that when a theory that explains these cases is formulated, it will also be applicable to the case of the heavier third bodies. However, the theory advanced here is sufficiently successful that we feel justified in advancing it at the present time.

**Acknowledgments.**—One of us (D.B.) is indebted to the National Science Foundation and the General Electric Company for Fellowships. We are grateful to Mr. Rolf Engleman and Mr. Ray Taylor for their assistance with the computations. We appreciate the support of the O.N.R. We are grateful to Dr. James Keck for constructive criticism and discussion.

Pasadena, Calif.

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[Contribution from Coates Chemical Laboratories, Louisiana State University, and the Department of Chemistry, The Florida State University]

# Energy Transfer in Molecular Complexes of *sym*-Trinitrobenzene with Polyacenes. I. General Considerations[1]

By S. P. McGlynn[2] and J. D. Boggus

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The emission spectra of $\pi$-complexes of aromatics with *sym*-trinitrobenzene have been studied. It is shown that after irradiation in the charge-transfer band, two emissions occur: one the reverse of the charge-transfer absorption, the other from a triplet level of the uncomplexed aromatic. Absorption spectra of complexes, their total emission spectra and phosphorescence emissions are described. Theoretical considerations of the processes involved lead us to presume that after excitation in the charge-transfer band, some intersystem crossing occurs to a dissociative triplet level of the complex. The resultant production of uncomplexed aromatic in its lowest triplet state then gives rise to the observed phosphorescence. State correlation diagrams and plots of ionization potential of aromatic *versus* the energy of the charge-transfer absorption are also described.

## Introduction

The origin of the emission spectrum characteristic of many $\pi$-complexes of *sym*-trinitrobenzene (TNB) with aromatics is to a large extent uncertain. Reid[3] observed a general parallelism of the emission spectra of such complexes with the T → S luminescence of the free uncomplexed aromatic component; since the anthracene–TNB complex had an emission extending from 5200 Å. into the infrared, he assigned, on the basis of the above parallelism, an energy of 19000 cm.$^{-1}$ to the lowest triplet state of anthracene. An energy of 14700 cm.$^{-1}$ already had been assigned to this state by Lewis and Kasha,[4] and this value was later affirmed[5] by vibrational analyses of the phosphorescence spectra of anthracene and its derivatives. Despite this exception of the anthracene–TNB complex, the great majority of the other complexes studied[6] did have emissions corresponding almost exactly to the T → S luminescence of the aromatic components. Indeed the remarkable spectral coincidence was interpreted as meaning that the triplet level of the aromatic was almost unaffected energy-wise in the complexing process.[7,8]

Bier and Ketelaar[9] noted that the emission and absorption spectra of both anthracene–TNB and phenanthrene–TNB were approximate "mirror images." They concluded that both processes involved the same two levels, that is that the emission process was the reverse (E → N) of the charge-transfer absorption (E ← N). This suggestion, however, did not meet with a general acceptance.[10] More recently Czekalla, Briegleb and collaborators[11] have extended the work of Bier and Ketelaar. These authors investigated the molecular compounds of hexamethylbenzene with each of eight different acceptor molecules ("acceptor" in the Lewis acid–base sense). The charge-transfer absorption of the complex shifted to the red as the electron affinity of the acceptor component increased; and the emission spectrum red-shifted similarly so that in each case the "mirror-image" relation was maintained. There remains then but little doubt that, at least for complexes of hexamethylbenzene, the emission is a charge-transfer (E → N) emission.

For the particular complex tetrachlorophthalic anhydride–naphthalene it was possible[11] because of a large spectral separation, to distinguish two emissions after excitation with Hg 3650: one the reverse of the charge-transfer absorption with half life $\tau = 10^{-9}$ sec, and the other corresponding to the phosphorescence of naphthalene with an unchanged half-life of a few seconds.[12,13]

In view of these experimental results, a reasonable interpretation would seem to be: absorption in the charge-transfer band is followed either by the converse emission, or by intersystem crossing[14] to a

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(1) Portions of this research are taken from S. P. McGlynn. Ph.D. Dissertation, The Florida State University, Jan., 1956, and J. D. Boggus, M.S. Thesis, The Florida State University, Jan., 1956. The research was done under Contract AF-18(600)-678 between the Office of Scientific Research, U. S. Air Force, and the Florida State University.

(2) Reprints available from SPM, Coates Chemical Laboratories, Louisiana State University, Baton Rouge 3, La.

