π-Complexes. I. Charge Transfer Spectra of π-Complexes Formed by Trinitrobenzene with Polycyclic Aromatic Compounds[1]

By Michael J. S. Dewar and Arthur R. Lepley[2]

The charge transfer spectra of the π-complexes formed by trinitrobenzene with a number of polycyclic aromatic hydrocarbons, and with derivatives of 10,9-borazarophenanthrene, have been measured in potassium bromide disks. The results are interpreted in terms of simple molecular orbital theory. The molecular orbital parameters for boron are discussed.

The molecular complexes formed by aromatic compounds with agents such as chloranil or picric acid have long presented an interesting theoretical problem. In recent years it has been shown[3] that their properties can be interpreted in terms of weak covalent interaction between the π-electrons of the donor and acceptor. Most of the work in this field has been based on the valence bond approximation in which the complex formed by a donor A and an acceptor B is represented as a resonance hybrid of the uncharged aggregate (I) and the ionic structure (II) formed from it by transfer of an electron from A to B. The appearance of a new band in the spectrum of such a complex is ascribed to a transition from the ground state which is mostly I mixed with a little II to an excited state which is mostly II mixed with a little I; this transition is of charge transfer type and the complexes have accordingly been termed charge transfer complexes.

$$\begin{array}{cc} \text{A \ B} & \text{A}^+ \ \text{B}^- \\ \text{I} & \text{II} \end{array}$$

This problem can also be approached in terms of the molecular orbital treatment. Here the complex A·B is represented as a π-complex formed by interaction of the π-orbitals of A and B; since the interaction is known to be small it can be conveniently treated by using perturbation theory.[4] Consider the orbitals of A and B (Fig. 1). Interactions between the filled bonding orbitals of A and of B lead to no change in their total energy and to no net transfer of charge between A and B. Interactions of the filled orbitals of A with the empty anti-bonding orbitals of B depress the former and raise the latter, leading to a net stabilization with a simultaneous transfer of negative charge from A to B; interactions of the filled orbitals of B with the empty orbitals of A likewise lead to stabilization with a net charge transfer in the opposite direction. These interactions are inversely proportional to the difference in energy between the interacting orbitals. In complexes of this kind one component is normally a molecule of donor type (i.e., with filled orbitals of relatively high energy), the other an acceptor (i.e., with empty orbitals of relatively low energy); the main interaction is therefore between the filled orbitals

of the donor and the empty orbitals of the acceptor, as indicated in Fig. 1; this leads to a net transfer of negative charge from the donor A to the acceptor B.

The heats of formation of complexes of this kind are at least an order of magnitude less than their lowest transition energies; this suggests that the changes in energy of the orbitals in forming the complex are small compared with the spacing between the filled (bonding) and empty (anti-bonding) orbitals. The energies of the orbitals in the complex should therefore be little different from those in the separate components; all the possible transitions observed in A and B should therefore appear in the spectrum of the complex AB, and this is commonly the case. Transitions of this type are described as *locally excited*.[5] There should also be *charge transfer transitions* of electrons from a filled orbital of A into an empty orbital of B, and from a filled orbital of B into an empty orbital of A. Figure 1 indicates that transitions of the former kind may occur at lower energies than the locally excited transitions and so lead to the appearance of new absorption bands at lower frequencies. This accounts for the new bands commonly observed in the spectra of such complexes and responsible for their color.

This treatment leads to conclusions similar to those given by the valence bond approach, but it seems preferable for two reasons. First, there are cases when more than one new charge transfer band appears in the complex AB; this can be explained at once in terms of the molecular orbital approach since there should be bands corresponding to transitions between any of the occupied orbitals of A and empty orbitals of B. Secondly, the term "charge transfer complex" is misleading in that very little charge is transferred in the ground states of such complexes and in that an appreciable part of their stability may be due to back-coordination involving interactions between the filled orbitals of the acceptor and the empty orbitals of the donor. The term "π-complex" seems preferable for compounds of this type.

If the interactions between donor and acceptor are small, the transition energy ΔE_0 for the first charge transfer band should by either treatment be given by

$$\Delta E_0 = I_A - A_B + \text{constant} \tag{1}$$

when I_A is the ionization potential of A (equal to the energy of the highest occupied MO in a naive molecular-orbital approach) and A_B is the electron affinity of B (likewise equal to the energy of its

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(2) Public Health Post-Doctoral Fellow; present address: Department of Chemistry, State University of New York, Long Island Center, Oyster Bay, N. Y.

