

ELECTROSTATIC AND CHARGE-TRANSFER CONTRIBUTION  
TO THE CHANGE OF  $C \equiv N$  AND  $C = C$  BAND INTENSITIES IN  
CHARGE-TRANSFER COMPLEXES OF  
TETRACYANOETHYLENE\*

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(Received January 28, 1975; revised version received March 15, 1977)

The methods of calculating electrostatic polarization, as well as the charge-transfer contribution to the infrared intensity of the acceptor bands in complexes has been extended to sandwich-type complexes: TCNE-benzene and TCNE-paraxylene. Due to the different selection rules for the electrostatic polarization and for the vibronic charge-transfer effect, the experiment renders possible a partial separation of the two effects. It has been demonstrated that the electrostatic polarization is responsible for the change in intensity of the allowed TCNE bands, and only partly for that of the forbidden bands; the high activity of the induced transition of the  $1554\text{ cm}^{-1}$  mode cannot be justified except by the admission of the charge-transfer vibronic effect described by the model of Friedrich and Person.

1. Introduction

The physical properties of the electron donor-acceptor (EDA) complexes, called (not quite properly) the "charge-transfer" complexes, constitute a very important problem for theorists as well as experimenters. During several years the major part of the effects, observed in the ground state of these complexes, e. g. the formation constant, the magnetic properties, the appearance of the induced dipole moment and its variation during vibration, manifested by the enhancement of the IR band — has been interpreted in terms of the Mulliken charge-transfer theory [1, 2].

The point of departure of this theory is the assumption, that the ground state wave function,  $\psi_N$ , can be obtained by the mixing in of a small admixture of the dative state wave function,  $\psi_1$ , corresponding to the complete electron transfer from donor to acceptor

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\* This work has been partly supported by the Polish Academy of Sciences, under project PAN-3.2.07.

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— to the no-bond state wave function,  $\psi_0$ , that includes all the classical interactions between a donor and an acceptor, i. e.

$$\psi_N = a\psi_0 + b\psi_1. \quad (1)$$

According to this theory the mixing coefficients,  $a$  and  $b$  would be the decisive parameters in determining the properties of the ground state of the complex. Unfortunately, this expectation has been not confirmed by experiment.

Due to this disaccordance, the Mulliken theory became since 1965 a subject of intense criticism [3, 4]. The main objection has concerned the restriction of the number of mixing states to only two (or three), while the general theory of intermolecular interaction between two arbitrary molecules should involve the mixing of all the excited states of both molecules.

Such a general theory of intermolecular interactions has been developed between 1965 and 1968, independently by the group of Pullman [5–7], and by Murrell [8, 9]. When the perturbation calculations for the interaction between two molecules  $A$  and  $B$  are executed up to the second order, with the zero order wave function taken as the product of  $\Phi_0^A$  and  $\Phi_0^B$  — then the interaction energy readily separates into three parts:

(i) the diagonal  $U$  matrix elements, associated with the state  $\Phi_0^A \cdot \Phi_0^B$ , giving the first order correction to the energy, which can be interpreted as the classical electrostatic interaction,

(ii) the second order correction to the energy, associated with the states of single excitation,  $\Phi_0^A \cdot \Phi_s^B$ , and  $\Phi_r^A \cdot \Phi_0^B$  which can be interpreted as the classical induction energy, and

(iii) the second order correction to the energy, associated with double excitation —  $\Phi_r^A \cdot \Phi_s^B$  states, which is the London dispersion energy.

These three contributions are sufficient to describe the long range interaction; for the medium range the orbital overlapping gives rise to the repulsion and charge-transfer energy. With the aim of including the overlap in the calculation, Murrell has introduced the wave function, which allows for the exchange of electrons between the two molecules; this zero order function is  $\mathcal{A} \cdot \Phi_0^A(i) \cdot \Phi_0^B(j)$  where  $\mathcal{A}$  is the antisymmetrizing operator. In the expansion of the states  $\Phi^A \cdot \Phi^B$ , apart from the locally excited states of the type  $\Phi_r^A \cdot \Phi_0^B$  and  $\Phi_0^A \cdot \Phi_s^B$ , the charge-transfer states of the type  $\Phi^{A+} \cdot \Phi^{B-}$  and  $\Phi^{A-} \cdot \Phi^{B+}$  appear.

The double perturbation expansion with  $U$  (an interaction energy) and  $S$  (an overlap between  $A$  and  $B$ ), as parameters, leads to the new energy formula, containing, besides the previously enumerated contributions also the additional terms:

(iv) the contribution of the first order in  $U$  and second order in  $S$ , plus the contribution of the second order in  $U$  and in  $S$ , named by the authors “the exchange energy” and “the exchange-polarization energy”, respectively,

(v) the contribution of second order in  $U$  and second order in  $S$ , originating from the ionic states, giving the charge-transfer stabilization energy.

This general formulation of the intermolecular interaction problem in the region of small overlap (up to 0.3) — suggests that the charge transfer interaction cannot constitute more, than a small part of the whole interaction energy.

The appearance of this theory has been followed by numerical calculations, in which the separate terms are approximated as far, as possible, by the expressions containing experimental parameters, such as dipole moment and polarizability. The calculations performed by Mantionne [10, 11] for several complexes of tetracyanoethylene (TCNE) with aromatic hydrocarbons and with a series of pentagonal heterocycles has demonstrated the dominant role of the Van der Waals interactions in the stabilization energy and in the dipole moment of the complex. The author did not try to compute the charge transfer contribution, estimating it as insignificant. Nevertheless, Lippert, Hanna and Trotter [12] have still compared the charge-transfer contribution calculated by the method of Murrell, Randic and Williams [8] to Van der Waals and repulsion contributions, and concluded that they are of comparable order.

Recently there were some attempts to treat the problem by the more sophisticated methods of quantum chemistry, but unfortunately without great success. The calculations of Chesnut and Wormer [13] using CNDO method suggest that the maximum stabilization energy for the TCNE-benzene complex occurs at interplanar distance, 1.75 Å i. e. about two times shorter than the experimental one. The calculations by Ohta and Fujikawa [14], performed using MINDO/2 method suggest that the potential energy curve of the interactions between TCNE and benzene has no minimum at all. Thus, at present these theories do not seem to be useful for large systems.