(3) C. Reid, *J. Chem. Phys.*, **20**, 1212, 1214 (1952).

(4) G. N. Lewis and M. Kasha, This Journal, **66**, 2100 (1944).

(5) S. P. McGlynn, M. R. Padhye and M. Kasha, *J. Chem. Phys.*, **23**, 593 (1955); M. R. Padhye, S. P. McGlynn and M. Kasha, *ibid.*, **24**, 588 (1956).

(6) M. M. Moodie and C. Reid, *ibid.*, **22**, 252 (1954).

(7) L. E. Orgel, *Quart. Rev.* (*London*), **8**, 442 (1954).

(8) It was assumed, of course, that emission occurred from a triplet level of the complex which was approximately described as a product of the ground state wave function (${}^1A_{1g}$) of TNB and the first excited triplet state (${}^3B_{2u}$) of anthracene. The energy of this level of the complex was supposed to be only slightly different from its energy at infinite separation of the components.

(9) A. Bier and J. A. A. Ketelaar, *Rec. trav. chim.*, **73**, 264 (1954); A. Bier, *ibid.*, **75**, 866 (1956).

(10) H. Sponer, *Ann. Rev. Phys. Chem.*, **6**, 193 (1955).

(11) J. Czekalla, G. Briegleb, W. Herre and R. Glier, *Z. Elektrochem.*, **61**, 537 (1957).

(12) J. Czekalla, *Naturwissenschaften*, **43**, 467 (1956).

(13) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955); J. Czekalla, A. Schmillen and K. J. Mager, *ibid.*, **61**, 1053 (1957).

(14) M. Kasha, *Faraday Soc. Disc.*, **9**, 14 (1950).

dissociative level of the complex which yields the aromatic in its first excited triplet state. The aromatic hydrocarbon then phosphoresces.

We have arrived at virtually the same conclusions from a study of complexes of TNB with naphthalene, anthracene, phenanthrene and carbazole. This study was both experimental and theoretical.

## Experimental Results

It is not our intention to report detailed experimental data here.[15] Rather we will give a brief resume of the more important experimental facts and then elaborate on these on the basis of the Mulliken charge-transfer theory of $\pi$-complexing.[16] The results are presented for the anthracene–TNB complex, which is fairly typical of the other complexes studied. The observations made on this system were:

(a) The charge-transfer absorption band of the complex occurs at 4,600 Å. with $\epsilon_{max}$ 1500.

(b) The complex was dissolved in a 1:1 v./v. ethyl ether–isopentane solution, cooled to −190° and irradiated with filtered light of band pass 4000–4800 Å. ($\lambda_{max}$ 4350 Å.) from a 1 kw. AH-6 water-cooled mercury lamp. Photography of the resultant emission required 15 minutes. The emission was a broad continuum extending from 5400 to 8200 Å. and similar in most respects to that obtained by Reid.[3] An overlying fine banded structure was observable in the longer wave length region of the continuum. The spectrograph was a Steinheil instrument in a Raman setting.

(c) Excitation of the complex under similar conditions to (b) above, but with a phosphoroscope interposed between light source and spectrograph, yielded an emission which required 2 hr. to photograph. This phosphorescence was very slightly blue shifted from that of pure anthracene,[5] but even though slightly more diffuse it corresponded accurately in vibrational detail to that of the anthracene.

(d) Excitation of pure anthracene dissolved alone in the ether–isopentane glass, and under the same conditions as (b) and (c) above, produced no observable emission, even with exposure times of 24 hr. and wide slit (1 mm.). Similar excitation of an ether–isopentane glass containing only TNB, and exposure for 20 hr., produced no trace of a photographic image.

(e) Subtraction of the phosphorescence (c), appropriately corrected, from the total emission (b) gave a resultant fluorescence which was a good "mirror-image" of the charge-transfer absorption.