(3) For a recent review and references see G. Briegleb and J. Czekalla, *Angew. Chem.*, **72**, 401 (1960).

(4) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

(5) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, (London), **68**, 601 (1955).

lowest unoccupied orbital). If then the acceptor is kept constant, ΔE_0 should vary linearly with the ionization potential of the donor; this relation has been observed in a number of cases.[3] In the molecular orbital approach eq. 1 is replaced by the more general relation

$$\Delta E_{ij} = A_i - B_j + \text{constant} \qquad (2)$$

when ΔE_{ij} is the transition energy for the charge transfer band involving the filled orbital i of A (energy A_i) and the empty orbital j of B (energy B_j). This is equivalent to eq. 1 in the case of the first charge transfer band, for the ionization potential of the donor should be equal to the energy of its highest occupied molecular orbital.

If eq. 2 is valid, the energies of the charge transfer transitions should be predictable from simple molecular orbital theory. Thus the energies of the first charge transfer transitions for a variety of donors with a given acceptor should be a linear function of the energies of the highest occupied orbitals of the donors. The obvious way to test this prediction is to use data for polycyclic hydrocarbons. The energies of the orbitals of such a compound are of the form $(\alpha + x\beta)$; the relative energies of the highest orbital depend on the product $x\beta$ where x is a number calculated theoretically and β is an empirical parameter (resonance integral). Hence if eq. 2 holds, a plot of ΔE_{ij} vs. x should be a straight line, independent of the values of any empirical parameters. The slope of this line should incidentally provide an estimate of β.

We became interested in this problem in another connection. A number of novel heteroaromatic boron compounds have been prepared recently[6] and we wished to see if their unusual properties could be interpreted by the simple molecular orbital approach. For this we needed to know the necessary parameters for a Hückel treatment, in particular the Coulomb integral of boron and the resonance integrals of bonds from boron to carbon, nitrogen, and oxygen. To do this we needed experimental estimates of quantities which could be calculated in terms of these parameters; if the arguments given above are correct, and if eq. 2 were calibrated by using data for a variety of hydrocarbons, the charge transfer spectra of our boron compounds would immediately provide estimates of the energies of their highest occupied molecular orbitals— which can of course be calculated theoretically.

Very few data of this kind are available at present. Nearly all the work on charge transfer spectra of complexes has been carried out with donors carrying substituents, e.g., polymethylbenzenes. This is because most of the previous work has been based on eq. 1; to use this one must know the ionization potentials of the donors—and these are known for only a few polycyclic aromatic hydrocarbons. However the limited evidence for these was encouraging. Their charge transfer bands had been shown[3] to follow eq. 1 and Streitwieser[7] has pointed out that their ionization potentials can be calculated quite well by the Hückel

(6) For a recent paper in the series and references see M. J. S. Dewar and P. M. Maitlis, J. Am. Chem. Soc., 83, 187 (1961).
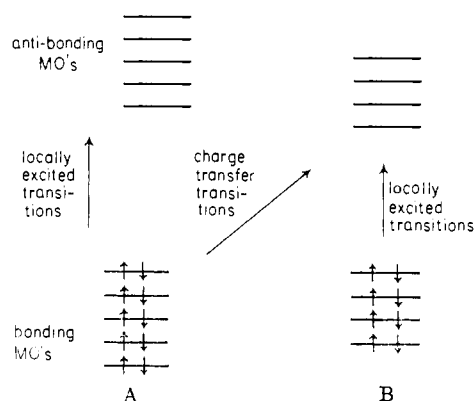
(7) A. Streitwieser, Jr., ibid., 82, 4123 (1960).

Fig. 1.—Orbital energies and transitions in a molecular complex formed by a donor A and acceptor B.

method on the assumption that the ionization potential is equal to the energy of the highest occupied orbital.

We have therefore measured the charge transfer spectra of the trinitrobenzene complexes formed by a wide range of polycyclic aromatic hydrocarbons containing up to seven fused rings. The spectra were measured in potassium bromide disks, a technique which was first introduced into ultraviolet spectroscopy by Wyman[8] and which proved particularly convenient here, for the complexes could usually be formed in situ by grinding together a mixture of the components with potassium bromide in a small ball mill.