The enhancement of the infrared forbidden band in complexes has been interpreted previously in terms of the charge-transfer model, suggested by Ferguson and Matsen [15] and developed by Friedrich and Person [16]. In 1967 Hanna and Williams [17] have proposed a method of calculating of the electrostatic contribution to the infrared intensity and frequency shifts of the induced bands. Their results suggest that this electrostatic contribution explicates the whole observed intensity of the halogen stretching band in halogen-benzene complexes. Mantionne however has pointed out [17], that these authors have taken a faulty value for the quadrupole moment of benzene. The value predicted by Mantionne by the transition moment factor,  $M_{N1, N0}$  for the  $I_2$  vibration in the TCNE-benzene complex is nearly four times lower, than that predicted by Hanna and Williams — but her final conclusions, concerning the role of the electrostatic contribution are similar.

On the other hand Szczepaniak and Person had demonstrated, [18], that the contribution to the intensity and frequency change of the HCl band for the HCl-benzene complex evaluated using the charge-transfer model is slightly more important, than that using the electrostatic model.

## 2. The setting up of the problem

The subject of this work is the competition of the charge-transfer and electrostatic contributions to the infrared intensity of the TCNE stretching bands in TCNE-benzene and TCNE-para-xylene complexes. The sandwich-type complexes (like the complexes under study) have an advantage over the halogen-aromatic complexes in the difference in the selection rules governing the electrostatic and charge-transfer contributions. The

electrostatic model permits in general the enhancement of the planar modes, allowed for an isolated molecule, as well as of the forbidden, induced transitions. The charge-transfer model does not allow but the totally symmetric induced transitions, which in a sandwich-type complex are polarized perpendicular to the plane of vibration [19, 20]. In this way the experiment renders possible a partial separation of the two effects.

In the previous paper [21] the author have demonstrated that the experimental intensity change of the infrared C—H stretching bands of naphthalene due to the formation of a complex with TCNE, is of the same order, as that, predicted by the calculations of the electrostatic contribution. Well, in ( $b\pi, a\pi$ ) complexes the electron transfer affects the delocalized  $\pi$ -electrons, and should not influence the infrared activity of the  $\sigma$ -bond vibration. The agreement of the experimental data with the data, calculated using the electrostatic model — can be treated as the verification of the adequacy of the theory adopted.

In this paper we have used the same method of calculation for the problem of TCNE infrared band intensity in complexes. The calculations of the contribution due to the electrostatic polarization will be based on the Hanna method, with the modifications proposed by Mantionne [17]. For the calculations of the charge-transfer contribution, the theory of Friedrich and Person [16] will be used, but the potential curves for the bond examined will be determined in another manner.

### 3. The estimation of the electrostatic polarization contribution

Two symmetrical configurations of the donor-acceptor pair, considered in this work — are presented in Fig. 1. For the C $\equiv$ N and C—C bond only configuration I has been taken into account; for the C=C bond the results obtained for the two configurations have been compared one to another. The interplanar distance has been assumed to be 3.5 Å.

The idea of Hanna is the following: The dipole moments of the bonds, as well, as the quadrupole moments of the  $2p$  orbitals of the carbon atoms of the donor create an electrostatic field on the acceptor molecule. This field induces in turn a dipole moment  $\vec{\mu}$  on a separate bond of TCNE,

$$\vec{\mu}_{\text{ind}} = \alpha \vec{E}, \quad (2)$$

where  $\alpha$  is the polarizability of the bond and  $\vec{E}$  — the electric field strength.

Since the electric field along the bond is both nonuniform and nonlinear, some kind of averaging procedure which distributes the polarizability over the bond must be used [22]. We have chosen the division of the polarizability  $\alpha$  into parts  $k_1\alpha$  and  $k_2\alpha$ , proportional to the atomic polarizabilities, located at each atom. The induced dipole moment will then be

$$\vec{\mu}_{\text{ind}} = k_1\alpha\vec{E}_1 + k_2\alpha\vec{E}_2, \quad (2)$$

where  $\vec{E}_1$  and  $\vec{E}_2$  are the electric field strengths at the atoms forming the bond and  $k_1$  and  $k_2$  fulfil the relation:  $k_1 + k_2 = 1$ .

The direction of the field forms a certain angle with the direction of the bond and therefore the field can be decomposed into two components: one parallel,  $E^{\parallel}$ , and the other perpendicular to the bond,  $E^{\perp}$ .

As the molecule vibrates, there will be two contributions to a change in the induced moment: a contribution due to the change of polarizability upon vibration, and a contribution due to the fact, that atoms 1 and 2 experience different fields. Thus, for the parallel component and for the perpendicular one

$$\begin{aligned} (\parallel) \left( \frac{\partial \mu^{\parallel}}{\partial r} \right) &= k_1 \left( \frac{\partial \alpha^{\parallel}}{\partial r} \right) E_1^{\parallel} + k_2 \left( \frac{\partial \alpha^{\parallel}}{\partial r} \right) E_2^{\parallel} + k_1 \alpha^{\parallel} + \frac{\partial E_1^{\parallel}}{\partial r} + k_2 \alpha^{\parallel} \frac{\partial E_2^{\parallel}}{\partial r}, \\ (\perp) \left( \frac{\partial \mu^{\perp}}{\partial r} \right) &= k_1 \left( \frac{\partial \alpha^{\perp}}{\partial r} \right) E_1^{\perp} + k_2 \left( \frac{\partial \alpha^{\perp}}{\partial r} \right) E_2^{\perp} + k_1 \alpha^{\perp} \frac{\partial E_1^{\perp}}{\partial r} + k_2 \alpha^{\perp} \frac{\partial E_2^{\perp}}{\partial r}. \end{aligned} \quad (3)$$

This procedure gives the set of  $\left( \frac{\partial \mu}{\partial r_j} \right)$  — the dipole moment derivatives with respect to the length of the bond:  $C \equiv N$ ,  $C-C$  and  $C=C$ . Now, these quantities have to be

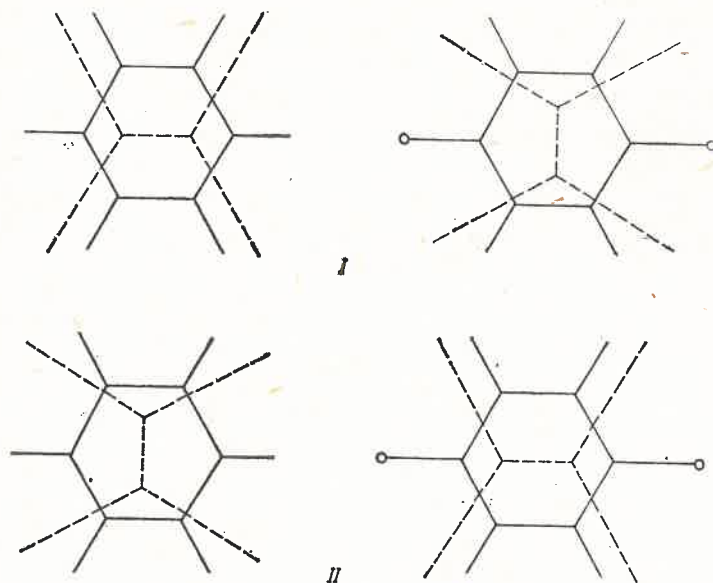


Fig. 1. Geometrical configurations of the TCNE-benzene and TCNE-paraxylene complexes used for calculations

transformed into appropriate dipole moment derivatives with respect to the normal coordinates; these are just the values which can be compared to the experimental values.