(f) The lifetime of the phosphorescence (c) was of the same order of magnitude as that of pure anthracene and certainly not less than $10^{-3}$ sec. as evidenced by its observation in a phosphoroscope of $10^{-4}$ sec. resolving time. The lifetime of the total emission (b), on the other hand, is $10^{-9}$ sec.[13]

## Theoretical Results

The most complete consideration of nitro-complexes thus far[13] suggests that charge-transfer interaction is responsible for some 50% of the stabilization energy of the ground state.[17] The wave function (WF) of the ground or normal state of a donor–acceptor complex may be approximately written[16]

$$\Phi_N = a\Phi_0 + b\Phi_1$$

where $\Phi_0$ is the no-bond WF $\Phi(A, B)$ and may be presumed descriptive of such dipole-induced dipole effects, closed shell repulsions and such perturbation effects of higher order (*i.e.*, London forces) as occur when the two components are brought together, each in its singlet ground state, to the equilibrium internuclear distance $r_{AB}$. A is the Lewis Acid and B the Lewis Base. $\Phi_1$ is the singlet dative WF, $\Phi(A^- — B^+)$, which includes the effect of attractive ionic forces, chemical bonding between the odd electrons, etc. We choose to ignore other structures such as $A^{*+} — B^-$ or $A^+ — B^{*-}$, where the star implies excited states of either $A^+$ or $B^-$, which may contribute to $\Phi_N$ or $\Phi_E$, also.[18] The WF of the charge-transfer excited state is now

$$\Phi_E = a^*\Phi_1 - b^*\Phi_0$$

where $a^* \simeq a \simeq 1$, and where $b^* \simeq b$ is very nearly zero.

The existence of a new absorption band characteristic of the complex alone and corresponding to the transition $\Phi_E \leftarrow \Phi_N$ (or E ← N absorption) can now be predicted. This absorption, despite the small resonance effect, can be expected to be intense because of the large transition moment lengths associated with it.

The no-bond WF may be written

$$\Phi_0 = (n!)^{-1/2} | \varphi_B(1)\bar{\varphi}_B(2)\varphi_3(3)\dots\bar{\varphi}_n(n) |$$

where $n$ is the total number of electrons in the complex, and the $\varphi$'s are the MO's, separately normalized. $\varphi_B$ is the *highest* energy *filled* MO of the *base* and $\varphi_3, \dots, \varphi_n$ are those MO's of either A or B which are unaffected by the excitation $\Phi_1 \leftarrow \Phi_0$. The *bar* denotes spin $\beta$; no *bar* denotes spin $\alpha$. The dative WF may be written

$$\Phi_1 = (\Phi_I + \Phi_{II})/(2 + 2S^2{}_{AB})^{1/2}$$

where

$$S_{AB} = \int \varphi_A{}^*\varphi_B d\tau$$

$$\Phi_I = (n!)^{-1/2} |\varphi_B(1)\bar{\varphi}_A(2)\varphi_3(3)\dots\bar{\varphi}_n(n) |$$

$\Phi_I$ differs from $\Phi_0$ only in that an electron has been transferred from $\varphi_B$ to the *lowest* energy *unfilled* MO of the *acid*, $\varphi_A$. $\Phi_{II}$ differs from $\Phi_I$ only in the orbital interchange of $\varphi_A$ and $\varphi_B$.

A triplet state also derives from the charge-transfer process, again describable approximately as

$$\Phi_2(M_S = 0) = (\Phi_1 - \Phi_{II})/(2 - 2S^2{}_{AB})^{1/2}$$

where $M_S = 0$ indicates this to be the component of the triplet state with spin component zero. In the cases we consider, the three components will be approximately degenerate. $\Phi_2$ will not interact with $\Phi_0$ because of spin-orthogonality.

A certain similarity between the formalism used here to describe the charge-transfer state and the simple Heitler–London treatment of $Li_2$ is to be noted. Our basis is MO's rather than AO's, yet the neglect of the core interactions in $Li_2$ is comparable to the neglect of all electron interactions in the complex except those in $\varphi_A$ or $\varphi_B$. In the case of weak interactions this neglect is expected to be quite valid, and it is on this basis that the triplet state ($^3E$) is drawn higher in energy than the $^1E$ state in Fig. 2.

Let us consider anthracene–TNB in particular. The three components of the presumed no-bond state of the complex which arises from the $^3B_{2u}$-

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(15) Paper II in this series. In preparation for publication.

(16) R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); *ibid.*, **74**, 811 (1952); *J. Chem. Phys.*, **19**, 514 (1951); *J. Phys. Chem.*, **56**, 801 (1952); *J. chim. phys.* (*France*), **51**, 341 (1954).

(17) In this respect see, however, earlier papers of Briegleb, for example: G. Briegleb and J. Kambeitz, *Naturwissenschaften*, **22**, 105 (1934), and the more recent work of H. Murakami, *Bull. Chem. Soc. Japan*, **26**, 441 (1953); **27**, 268 (1954); **28**, 577 (1955).