Experimental

Materials.—Sym-Trinitrobenzene was purified by heating with dilute nitric acid followed by repeated recrystallization from alcohol. Phenanthrene was purified by treatment with maleic anhydride in hot xylene. Anthracene was codistilled with ethylene glycol and then crystallized from 95% ethanol. Pyrene was zone-refined. Other hydrocarbons were used in the form obtained from the Aldrich Chemical Co. The preparation of the borazarophenanthrene derivatives has been reported elsewhere.[6]

Spectra.—Measurements were made from 300–700 mμ in potassium bromide disk[8] using a Cary model 14 spectrometer. Samples were prepared by weighing about 10^{-5} mole (2–5 mg.) of the hydrocarbon and trinitrobenzene, or of the preformed π-complex, and grinding for 15 seconds with an accurately known amount (approximately 430 mg.) of infrared quality potassium bromide. Mixtures for pellet preparation were made by diluting a weighed amount (5–40 mg.) of sample to 150 mg. with potassium bromide and grinding. Standard infrared techniques were used in pressing pellets. The clear disks (concentration 5×10^{-4} to 4×10^{-6} molar) were dipped in paraffin oil and balanced against standard potassium bromide blanks at 700 mμ. No attempt was made to compensate for uncomplexed material. Spectra were measured on pure 1,3,5-trinitrobenzene, each pure donor and the 1:1 molar mixture or complex of 1,3,5-trinitrobenzene with each donor.

Results

Table I lists the wave lengths of the charge transfer bands for the twenty π-complexes studied, together with values reported previously by Bier[9] for the complexes of benzene and naphthalene. The listed limits of error were estimated visually from the spectrometer traces. The fourth column gives the measured extinction coefficients; these are of course lower limits since we could not estimate the extent to which the hydrocarbon and trinitro-

(8) G. M. Wyman, J. Opt. Soc. Am., 45, 965 (1955).
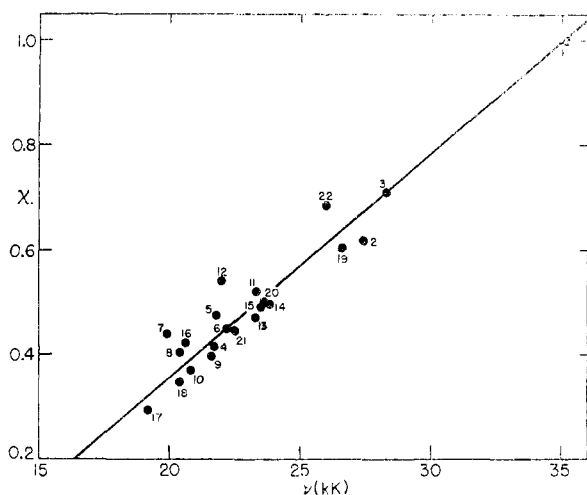
(9) A. Bier, Rec. trav. chim., 75, 866 (1956).

Fig. 2.—Plot of the frequencies (v) of the charge transfer bands of trinitrobenzene complexes against the molecular orbital parameter x of eq. 3.

benzene had interacted to form a complex. However, the remarkable uniformity of the extinction coefficients suggests the complex formation may well have been essentially complete. The last column lists energies calculated for the highest occupied orbitals by the Hückel method with neglect of overlap. The values given are those for x in the expression for the orbital energy E_m.

TABLE I

CHARGE TRANSFER SPECTRA FOR HYDROCARBON TRINITRO-
BENZENE COMPLEXES AND ENERGIES OF HIGHEST OCCUPIED
MO'S OF THE HYDROCARBONS