The calculations fall into three steps:

a. The evaluation of the field strengths on all the atoms forming the  $C \equiv N$ ,  $C=C$  and  $C-C$  bonds.

b. The evaluation of the dipole moment derivatives with respect to the bond length, polarized parallelly and perpendicularly to the bond.

c. The transformation to normal coordinates for the infrared active vibrations of the complex.

#### a. The evaluation of the field components

As has been mentioned above the field created by the benzene molecule can be due: to the dipole moment of the C—H bonds and to quadrupole moments of the carbon  $2p_z$  and  $sp^2$  orbitals.

As customary, we divide the dipole moment of the C—H bond into appropriate charges localized on the carbon and hydrogen atoms. There is a considerable discrepancy about the magnitude and even the sign of these charges. This subject has been widely treated in the paper by Hanna [23]. The extended Huckel method, the method of del Re [24] and the SCF method, developed by Lipscomb [25] give values from 0.04 to 0.10, with the “+” sign on hydrogen. The recent CNDO/2 calculations, performed by Boucher and Cremashi [26] give a negative charge of about 0.01 on hydrogen; the opinion of many theorists is however that the results obtained by the CNDO and MINDO method have no absolute significance, but can be treated only as comparative values within a series of compounds; the method based more directly on the experimental parameters, as that of Orville-Thomas [27], utilizing the infrared intensity data, and considering the rehybridization effect during the C—H bond bending, as well, as the del Re method — inspire more confidence [28]. This being so we have adopted the values  $-0.053$  and  $+0.053$  for the net charges on the C and H atoms respectively of the C—H bond in isolated molecules of benzene and para-xylene according to the calculations of Mantionne based on the extended Del Re method. Besides, it is necessary to account for the supplementary net charges, originating from the dipole moment induced on the C—H bonds of the donor, by the acceptor molecule. For these induced charges on the C and H atoms of the C—H bonds we have adopted the value  $\pm 0.010$ , calculated from data of our previous paper [22] for naphthalene-TCNE complex.

Finally, the net charges on C and H are:  $-0.063$  and  $+0.063$ , respectively.

The  $\pi$ -charges on the carbon atoms for para-xylene as evaluated by Krygowski [29], using the Hückel method are  $+0.033$  on the carbon atom of the methyl group,  $+0.016$  on the neighbouring ring carbon atom and  $-0.025$  on the four remaining carbon atoms.

The role of the quadrupole moment of the charge distribution on the carbon atom has been first recognized by Hanna [23]. He has considered the quadrupole moment of the  $2p\pi$  orbitals, while neglecting the potential due to the quadrupole moment of the  $sp^2$  orbitals. Mantionne has claimed [18], that this procedure is not legitimate. Claverie [30] has pointed out, that, if for the neutral, trigonally hybridized carbon atom all the  $2p$  atomic orbitals are supposed to be identical, the quadrupole moment of a  $2p\pi$  orbital is exactly cancelled by the combined quadrupole moment of the three  $sp^2$  orbitals. The value of the quadrupole moment of benzene, obtained from the analysis of virial coefficients is still larger than can be expected if accounting but the quadrupole moment, resulting from the three quadrupoles formed by the charge distribution  $H^+ - C^- \dots C^- - H^+$ . To

justify this experimental fact, Mantionne has adopted different Slater coefficients for the  $2p\pi$  and  $2p\sigma$  orbitals of benzene, namely  $\xi_\pi = 1.59$  and  $\xi_\sigma = 2.01$ , similiary, as Griffith and Goodman [31] have done for acetylene.

The resultant quadrupole moment parallel to the  $z$ -axis due to the charge distribution of the three  $sp^2$  and one  $2p_z$  orbitals would then have the value

$$Q_i = Q_{2p\pi} - Q_{2p\sigma} = -12 \left[ \left( \frac{1}{2\xi_\pi} \right)^2 - \left( \frac{1}{2\xi_\sigma} \right)^2 \right] = -0.444 \text{ au.} \quad (4)$$

(the value used by Hanna was 1.14 au.)

This value has been used in our calculations for the TCNE-benzene and TCNE-para-xylene complexes.

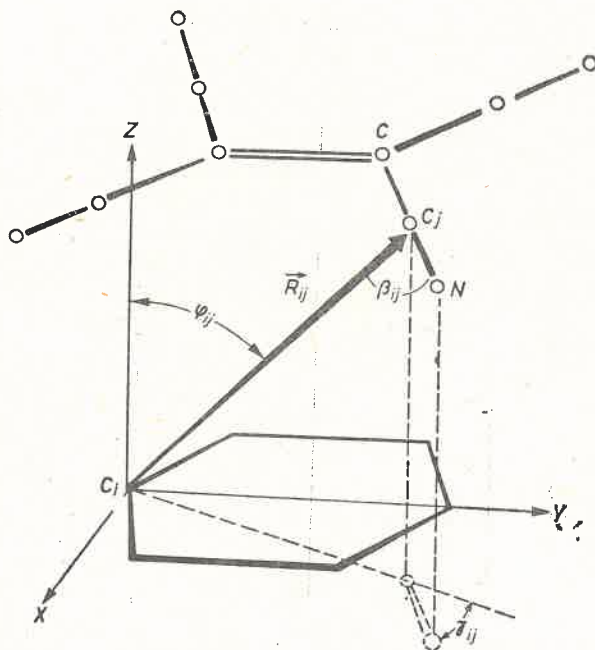


Fig. 2. Coordinates used in the calculations of the field strengths on the atoms of TCNE

The electrostatic potential resulting from the quadrupole moments of the aromatic ring at a point, localized at  $C_j$  atom of the C—C group of TCNE molecule would be [32]

$$V_{C_j} = \sum_i \frac{1}{2R_{ij}^3} \{Q_i(3 \cos^2 \varphi_{ij} - 1)\}, \quad (5)$$

where  $R_{ij}$  is the distance of the  $C_j$  atom of TCNE from the  $i$ -th carbon atom,  $C_i$ , of benzene (or, para-xylene), and  $\varphi_{ij}$  — the angle between  $R_{ij}$  and the  $z$ -axis.