(18) However, in the future in expanding $\Phi_0$ or $\Phi_1$ in terms of MO's we will consider these MO's as the one electron eigenfunctions of the Hamiltonian for either TNB alone or anthracene alone. This is done to facilitate symmetry considerations and is not expected to introduce any error.

$(D_{2h})$ state of anthracene and the $^1A_{1g}(D_{3h})$ ground state of TNB may be written

$$\Phi_3(M_S = 0) = (\Phi_{111} - \Phi_{IV})/(2 - 2S^2_{BB'})^{1/2}$$

where

$$S_{BB'} = \int \varphi_B{}^* \varphi_B{}' d\tau$$
$$\Phi_{111} = (n!)^{-1/2} |\varphi_B(1)\overline{\varphi}_B{}'(2)\varphi_3(3)\ldots\overline{\varphi_n}(n)|$$

and differs from $\Phi_{IV}$ only in the orbital interchange of $\varphi_B$ and $\varphi_{B'}$. $\varphi_B$ and $\varphi_{B'}$ are the two unfilled MO's of that configuration of anthracene which gives rise to the $^3B_{2u}$ state. A knowledge of the geometry of the complex is necessary before we can say to what symmetry species $\Phi_3$ belongs. In any case $\Phi_2$ will not interact with $\Phi_3$ unless $\Phi_3$ is totally symmetric with respect to the point group of the complex.[19] It is expected that these two triplet states will be important in considerations of energy degradation. There is a corresponding singlet state of the complex given by

$$\Phi_4 = (\Phi_{111} + \Phi_{IV})/(2 + 2S^2_{BB'})^{1/2}$$

It is of energy 26700 cm.$^{-1}$ when the complexing coördinate is infinity.[20] It should be noted that there is no *a priori* reason why the WF's $\Phi_3$ and $\Phi_4$ should be of no-bond type. They are such only because we assume no unpairing of the TNB electrons. This assumption is probably not quite true.

The energies of the combinations A,B, A,B($^3B_{2u}$) and A,B($^1B_{2u}$) at $r_{AB} = \infty$ are known experimentally. Thus, if the minimum in the potential energy curve of the ground state of the complex is designated the zero of energy, the energy of A,B is[13] 1540 cm.$^{-1}$, of A,B($^3B_{2u}$) 16470 cm.$^{-1}$ and A,B-($^1B_{2u}$) 28240 cm.$^{-1}$. The energy of the $A^-,B^+$ combination at $r_{AB} = \infty$ is approximately 55500 cm.$^{-1}$, a value which may be arrived at in two ways. Thus from the ionization potential[21] of 7.83 e.v. and an estimate of 1.1 e.v. for the electron affinity of TNB (see appendix), we obtain a value of 55640 cm.$^{-1}$ Conversely, we may work backward. The position of the charge-transfer state, $^1E$, is 22300 cm.$^{-1}$; the electrovalent attractive force between the two ionic species in the $^1E$ state as estimated from the orbital charge distributions in TNB$^-$ and in the anthracene cation is 3.4 e.v. ($r_{AB}$ = 3.5 Å.); the overlap[22] of two $2p_z$ orbitals at a distance of centers of 3.5 Å. is $S(2p_z, 2p_z) = 0.09$, leading to a covalent binding energy for six such orbital pairs of about 0.5 e.v.; in this manner a value of 54000 cm.$^{-1}$ is obtained for the energy of $A^-$, $B^+$.

It now remains to introduce symmetry considerations. Two possible highest symmetry structures are envisioned for the complex. These are of sandwich type with the planes of both the partners parallel because of the dipole–induced-dipole orientation effects. They belong to point groups $C_{1h}$ and $C'_{1h}$, respectively (see Table I). The axes are defined in Fig. 1. The ground state of TNB$^-$ (see Appendix) is $^2E''$ in $D_{3h}$, and that of the anthracene cation is $^2B_{2g}$ in $D_{2h}$. These transform as

$$^2E''(D_{3h});\ ^2A', ^2A''(C_{1h} \text{ or } C'_{1h})$$
$$^2B_{2g}(D_{2h});\ ^2A'(C_{1h}),\ ^2A''(C'_{1h})$$

in the point group defined by the complex. The lowest excited states of anthracene $^{1,3}B_{2u}(D_{2h})$ transform as $^{1,3}A''$ $(C'_{1h})$. The lowest excited singlet state of TNB of $n,\pi^*$ type is either $^1A'$ or $^1A''$ $(C'_{1h})$.