Compound	Symbol	Wave length of charge transfer band, mμ	log ϵ	Calcd. energy of highest occupied MO[a]
Benzene	1	284[b]	..	1.000
Naphthalene	2	365[b]	..	0.618
Acenaphthylene	3	353 ± 10	3.3	.637
Anthracene	4	460 ± 5	3.3	.414
Azulene	5	458 ± 5	3.0	.477
1,2-Benzanthracene	6	450 ± 10	3.02	.452
1,12-Benzoperylene	7	503 ± 10	3.23	.439
3,4-Benzotetraphene	8	490 ± 15	3.09	.405[c]
1,2-Benzopyrene	9	464 ± 10	3.2	.497[c]
3,4-Benzopyrene	10	480 ± 15	3.43	.371[c]
Chrysene	11	430 ± 10	3.05	.520
Coronene	12	455 ± 10	3.47	.539
1,2,5,6-Dibenzanthracene	13	430 ± 15	3.43	.473
1,2,3,4-Dibenzanthracene	14	420 ± 30	3.3	.499
1,2,7,8-Dibenzanthracene	15	425 ± 10	3.26	.491
1,2,4,5-Dibenzopyrene	16	485 ± 15	3.42	.422[c]
Naphthacene	17	520 ± 2	3.56	.294
Perylene	18	490 ± 15	3.42	.347
Phenanthrene	19	376 ± 5	3.1	.605
Picene	20	422 ± 30	..	.501
Pyrene	21	445 ± 5	2.84	.445
Triphenylene	22	384 ± 5	3.2	.684
10-Hydroxy-10,9-boraza-rophenanthrene		425 ± 10	2.9	...
10-Methyl-10,9-boraza-rophenanthrene		420 ± 10	2.7	...

[a] Ref. 10. [b] Ref. 9. [c] Dr. L. Snyder, private communication.

$$E_m = \alpha + x_m\beta \qquad (3)$$

Most of the values for x_m were taken from a recent compilation[10]; other values were calculated by Dr. L. Snyder at Bell Telephone Laboratories.

Discussion

Figure 2 shows a plot of the frequencies of the charge transfer bands against the calculated orbital energies (as measured by the parameter x). The points are identified by numbers following the code in the second column of Table I.

All but four of the points lie on a straight line within the estimated limits of error; the exceptions are azulene (5), 1,12-benzoperylene (7), coronene (12) and triphenylene (22). The point for naphthalene (2) also lies some way off the line, but no limits of error were quoted in the measurement reported[9] for the charge transfer spectrum of its trinitrobenzene π-complex.
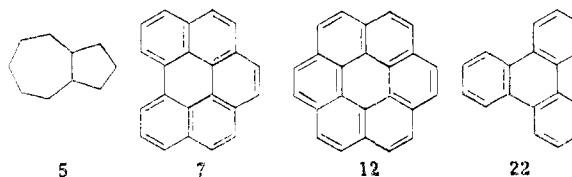
It is difficult to see any common feature that might distinguish these compounds from the rest. The deviations are in any case quite small and can probably be ascribed to the general inaccuracy of the simple Hückel method. Streitwieser[7] has pointed out that the simple Hückel method should not be used to estimate ionization potentials since it neglects the changes in electronegativity of carbon atoms due to the positive charges they acquire in the resulting ion. Allowance can be made for these by a method originally due to Wheland and Mann[11]; Streitwieser found that in many cases this refinement gave improved estimates of ionization potentials. In the case of polycyclic aromatic hydrocarbons, however, the Wheland–Mann procedure (ω-technique) gave results almost identical with those from the simple Hückel treatment. We are investigating this matter further but without much hope that the use of ionization potentials calculated by Streitwieser's ω-technique will lead to any noticeable improvement. Extrapolation of the straight line in Fig. 2 to $\nu = 0$ should give an estimate of the energy (E_0) of the lowest unoccupied molecular orbital of trinitrobenzene

$$E_0 = \alpha - 0.46\beta \qquad (4)$$

This value seems reasonable. From the slope of the line we may estimate the value of the parameter β

$$\beta = -3.00 \text{ e.v.} \qquad (5)$$

This lies nicely in the range of "spectroscopic" values for β. Thus the average excitation energy for the first four singlet–singlet transitions in benzene should be equal to 2β in the Hückel approximation; this gives a value of -3.1 e.v. for β.

(10) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants."

(11) G. W. Wheland and D. E. Mann, J. Chem. Phys., 17, 264 (1949).