For the projection of the field strength, due to the quadrupole moment, plus that, due to the dipole moments, on the directions: parallel, ( $\parallel$ ) and perpendicular ( $\perp$ ) to the

bond we have obtained

$$(\parallel) E_{C_j} = \sum_i \left\{ \frac{-q_i}{R_{ij}^2} \cos \beta_{ij} - \frac{3Q_i}{2R_{ij}^4} \sin \varphi_{ij} (5 \cos^2 \varphi_{ij} - 1) \cos \gamma_{ij} \right\} \quad (6)$$

$$(\perp) E_{C_j} = \sum_i \left\{ \frac{-q_i}{R_{ij}^2} \cos \varphi_{ij} - \frac{3Q_i}{2R_{ij}^4} \cos \varphi_{ij} (5 \cos^2 \varphi_{ij} - 3) \right\}, \quad (7)$$

where  $\beta_{ij}$  is the angle between  $R_{ij}$  and the direction of the bond examined (C—C, C=C or C≡N),  $\varphi_{ij}$  is an angle between  $R_{ij}$  and the z-axis, and  $\gamma_{ij}$  — the angle between the direction of the bond and the projection of  $R_{ij}$  on the  $xy$ -plane (Fig. 2).

TABLE I

The electric field strengths on the TCNE atoms

		Field strength $E \times 10^{-5}$ esu/cm <sup>2</sup>			$\frac{\partial E}{\partial r} \times 10^{-13}$ esu/cm <sup>3</sup>
		due to point charges	due to quadrupole mom.	total	
TCNE- benzene	$E_N(\parallel)$	0.140	0.135	0.275	-0.12
	$E_{C_1}(\parallel)^1$	0.182	0.165	0.347	±0.01
	$E_{C_2}(\parallel)$	0.037	0.082	0.119	±0.18
	$E_N(\perp)$	0.031	0.038	0.069	-0.10
	$E_{C_1}(\perp)$	0.184	0.180	0.364	±0.12
	$E_{C_2}(\perp)^2$	0.334	0.332	0.666	-0.04
TCNE- p-xylene	$E_N(\parallel)$	0.171	0.133	0.304	-0.05
	$E_{C_1}(\parallel)$	0.160	0.176	0.336	-0.01
	$E_{C_2}(\parallel)$	0.014	0.128	0.142	±0.15
	$E_N(\perp)$	0.051	0.025	0.076	-0.10
	$E_{C_1}(\perp)$	0.147	0.190	0.337	±0.11
	$E_{C_2}(\perp)^2$	0.326	0.335	0.661	-0.04

<sup>1</sup>  $C_1$  is a carbon atom forming the C≡N bond,  $C_2$  — the carbon atom forming the bond C=C.

<sup>2</sup> These are the mean values for two configurations examined.

The hydrogen atoms and the methyl groups create at the  $C_j$  atom of TCNE the fields of strength

$$(\parallel) E_{C_j} = \sum_i \frac{+q_i}{R_{ij}^2} \cos \beta_{ij}, \quad (8)$$

$$(\perp) E_{C_j} = \sum_i \frac{+q_i}{R_{ij}^2} \cos \varphi_{ij}. \quad (9)$$

In Table I the electric field strengths obtained in this way are given for all the atoms of the C≡N, C=C and C—C bonds.



b. The evaluation of the dipole moment derivatives with respect to the bond length coordinates

With the aim of evaluating the dipole moment derivatives with respect to the bond length coordinates knowledge of the following parameters is needed:  $\alpha^{\parallel}$ ,  $\alpha^{\perp}$ ,  $\frac{\partial\alpha^{\parallel}}{\partial r}$  and  $\frac{\partial\alpha^{\perp}}{\partial r}$ . The values of the bond polarizability has been taken from the monography of Hirschfelder, Curtis and Bird [32]. For the polarizability derivatives parallel to the bond, the values, estimated using the  $\delta$  function model by Lippincott and Nagarajan [33] has been utilized. The perpendicular component of the polarizability derivatives can be evaluated from the degree of depolarization,  $\rho$ , of an appropriate Raman line. For linearly polarized incident light the degree of the depolarization  $\rho_p$  is expressed by

$$\rho_p = \frac{3\gamma'^2}{45\alpha'^2 + 4\gamma'^2} \quad (10)$$

where  $3\alpha' = \left(\frac{\partial\alpha^{\parallel}}{\partial Q} + 2\frac{\partial\alpha^{\perp}}{\partial Q}\right)$  is the trace, and  $\gamma = \left(\frac{\partial\alpha^{\parallel}}{\partial Q} - \frac{\partial\alpha^{\perp}}{\partial Q}\right)$  — the anisotropy of the tensor of the polarizability derivatives with respect to the normal coordinates.

We have assumed approximately that the ratio  $\frac{\partial\alpha^{\perp}}{\partial r_j} : \frac{\partial\alpha^{\parallel}}{\partial r_j}$  is equal to the ratio  $\frac{\partial\alpha^{\perp}}{\partial Q_i} : \frac{\partial\alpha^{\parallel}}{\partial Q_i}$  for the appropriate  $Q_i$ ; the last ratio can be evaluated from the experimental value of  $\rho_p$  using formula (10).

The degree of depolarization of the Raman line  $2220\text{ cm}^{-1}$  of TCNE in the benzene and para-xylene solutions, as well, as of the line  $1554\text{ cm}^{-1}$  in the benzene solutions has

TABLE II

Parameters used in the calculation of the dipole moment derivatives due to the electrostatic polarization

Bond	C=C	C-C	C≡N
$\alpha^{\parallel} \times 10^{25} \text{ cm}^3$	28.6	18.8	31.0
$\alpha^{\perp} \times 10^{25} \text{ cm}^3$	10.6	0.2	14.0
$\frac{\partial\alpha^{\parallel}}{\partial r} \times 10^{16} \text{ cm}^2$	6.7	4.4	6.9
$\rho$ { in benzene	$0.078 \pm 0.008$	0.10	$0.065 \pm 0.007$
{ in p-xylene	—	0.10	$0.060 \pm 0.008$
$\left(\frac{\partial\alpha^{\perp}}{\partial r}\right) : \left(\frac{\partial\alpha^{\parallel}}{\partial r}\right)$ { in benzene	0.36	0.31	0.39
{ in p-xylene	—	—	0.40
$\left(\frac{\partial\alpha^{\perp}}{\partial r}\right)$ { in benzene	2.4	1.35	2.70
{ in p-xylene	—	—	2.75

been measured with the aid of the Goderg PHO Spectrophotometer, using the 6471 Å krypton laser line as the exciting line<sup>1</sup>. For the C—C stretching line of TCNE the value of  $\rho$  given by Sviertlov, Kovner and Krainov [34] for the analogical line of tetracyanoethylene has been used. All the parameters are given in Table II.