TABLE I

POINT GROUPS DEFINED

| $C_1h$ | E | $\sigma_{zx}$ | Axes | $C'_1h$ | E | $\sigma_{zy}$ | Axes |
|---|---|---|---|---|---|---|---|
| A′ | 1 | 1 | $z,x$ | A’ | 1 | 1 | $z,y$ |
| A″ | 1 | −1 | $y$ | A″ | 1 | −1 | $x$ |

Using the above energy and symmetry considerations, we have plotted Fig. 2 for the anthracene–TNB complex belonging to point group $C'_{1h}$. A number of points are to be noted. Potential crossing occurs between the $^3N^*(^3A'')$ state which correlates with $^3B_{2u}$ of anthracene, and the $^1E$ state which is shown correlating with $^2B_{2g}$ of $B^+$. Thus immediately following the charge-transfer (E ← N) absorption, process (i), energy should revert by intersystem crossing from the $^1E(^1A')$ state of the complex to the $^3N^*(^3A'')$ state. The vibrational energy of this state is now greater than its dissociation energy; accordingly production of free anthracene in its $^3B_{2u}$ state and of free TNB in its ground state should occur rather rapidly after crossover. The phosphorescence emission of anthracene, $^3B_{2u} \rightarrow {}^1A_{1g}$, should then occur with practically the same lifetime as that of pure anthracene. This is denoted process (iii) in Fig. 2. This intersystem conversion of energy competes of course with the emission process (ii), which is a charge-transfer fluorescence. We thus conclude that immediately following excitation in the E ← N band, there should occur not only a strongly allowed fluorescence (ii), but also the lowest energy T → S emission (iii) of the uncomplexed anthracene. These conclusions accord well with experiment. The slight diffuseness of the phosphorescence may be due to some vibrational inactivation of the $^3N^*$-$(^3A'')$ state of the complex and consequent emission before dissociation.

It is perhaps appropriate to make the following point here. If ionic–no-bond resonance is a primary stabilizing effect in the ground state of the complex, the charge-transfer state must be of the totally symmetric species. This condition can be fulfilled for any 1:1 complex of anthracene since the maximal geometric symmetry is so low. It will not, however, be generally the case for complexes where higher geometric symmetries are possible (*cf.* benzene–$Cl_2$). In this particular instance the maximal geometric symmetry will be limited by the necessity of resonance. However, any configuration of lesser symmetry, where permitted, can exist. All that the resonance condition implies is a knowledge of the higher geometries possible. All other appropriate geometric configurations will exist to some extent in thermodynamic equilibrium.

**Benzene–TNB Complex.**—The maximal geometric symmetry is $C_{3v}$. The ground states of

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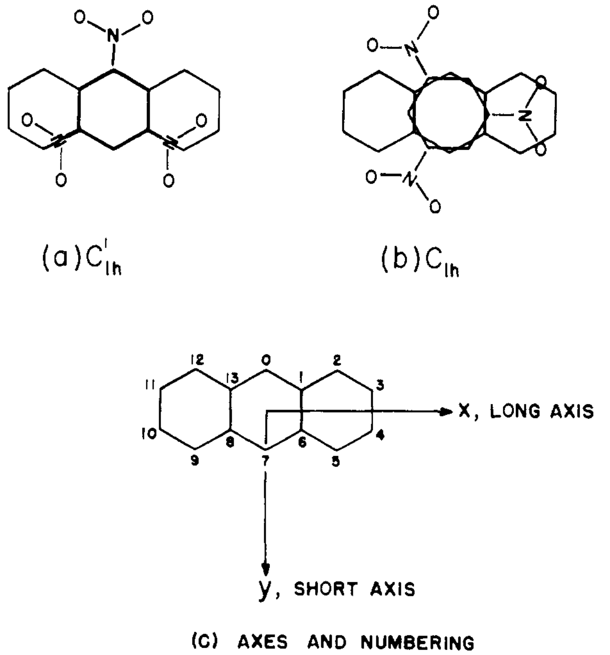
[19] This assertion is true only if we presume the ionic–no-bond resonance necessary for complex formation.

[20] E. Clar and Ch. Marschalk, *Memoires Presentes a la Soc. Chim.*, **17**, 434 (1950).