If eq. 2 holds and can be embodied in the straight line of Fig. 2, we may estimate the energies of the highest occupied molecular orbitals of the borazarophenanthrene derivatives from the frequencies of the charge transfer bands of their trinitrobenzene π-complexes; we find in this way

10-hydroxy-10,9-borazarophenanthrene, $\alpha + 0.515\beta$ (6)

10-methyl-10,9-borazarophenanthrene, $\alpha + 0.525\beta$ (7)

Since the effect of hydroxyl should be much greater than that of methyl we may estimate that for the parent compound the energy of the highest occupied molecular orbital is given by

$$10,9\text{-borazarophenanthrene, } \alpha + 0.53\beta \qquad (8)$$

For the isoconjugate hydrocarbon, phenanthrene, the energy of the highest occupied molecular orbital is

$$\text{phenanthrene, } \alpha + 0.605\beta \qquad (9)$$

The difference between these can be estimated in terms of the various integrals involving boron by the perturbation method introduced by Coulson and Longuet-Higgins.[12] The perturbations are of two kinds; those arising from the difference in electronegativity between carbon and boron or nitrogen, and those arising from differences between the resonance integrals for the various kinds of bonds. The over-all change δE_1 in orbital energy due to the first set of terms is given by

$$\delta E_1 = a_9{}^2 (\alpha_C - \alpha_N) + a_{10}{}^2(\alpha_C - \alpha_B) \qquad (10)$$

where α_C, α_N, α_B, are the coulomb integrals of carbon, nitrogen and boron, respectively, and a_i is the coefficient of the $2p$-orbital of atom i in the molecular orbital in question. The corresponding contribution δE_2 due to changes in the resonance integrals is given by

$$\delta E_2 = a_9 a_{10} (\beta_{BN} - \beta_{CC}) + a_9 a_{14} (\beta_{CN} - \beta_{CC}) + \\ a_{10} a_{11} (\beta_{CB} - \beta_{CC}) \qquad (11)$$

where β_{XY} is the resonance integral for the bond XY. The values of the various coefficients are[10]

$$a_9 = a_{10} = 0.415 \qquad (12)$$

$$a_{11} = a_{14} = 0.164 \qquad (13)$$

Now the differences in ionization potential between carbon and boron and between nitrogen and carbon are similar; the same should be true for their coulomb integrals. Since $a_9 = a_{10}$, δE_1 should therefore vanish. One might likewise expect the second and third terms in eq. 11 to cancel. This conclusion is supported by a comparison of the transition energies of the first π–π transitions for phenanthrene and 10,9-borazaro-

(12) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **A192**, 16 (1947); **A193**, 447, 456 (1948); **A195**, 188 (1948).
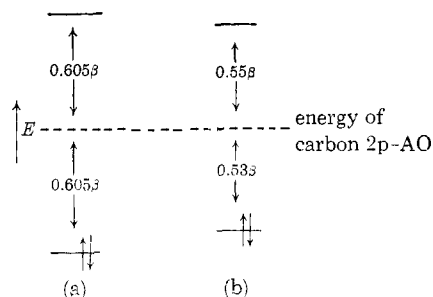

Fig. 3.—Energies of highest occupied and lowest unoccupied MO's for phenanthrene (a) and 10,9-borazarophenanthrene (b).

phenanthrene. The energies of the highest occupied and lowest unoccupied orbitals of phenanthrene are, respectively, 0.605β and -0.605β, corresponding to a transition energy of 1.21β. The experimental value is 4.24 e.v. The experimental value for the transition energy of 10,9-borazarophenanthrene is 3.79 e.v., which should correspond to an energy difference of 1.08β. Since the highest occupied orbital has been estimated to have an energy of 0.53β, that of the lowest unoccupied orbital should be -0.55β. These conclusions are summarized in Fig. 3.

It will be seen that the center of gravity of the two orbitals for borazarophenanthrene is almost identical with that for phenanthrene. Any changes in the electronegativity of atoms in phenanthrene should alter the energies of both the highest occupied and the lowest unoccupied orbitals in a similar manner with corresponding changes in the center of gravity of the two. The fact that the center of gravity is not shifted appreciably in borazarophenanthrene is therefore consistent with the idea that the effects of boron and nitrogen are equal and opposite.

The whole of the difference (0.075β) between the energies of the highest occupied orbitals of phenanthrene and of 10,9-borazarophenanthrene must then be ascribed to the first term in eq. 11. Hence

$$\beta_{BN} = \beta \left(1 - \frac{0.075}{(0.415)^2}\right) = 0.57\beta \qquad (14)$$

This seems not unreasonable, for the resonance interactions across the 9,10-band will be inhibited in borazarophenanthrene by the charge separation involved; the 9,10-bond should consequently be much longer than that in phenanthrene and its resonance integral correspondingly less.