TABLE III

Dipole moment derivatives with respect to the internal coordinates

	$(k_1 E_1 + k_2 E_2) \frac{\partial \alpha}{\partial r}$	$\left( k_1 \frac{\partial E_1}{\partial r} + k_2 \frac{\partial E_2}{\partial r} \right) \alpha$	$\frac{\partial \mu}{\partial r} (\text{D } \text{Å}^{-1})$
TCNE-benzene			
C≡N	0.218	-0.014	0.204
C—C	0.102	-0.016	0.086
⊥ C≡N	0.064	0.009	0.073
⊥ C—C	0.069	0.000	0.069
⊥ C—C	0.160	-0.016	0.144
TCNE-p-xylene			
C≡N	0.222	0.005	0.217
C—C	0.105	-0.013	0.092
⊥ C≡N	0.062	+0.003	0.065
⊥ C—C	0.159	-0.004	0.155
⊥ C—C	0.067	0.000	0.067

The dipole moment derivatives with respect to the bond length coordinates has been calculated from formula (3) with the parameters:  $k_1 = k_2 = \frac{1}{2}$  for C—C and C=C bonds, and  $k_N = \frac{3}{7}$ ,  $k_C = \frac{4}{7}$  for the C≡N bond. The results are presented in Table III; the contribution due to the change of the polarizability and that, due to the field change upon vibration, are separately given.

### c. The evaluation of the dipole moment derivatives with respect to the normal coordinates

The set of the four C≡N bonds, as well as the set of the four C—C bonds gives rise to four vibrations of the symmetry species  $a_{1g}$ ,  $b_{3g}$ ,  $b_{1u}$  and  $b_{2u}$ . For the transitions associated with the polarizability change along the bond direction, the transformation from the dipole moment derivatives with respect to the internal coordinates, into these with respect to the symmetry coordinates — will be the same in complex, as in the isolated TCNE molecule, namely:

$$b_{1u} \frac{\partial \mu}{\partial S_{10}} = -2 \frac{\partial \mu^{\parallel}}{\partial r} \cos 120^\circ, \quad \text{where } r \parallel \text{C} \equiv \text{N}$$

<sup>1</sup> These measurements have been performed during the author's stay in the Laboratory of Molecular and Crystal Spectroscopy of the Paris University V, directed by prof. J. P. Mathieu.

$$\begin{aligned}
 \frac{\partial \mu}{\partial S_{11}} &= -2 \frac{\partial \mu^{\parallel}}{\partial r} \cos 120^{\circ}, & \text{where } r \parallel \text{C}-\text{C}, \\
 b_{2u} \frac{\partial \mu}{\partial S_{14}} &= 2 \frac{\partial \mu^{\parallel}}{\partial r} \sin 120^{\circ}, & \text{where } r \parallel \text{C} \equiv \text{N} \\
 \frac{\partial \mu}{\partial S_{15}} &= 2 \frac{\partial \mu^{\parallel}}{\partial r} \sin 120^{\circ}, & \text{where } r \parallel \text{C}-\text{C}.
 \end{aligned} \tag{11}$$

All the  $b_{3g}$  and  $a_{1g}$  transitions, (the C=C stretching vibration included), associated with the parallel dipole moment derivatives remain infrared inactive.

On the other hand the transitions associated with the component of the polarizability derivative perpendicular to the bond are different from zero just for the totally symmetric vibrations, and the new transformation relations hold

$$\begin{aligned}
 a_{1g} \frac{\partial \mu}{\partial S_1} &= \frac{\partial \mu^{\perp}}{\partial r}, & \text{where } r \perp \text{C} = \text{C} \\
 \frac{\partial \mu}{\partial S_2} &= 2 \frac{\partial \mu^{\perp}}{\partial r}, & \text{where } r \perp \text{C}-\text{C} \\
 \frac{\partial \mu}{\partial S_3} &= 2 \frac{\partial \mu^{\perp}}{\partial r}, & \text{where } r \perp \text{C} \equiv \text{N}.
 \end{aligned} \tag{12}$$

The dipole moment derivatives with respect to the symmetry coordinates will in turn be transformed into these with respect to the normal coordinates through the  $L$ -matrix, according to the formula [35, 36].

$$\frac{\partial \mu}{\partial Q_j} = \sum_i^n L_{ij} \left( \frac{\partial \mu}{\partial S_i} \right), \tag{13}$$

where  $n$  is the number of the vibrations belonging to the same symmetry species. In general the summation is extended over all the coordinates of the same symmetry species. In practice, however, contributions from some vibrations are insignificant. We feel that in our case the bending modes do not contribute to the induced absorption and therefore only the contribution from the stretching modes have been considered.

TABLE IV

Symmetrized  $L$ -Matrix for TCNE

$B_{1u}$	$Q_{10}$	$Q_{11}$	$B_{2u}$	$Q_{14}$	$Q_{15}$	$A_{1g}$	$Q_1$	$Q_2$	$Q_3$
		2230		952			2253	1152	
$S_{10}$	0.2478	0.2261	$S_{14}$	0.2941	0.3486	$S_1$	-0.0627	-0.3966	0.0046
$S_{11}$	-0.3898	0.0486	$S_{15}$	-0.3841	0.0848	$S_2$	0.2578	0.1874	0.1249
						$S_3$	-0.3870	0.0645	0.0228

Electrostatic contribution to the IR intensity

Symmetry	Mode	Polarization	TCNE-benzene		TCNE-para-xylene	
			Freq.	$\left(\frac{\partial\mu}{\partial Q_i}\right)^a$	Freq.	$\left(\frac{\partial\mu}{\partial Q_i}\right)$
$a_{1g}$	$\nu_1$	$\perp$	2220	0.026	2220	0.025
$a_{1g}$	$\nu_2$	$\perp$	1554	0.022	1554	0.025
$a_{1g}$	$\nu_3$	$\perp$	557	0.021	557	0.025
$b_{1u}$	$\nu_{10}$	$\parallel$	2216	0.058	2217	0.062
$b_{1u}$	$\nu_{11}$	$\parallel$	950	0.029	950	0.031
$b_{2u}$	$\nu_{14}$	$\parallel$	2251	0.092	2250	0.097
$b_{2u}$	$\nu_{15}$	$\parallel$	1150	0.070	1150	0.087

<sup>a</sup>  $\frac{\partial\mu}{\partial Q_i}$  are in (D/Å (amu<sup>-1/2</sup>)).