[21] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[22] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949). Self-consistent-field $2p_z$ AO overlap integrals were used. These SCF AO's give quite different, and presumably better, $S$ values than the corresponding Slater AO's at large $r_{AB}$ distances.



(a)$C'_{1h}$ (b)$C_{1h}$

(C) AXES AND NUMBERING

Fig. 1.—The two highest geometrically symmetric forms of the anthracene–TNB complex are depicted in (a) and (b). The heavy lines in the case of (a) merely indicate the positioning of TNB *directly* above the central hexagon of anthracene. The choice of axes in (c) is that of McClure, Craig, Ross and Sponer and is to be distinguished from that of Moffitt and Platt.

$TNB^-$ and the benzene cation transform as

$$^2E''(D_{3h});\ ^2E(C_{3v})$$
$$^2E_{1g}(D_{6h});\ ^2E(C_{3v})$$

Geometry $C_{3v}$ is thus quite allowed by the ionic-no-bond resonance condition. The lowest triplet state of benzene, $^3B_{1u}(D_{6h})$ or $^3A_1(C_{3v})$, lies at 30574 cm.$^{-1}$. The E ← N transition is of energy 33300 cm.$^{-1}$. The lowest singlet state of TNB ($n,\pi^*$ type) is at energy higher than 25000 cm.$^{-1}$ and can be of species E,$A_1$ or $A_2$ in $C_{3v}$. Consequently, since incipient crossing of either of the potential curves correlating with $A^*(^1E)$,B or $A^*(^1A_2)$,B can occur with the charge-transfer potential curve, energy transfer should occur to some extent to yield TNB in an excited singlet state. However, TNB does not fluoresce or phosphoresce, this probably being due to energy localization in, and subsequent disruption of, the aryl–$NO_2$ bond[23] (for which $D_E \simeq$ 58 kcal./mole).

The emission properties of benzene–TNB have not thus far been investigated. The study should prove valuable, since if any emission is observed it will be explicable only by competition of processes (ii) or (iii) with the aryl–$NO_2$ bond dissociative process.

**Naphthalene–TNB, Naphthacene–TNB and Phenanthrene–TNB Complexes.**—These complexes can belong to point groups $C_{1h}$, $C'_{1h}$ or lower. Since the E ← N absorption of the naphthalene–TNB complex is at 27600 cm.$^{-1}$, energy localization in the aryl–$NO_2$ bond may compete with the E → N and T → S processes. However, we have observed both of these latter emissions.[24]

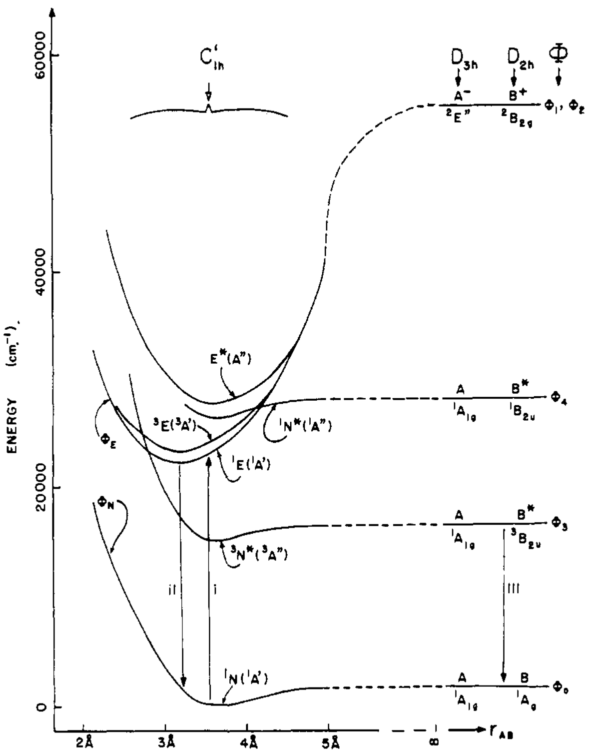


Fig. 2.—A correlation diagram for the electronic states of the anthracene–TNB complex—for which geometry $C'_{1h}$ is assumed. A refers to Lewis acid, B to Lewis base. Symmetries of the excited states for each of the three species present are shown in columnar form under the appropriate point group symbol. Text should be consulted for more detail.

