. Tables VI-IX list the relative symmetry(s) under which

the first CT state  $|D^+A^- \rangle$  has the correct representation to allow CT stabilization of the ground state. Both must be of the totally symmetric representation ( $A_1$ ,  $A$ , or  $A'$ ). From reported crystal structure data of DA solids, this  $A_1$  symmetry criterion is always found to hold. As a consequence, the benzidine-chloranil complex is predicted *not* to have symmetries  $C_{2v}^{90}$ ,  $C_s^{90}(y)$ , or  $C_s^{90}(x)$ . From the incomplete list of molecules surveyed, one can make many other interesting predictions worth experimental verifications.

Finally if the DA structure *and* spectra are known as it is for the perylene-fluoranil complex, molecular orbital information on the  $D^-$  and  $A^-$  components can be extracted. Under the approximate  $C_s(x)$  symmetry of the complex the important orbitals involved with the first and second CT bands are assigned as follows: perylene,  $a_u$  (first) and  $b_{2g}$  (second) donor orbitals; fluoranil,  $b_{2g}$  acceptor orbital. Accidental degeneracies of the second donor orbital of perylene made the origin of that state in doubt.

**Acknowledgments.** I am pleased to acknowledge the two laboratories (above) at which this work was carried out and from which the author received full support and cooperation.

## Ion-Molecule Reactions of Hydrogen Sulfide with Ethylene and Acetylene

S. E. Buttrill, Jr.<sup>1</sup>

*Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received October 16, 1969*

**Abstract:** Ion cyclotron resonance spectroscopy has been used to study the ion-molecule reactions in mixtures of hydrogen sulfide with ethylene and acetylene. In ethylene the major products at 12.5 eV are  $CH_2S^+$  and  $CH_2SH^+$ . Small amounts of  $HCS^+$  are observed at higher electron energies. Deuterium labeling of ethylene shows that two of the hydrogens in  $CH_2SH^+$  and the two hydrogens in  $CH_2S^+$  come from the same ethylene carbon atom. The third hydrogen in  $CH_2SH^+$  originates from the hydrogen sulfide. The hydrogen sulfide-ethylene reaction complex has an ethanethiol molecular ion structure and hydrogen rearrangement within the complex is slow compared to fragmentation to the reaction products. The products of the reaction of hydrogen sulfide ion with acetylene are  $HCS^+$  and  $C_2H_3S^+$ . The acetylene ion does not react with hydrogen sulfide except by charge transfer. The reactions of hydrogen sulfide ion with acetylene- $d_2$  indicate that the reaction complex is best represented as the enol form of the sulfur analog of acetaldehyde molecular ion. Charge localization on sulfur in the reaction complex inhibits the extensive hydrogen rearrangement usually found in unsaturated hydrocarbon ion-molecule reactions.

**I**on cyclotron resonance (icr) spectrometry has been used to study the ion-molecule reactions occurring in a variety of compounds.<sup>2-9</sup> There are two characteristics of the icr spectrometer which make it par-

ticularly well suited to this type of study: (1) spectra may be taken at high enough pressures ( $10^{-6}$ - $10^{-4}$  Torr) that ion-molecule reactions are readily observed, and (2) the pulsed-double-resonance technique<sup>10</sup> makes possible the verification of ion-molecule reaction sequences.

Previous work with deuterium-labeled ethylene using icr,<sup>5</sup> tandem,<sup>11</sup> and high-pressure<sup>12</sup> mass spectro-

(1) National Science Foundation Graduate Fellow 1966-1969. Address correspondence to: 139 Chemistry Building, University of Minnesota, Minneapolis, Minn. 55455.

(2) J. L. Beauchamp, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1967.

(3) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(4) R. C. Dunbar, *J. Amer. Chem. Soc.*, **90**, 5676 (1968).

(5) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968).

(6) J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

(7) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *ibid.*, **89**, 4569 (1967).

(8) G. Gray, *ibid.*, **90**, 2177, 6002 (1968).

(9) J. I. Brauman and L. K. Blair, *ibid.*, **90**, 5636 6561 (1968).

(10) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966); J. L. Beauchamp and S. E. Buttrill, Jr., *ibid.*, **48**, 1783 (1968).

(11) T. O. Tiernan and J. H. Futrell, *J. Phys. Chem.*, **72**, 3080 (1968).

(12) J. J. Myher and A. G. Harrison, *Can. J. Chem.*, **46**, 101 (1968); "Ion-Molecule Reactions in the Gas Phase," *Advances in Chemistry Series*, No. 58, American Chemical Society, Washington, D. C., 1966, Chapter 14.