We have utilized the  $L$  matrix supplied kindly by professor J. P. Devlin, from Oklahoma State University; the elements  $L_{ij}$  relating to the modes of interest are given in Table IV, and the final results in Table V.

#### 4. The evaluation of the charge-transfer contribution

The vibronic charge-transfer effect is included in the framework of a general theory of the electron delocalization contribution to the infrared intensity [37, 38]. The idea of this theory is, that motion during a particular vibration may cause an extensive reorientation of electrons, as the electronic wavefunctions change with changing nuclear configurations. According to the formalism developed by Friedrich and Person [16], this change is associated, in charge-transfer complexes with the change of mixing coefficients during a particular vibration. The difference between the dipole moment derivative,  $\frac{\partial\vec{p}}{\partial R_j}$ , and the intrinsic dipole moment derivative (that for an isolated molecule),  $\frac{\partial\vec{\mu}_N}{\partial R_j}$ , named "delocalization moment", or "delocalization charge" — is obtained in the form

$$\left(\frac{\partial\vec{p}}{\partial R_j}\right) - \left(\frac{\partial\vec{\mu}_N}{\partial R_j}\right) \approx 2b \left(\frac{\partial b}{\partial R_j}\right) [\vec{\mu}_1 - \vec{\mu}_0] = \vec{M}'_d, \quad (14)$$

where  $\vec{\mu}_1$  and  $\vec{\mu}_0$  are dipole moments of the no-bond and dative structure, respectively;  $b$  is depending on  $R_j$  through  $\beta_0$  — the resonance integral and through  $\Delta$  — the energy difference in the dative and no-bond states. The last quantity is expressed by

$$\Delta = I_D^v - E_A^v + (G_1 - G_0), \quad (15)$$

where  $I_D^v$  and  $E_A^v$  are the vertical ionization potential and the vertical electron affinity, respectively, and  $G_1 - G_0$  — the change in the electrostatic energy, that occurs when acceptor and donor molecules are brought together in the complex.

It is generally assumed, that the resonance integral  $\beta_0$ , (including the overlap integral), does not change during a symmetrical planar vibration. In the case of an acceptor molecule  $b$  is therefore dependent on  $R_j$  mainly through the vertical electron affinity. The final relation will be

$$\vec{M}'_d = 2a^2b^2 \left( \frac{\partial E_A^v}{\partial R_j} \right) \cdot \frac{1}{\Delta} [\vec{\mu}_1 - \vec{\mu}_0]. \quad (16)$$

The values  $\Delta$  and  $\mu_1 - \mu_0$  needed in our calculations have been taken from the paper by Chan and Liao [39].

How to estimate the quantities  $\frac{\partial E_A^v}{\partial R_j}$ ,  $a$  and  $b$  constitutes, however, a separate problem.

According to Friedrich and Person [16] the quantity  $\frac{\partial E_A^v}{\partial R_j}$  is equal to the slope of the tangent line to the acceptor potential curve for the dative state in the equilibrium point for the no-bond state. In the case of the diatomic acceptor molecule (that a halogen molecule is), there is one potential curve for each of the dative and the no-bond state. In the case of a polyatomic molecule (as TCNE molecule) — separate potential curves for different bonds are needed.

Next, in the case of a diatomic acceptor molecule the orbital into which an electron is transferred in the dative state, is associated with only one bond. In the case of a TCNE molecule the charge of the electron transferred in the first vacant orbital is distributed over all the existing 9 bonds. Therefore, to obtain the proper values of the quantities  $a^2$  and  $b^2$  we have to find the rates at which electron charge is concentrated on separate TCNE bonds.

Now, if the potential curve for a definite bond of  $\text{TCNE}^-$  is given by a Morse potential, the derivative evaluated in  $r_e$  is

$$\left( \frac{\partial E_A^v}{\partial r} \right)_{r=r_e} = 2D_a(\text{TCNE}^-) \cdot \beta_a \cdot \{1 - \exp[-\beta_a(r_e - r_a)]\} \cdot \exp[-\beta_a(r_e - r_a)]. \quad (17)$$

Here  $D_a(\text{TCNE}^-)$  is the dissociation energy of  $\text{TCNE}^-$ ,  $\beta_n$  is the Morse constant for  $\text{TCNE}^-$ ,  $r_e$  is the equilibrium bond distance and  $r_a$  is the anion equilibrium bond distance.

The evaluation of the set of parameters  $D_a$ ,  $\beta_a$  and  $r_a$  for the bond  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{N}$  has been based on the data obtained by Hinkel and Devlin [40] for the radical anion salts of TCNE, namely  $r_a$  has been obtained from  $r_e$  and the force constant  $k$  and  $k_a$  for the appropriate bond in TCNE and  $\text{TCNE}^-$  respectively, using the relation [41]

$$k = A \cdot e^{-Br} \quad \text{where } A \text{ and } B \text{ are constants.} \quad (18)$$

$\beta_a$  is calculated from [42]

$$\beta_a = 1.2177 \times 10^7 \omega_a \sqrt{\frac{\mu_A}{D_a}}, \quad (19)$$

where  $\mu_A$  is the reduced mass,  $\omega_a$  — the frequency in the anion and  $D_a$  is expressed in  $\text{cm}^{-1}$ .  $D_a$  is obtained from the correlation between the dissociation energy and bond length in diatomic molecules. The potential curves for the C=C bond are shown in Fig. 4.

TABLE VI

Parameters used for the estimation of the delocalization moment

a. Parameters of the potential energy curves

	C=C	C≡N
Dissociation energy in TCNE <sup>-</sup>	31200 cm <sup>-1</sup>	74.300 cm <sup>-1</sup>
Symm. stretching freq. in TCNE	1569 cm <sup>-1</sup>	2235 cm <sup>-1</sup>
Symm. stretching freq. in TCNE <sup>-</sup>	1392 cm <sup>-1</sup>	2200 cm <sup>-1</sup>
Change in bond length	0.098 Å	0.011 Å
Electron affinity derivative $\frac{\partial E_A^0}{\partial Q_i}$	2.91 eV Å <sup>-1</sup>	0.48 eV Å <sup>-1</sup>

b. Parameters associated with the complexes

	TCNE-benzene	TCNE-p-xylene
Dipole mom. in dative state	16.8 D.	16.8 D.
Energy difference, $\Delta$ ,	2.91 eV	2.50 eV
Weight of the dative structure		
C=C	0.0217	0.029
C≡N	0.0023	0.003

The total value of the approximate weight of the dative structure,  $b^2$  is assumed equal, to 0.031 for the TCNE-benzene and 0.041 for the TCNE-paraxylene complex, according to Chan and Liao [39].