The E ← N absorption of naphthacene–TNB should occur at 17500 cm.$^{-1}$, somewhat lower in energy than the 2nd excited triplet state of naphthacene at 19600 cm.$^{-1}$. Accordingly, excitation in the charge-transfer band might afford a means of excitation of the lowest triplet state of naphthacene which has been observed in absorption at 10250 cm.$^{-1}$ but which has not yet been detected in emission.[5,25]

**Acknowledgments.**—Much of the work reported here was initiated by Michael Kasha. We are grateful for his advice and criticism. We also thank Professor R. S. Mulliken and Professor W. T. Simpson for many helpful suggestions and comments. We thank Ethyl Corporation of Baton Rouge for drawing the diagrams.

## Appendix

**(A) Energies of Catacondensed Cations.**—This question may be approached by the perimeter method of Mofitt.[26] We consider a cyclic polyene

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(23) Th. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen, Germany, 1951, p. 117f; Th. Förster, *Z. Electrochem.*, **56**, 716 (1952); E. Lippert, *Z. physik. Chem.* (*Neue Folge*), **2**, 5, 328 (1954); *J. phys. radium*, **15**, 627 (1954).

(24) R. V. Nauman and C. Garrett, in this Laboratory, have observed two emissions from thianaphthene–TNB complex. One is a fluorescence (presumably E → N), the other a phosphorescence probably of the thianaphthene. Excitation was selective, but the phosphorescence was not photographed.

(25) S. P. McGlynn and M. Kasha, in preparation for publication.

(26) W. Mofitt, *J. Chem. Phys.*, **22**, 320 (1954). This paper should be consulted for details.

of general formula $C_{4\nu+2}H_{4\nu+2}$. The carbon atoms are numbered serially from 0 to $4\nu + 1$ on going around the ring, with carbon zero on the *y*-axis. The MO's may be specified immediately as linear combinations of $2p\pi$ carbon AO's $X_k$

$$\varphi_j = \sigma_j \sum_{k=0}^{4\nu+1} e^{2\pi ijk/4\nu+2} X_k,\ j = 0, \pm1, \ldots, \pm2\nu, 2\nu + 1$$

The one electron energy $\epsilon_j$ associated with $\varphi_j$ is a monotonically increasing function of $j$ with $\epsilon_j = \epsilon_{-j}$. We may thus specify two isoenergetic electron configurations for the cyclic polyene $C_{4\nu+2}H^+_{4\nu+2}$. These are $^2\Theta_1$ and $^2\Theta_2$, two of the interacting components of which are

$$^2\Theta_1{}^\alpha = |\ldots\varphi_{+\nu}(1)\bar{\varphi}_{+\nu}(2)\varphi_{-\nu}(3)|$$
$$^2\Theta_2{}^\alpha = |\ldots\varphi_{-\nu}(1)\bar{\varphi}_{-\nu}(2)\varphi_{+\nu}(3)|$$

To complete the distortion of the $D_{(4\nu+2)h}$ polyenic cation to the point group of the cation of interest we make use of the one electron Hermitian operators

$$P = \sum_{j=1}^{4\nu+1} p_j$$

The first-order interaction matrix is

$$\begin{array}{c} ^2\Theta_1 \\ ^2\Theta_2 \end{array} \begin{vmatrix} q - p_{-\nu,-\nu} & -p_{\nu,-\nu} \\ -p_{-\nu,\nu} & q - p_{\nu,\nu} \end{vmatrix} = 0$$

The configurational splitting is then $2|p_{\nu,-\nu}|$, where $q$ is the diagonal element corresponding to the first-order ground state of the non-ionized polyacene in the matrix representing the perturbation

$$P' = \sum_{j=1}^{4\nu+2} p_j$$

The ground state WF is given by

$$^2\Theta_G = 1/\sqrt{2}(^2\Theta_1 - (-1)^\nu\ {}^2\Theta_2)$$

and the excited state by

$$^2\Theta_E = 1/\sqrt{2}(^2\Theta_1 + (-1)^\nu\ {}^2\Theta_2)$$

The transformation properties of these states of the cations are easily derived from those in the $D_{(4\nu+2)h}$ point group. These are given in Table II for appropriate operations.

On this basis the cations of naphthalene, anthracene, naphthacene and phenanthrene have ground states of species $^2A_{1u}(D_{2h})$, $^2B_{2g}(D_{2h})$, $^2A_{1u}(D_{2h})$ and $^2B_2(C_{2v})$, respectively. The configurational splitting in the case of the *linear* polyacenes is given by $(2\nu - 2)\beta/(2\nu + 1)$ and for phenanthrene is $0.127\ \beta$, where $\beta$ is the resonance integral.