TABLE VII

Charge-transfer contribution to the IR intensity

Complex	Delocalization moment	
	TCNE-benzene	TCNE-p-xylene
$M_d(r)$ for C≡N bond (D Å <sup>-1</sup> )	0.013	0.018
$M_d(r)$ for C=C bond (D Å <sup>-1</sup> )	0.722	0.095
$M_d(Q)$ for 2220 cm <sup>-1</sup> (D Å <sup>-1</sup> amu <sup>-1/2</sup> )	0.090	1.138
$M_d(Q)$ for 1554 cm <sup>-1</sup> (D Å <sup>-1</sup> amu <sup>-1/2</sup> )	0.286	0.432

The very critical point is the division of the charge between the C=C and C≡N bonds. The simplest way would seem to divide it proportionally to the bond orders, evaluated using MO coefficients. Unfortunately, as Hinkel and Devlin have pointed out, [40], the available molecular orbitals for TCNE fail in estimating the proper force constants for the anion. Therefore we have decided to base our division on the experimental data: the rate at which charge is transferred is assumed proportional to the change in the bond length, evaluated from the experimental force constants. Moreover it has been assumed, that, when an electron is transferred to the first vacant orbital of TCNE, the charge is distributed between the C=C and C≡N bonds, but does not affect the C—C bonds.

All the parameters used in the calculations are collected in Table VI. The values of the delocalization moment ( $M'_d$ ), represented with respect to the internal coordinates, as well as those, evaluated with respect to normal coordinates ( $M_d$ ) — are given in Table VII.

### 5. Experimental data

The infrared absorption spectra of TCNE solutions in benzene, para-xylene and ethyl acetate in the region of the C≡N stretching vibrations have been obtained with the help of the Hilger H 800 spectrophotometer. The concentrations ranged from 0.015 to 0.023

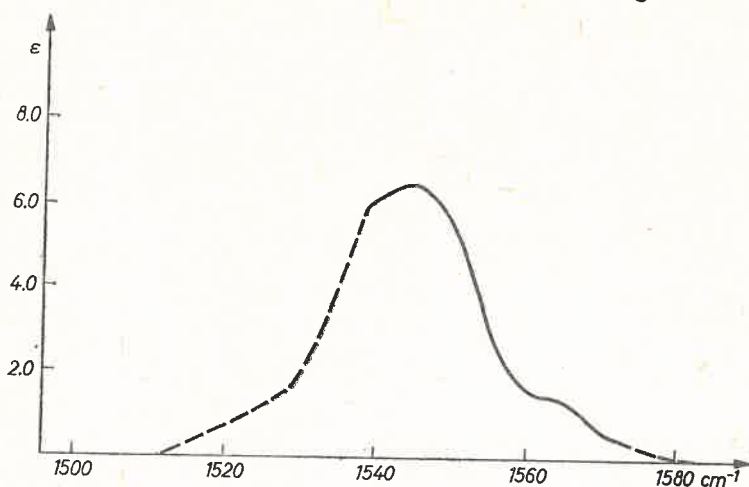


Fig. 3. The induced band in the 1500  $\text{cm}^{-1}$  region. The low frequency wing has been corrected on the basis of the assumption, that the band is symmetrical

$\text{mmol}/\text{cm}^3$ . The two observed bands near 2215 and 2250  $\text{cm}^{-1}$  have been separated graphically. The investigation of the forbidden C=C band is very difficult, because in this region there occur strong solvent bands. We have succeeded except for the case of the benzene solution. Two methods have been used:

1) the method of compensation by the absorption of the solvent placed in the reference beam; the band contour obtained in this way with the Perkin-Elmer 577 type spectrophotometer is shown in Fig. 3,

2) the method of graphical subtraction of the solvent absorption from the absorption of the solution; this time the UR20 spectrophotometer has been used.

The theoretical considerations concern a donor-acceptor pair. In the experiment however we deal with donor-acceptor pair surrounded with the donor molecules. With the aim of eliminating the effect of the internal field created by this surrounding, we have utilized the Hirota equation [43]

$$\frac{B_g}{B_{\text{sol}}} = \frac{3(2\varepsilon^2 + n^2)}{(n^2 + 2) \cdot (2\varepsilon + 1)^2}, \quad (20)$$

where  $B_g$  is the intensity in the gaseous phase and  $B_{\text{sol}}$  — the intensity in solution. The Hirota equation has this advantage over the other ones, that it accounts for the polarity

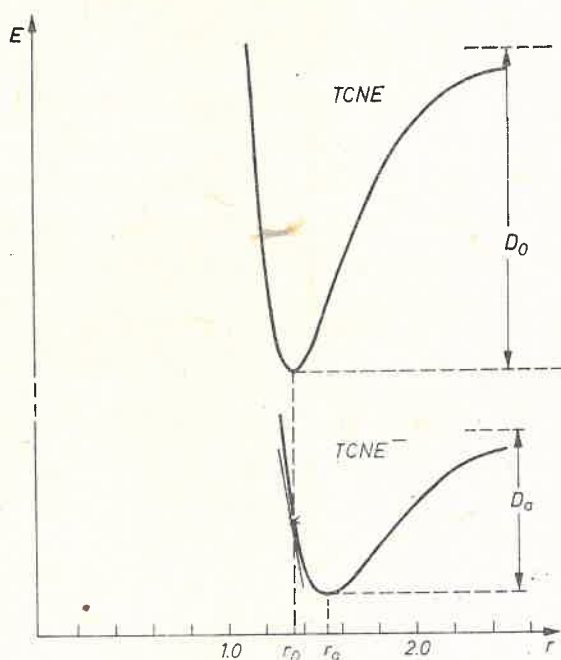


Fig. 4. The potential curves for the C=C bond of TCNE and TCNE<sup>-</sup>. The value of  $\left(\frac{\partial E_A^0}{\partial R}\right)$  is equal to the slope of the tangent line

of the solvent (important for the case of ethyl acetate). We have assumed that the intensity of the donor-acceptor pair is approximately given by the intensity evaluated for the gaseous phase. The values of the dipole moment derivatives with respect to the normal coordinates are approximately equal to  $1.1936 \sqrt{\frac{B}{N_0}} \times 10^{10} \text{ D/\AA amu}^{-1/2}$ , where  $B$  is the band intensity in cm/m mole, and  $N_0$  is the Avogadro number.



TABLE VIII

## Experimental results

Solvent	$\nu$	$B_{\text{exp}}$	$\left(\frac{\partial\mu}{\partial Q}\right)_{\text{exp}}$	$\Delta\left(\frac{\partial\mu}{\partial Q}\right)$
	cm <sup>-1</sup>	darks	$D/\text{\AA} (\text{amu}^{-1/2})$	
p-xylene	2250	2047 ± 98	0.602 ± 0.028	0.098 ± 0.046
p-xylene	2217	1296 ± 60	0.479 ± 0.022	0.130 ± 0.055
benzene	2251	1872 ± 29	0.576 ± 0.016	0.076 ± 0.034
benzene	2216	1337 ± 37	0.487 ± 0.014	0.138 ± 0.056
ethyl acetate	2256	1577 ± 56	0.504 ± 0.018	—
ethyl acetate	2221	970 ± 93	0.349 ± 0.033	—
benzene	1554	406 ± 39	0.268 ± 0.025	0.268 ± 0.025

The experimental intensity ( $Q_{\text{sol}}$ ), and the dipole moment derivatives, evaluated for the donor-acceptor pairs,  $\left(\frac{\partial\mu}{\partial Q}\right)_{\text{exp}}$  are given in Table VIII.

The experimental values,  $\left(\frac{\partial\mu}{\partial Q}\right)_{\text{exp}}$  is the sum of the intrinsic moment derivative, characteristic of an isolated molecule and a supplementary moment derivative, due to the complex formation. Since the intensity values of the gaseous TCNE are not available, we have assumed that they are not higher than the intensity in the ethyl acetate solution: the difference between the band intensity in the benzene or para-xylene solution, and that in ethyl acetate solution (the last column of Table VIII) is then considered as the lower limit of the intensity change due to the EDA complex formation.

### 6. Discussion of the results

The comparison of Table V and VII shows, that for the TCNE-benzene complex the values of the dipole moment derivative for the forbidden vibration 1554 cm<sup>-1</sup>, predicted by the charge transfer model is 12 times larger than the values predicted by the electrostatic model. This ratio is still higher for the TCNE para-xylene, complex. In the case of the forbidden vibration 2220 cm<sup>-1</sup> this ratio is nearly 2 for TCNE-benzene and nearly 3 for the TCNE-paraxylene complex.

It must be remembered however, that the values of the dipole moment derivatives, given in Table V have been calculated using the net charges +0.063 and -0.063 on the H and C atoms, respectively. The values, obtained with these parameters can be treated as the upper limit. As the lower limit — the charges evaluated by Boucher and Cremashi (-0.01 on the H atom, and +0.01 on the C atom) can be adopted. Since the dipole moment induced on the CH bond by the TCNE molecule is equal and opposite in sign, the resulting

bond dipole moment would be zero; the only electrostatic contribution to the dipole moment derivatives is then originated by the quadrupole moment, and contributes about one half of the upper limit value. In this case the predominance of the dipole moment derivative values, predicted by the charge transfer model, over those, predicted by the electrostatic model is even more drastic.

Inspection of the last column of Table VIII shows that in the case of the transition, associated with the vibration  $1554\text{ cm}^{-1}$ , the experimental value correlates very well with that, obtained using the charge-transfer model. The problem is more complicated in the case of the transition, associated with the symmetrical stretching vibration  $2220\text{ cm}^{-1}$ . The experiment does not give explicit evidence of this band, because of an allowed band occurs at  $2216\text{ cm}^{-1}$ . Table V shows, however, that the electrostatic model predicts a higher increase in dipole moment derivative for the band at  $2250\text{ cm}^{-1}$ , than for the band at  $2216(7)\text{ cm}^{-1}$ ; the experimental evidence is to the contrary. The experimental values in the last column of Table VIII for the  $2216$  (or  $2217$ )  $\text{cm}^{-1}$  vibration, (giving the lower values of the increase in the dipole moment derivative), are sufficiently high to justify the existence of the weak induced perpendicular band in this region. These conclusions are even more valid for the lower limit values of the electrostatic contribution.

It is not out of place to emphasise, that the weights  $a^2$  and  $b^2$  used in the calculations of the delocalization moment given in Table VII have been obtained upon the assumption, that all the formation energy of the complexes under study are due to the charge transfer interaction. Such an assumption is inadmissible in our case. Nevertheless the assumption of half of this  $a^2$  and  $b^2$  values would still give a sufficient conformity with the experiment.

The admissible modifications of the other parameters used, cannot refute the main conclusions of our study, which are:

1) Both models, the electrostatic and charge-transfer, are indispensable for the interpretation of the intensity change the infrared bands in our complexes.

2) In the case of the induced band at  $1554\text{ cm}^{-1}$  the role of charge-transfer is predominant.

3) The activity of the forbidden band at  $1554\text{ cm}^{-1}$ , associated mainly with the  $\text{C}=\text{C}$  valence vibration, is several times higher, than the activity of the band at  $2220\text{ cm}^{-1}$ , associated mainly with the  $\text{C}\equiv\text{N}$  valence vibration. This predominance is similar to that experimentally demonstrated for the case of the TCNE-HMB complex in a former paper by this author about the study of single crystal in polarized light (see Fig. 1 in paper [44]). As is evident from Table V this feature cannot be explained by the electrostatic polarization model.

4) The increase in intensity of the allowed  $\text{C}\equiv\text{N}$  bands is due to the electrostatic polarization by the donor molecule.

There remains the question of the change in intensity of the bands associated mainly with the  $\text{C}-\text{C}$  stretching vibration. Devlin et al., [45] have observed that the band at  $1150\text{ cm}^{-1}$  loses activity in complexes. Our calculations however predict the increase in intensity. These facts can be explained by the opposite sign of the dipole moment derivatives in an isolated molecule, which means, that the carbon atom of the  $\text{C}\equiv\text{N}$  bond becomes more positive, as the bond is stretched.

It may be noticed, that the values of the dipole moment derivatives obtained with the aid of the electrostatic model are nearly the same for the solution in benzene and in para-xylene, On the contrary, the delocalization moment depends strongly upon the donor strength. In this way the experiment on a series of complexes would allow one to determine the nature of the effect observed.

Investigations on this topic are in progress.

The author is indebted to Professor H. Poulet and Professor S. Odjot from the Paris University V and to dr P. Claverie from the Institut de Biologie Physico-Chimique in Paris for valuable, fruitful discussions. Special gratitude is due to Professor J. P. Devlin for allowing the use of his *L*-matrix for the TCNE molecule and to dr M. Krygowski for having evaluated the net charges for the para-xylene. The author is most thankful to Professr J. P. Mathieu for the use of the Coderg spectrophotometer.

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