These quantities are defined

$$p_{\nu,\nu} = (\beta/2\nu + 1) \sum_m \sum_{n>m} \cos\frac{\pi(n - m)\nu}{2\nu + 1} = p_{-\nu,-\nu}$$

$$p_{\nu,-\nu} = (\beta/2\nu + 1) \sum_m \sum_{n>m} e^{-\pi i(n+m)\nu/2\nu+1} = p^*_{-\nu,\nu}$$

The summation extends in each case over pairs of serial numbers between which bonds are formed in the distortion process. Thus for anthracene (Fig. 1), there are two terms in the summation: $m = 1$, $n = 6$ and $m = 8$, $n = 13$.

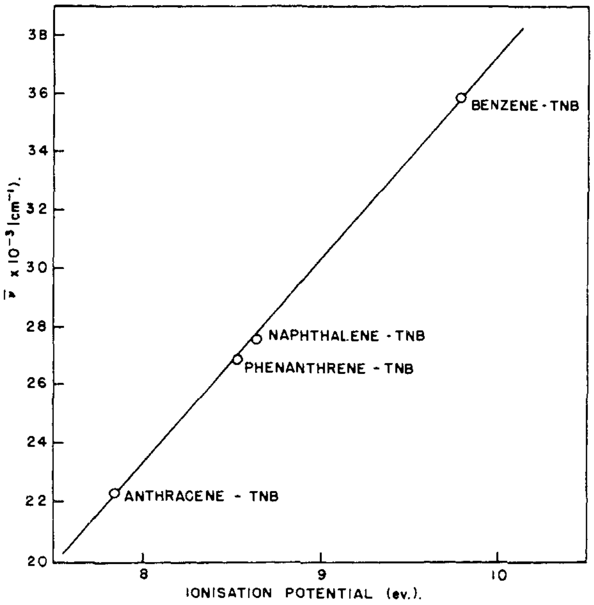

Fig. 3.—A plot of $\bar{\nu}_{max}$ of the E←N absorption band of the complex *versus* the ionization potential of the base. The values of $\bar{\nu}_{max}$ used are from the present work except that for benzene–TNB, which is taken from D. M. G. Lawrey and H. McConnell, This Journal, **74**, 6175 (1952).

**(B) The Relation of E—N Transition Energy to Ionization Potential for Aromatic–TNB Complexes.**—A linear relation between the ionization potential of the base and $\bar{\nu}_{max}$ of the E←N transition is a general characteristic of charge-transfer complexes of the same acid with different bases.[27] It is to be noted that this linearity has very little basis in theory[28] and that many experimental deviations from it have been noted.[29] However, within a group of closely related donors, especially when the ionization potential ($I_p$) range spanned is relatively small, linearity is not entirely unexpected.

Table II

Transformation Properties of Configurational and State WF's

| | $\Theta_1$ | $\Theta_2$ | $\Theta_G$ | $\Theta_E$ |
|---|---|---|---|---|
| $\sigma_{yz}$ | $\Theta_2$ | $\Theta_1$ | $-\Theta_G$ | $(-1)^\nu\Theta_E$ |
| $\sigma_{xz}$ | $(-1)^\nu\Theta_2$ | $(-1)^\nu\Theta_1$ | $(-1)^{\nu+1}\Theta_G$ | $(-1)^\nu\Theta_E$ |
| $\sigma_{xy}$ | $-\Theta_1$ | $-\Theta_2$ | $-\Theta_G$ | $(-1)^{\nu+1}\Theta_E$ |

Unfortunately experimental values of $I_p$ are not known for many aromatics. They may be evaluated readily in terms of the discussion of (a); however, we choose to use the "better theoretical" values of Hush and Pople.[21] These are plotted against $\bar{\nu}_{max}$ in Fig. 3. The excellent linearity obtaining affords good confirmatory support of the charge-transfer origins of this absorption band.

**(C) *sym*-Trinitrobenzene and its Conjugate Anion.**—The $\pi$-group orbitals (GO's) of the hexagonal carbon skeleton of TNB are just the $\pi$-MO's of benzene. The $NO_2$ groups are each replaced by a negative carbon atom $C^-$ as the initial step in the calculations. In the sense of the skeletal carbon atoms these $C^-$ atoms are not nearest neighbors, and the two GO's embracing these cen-

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[27] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, This Journal, **75**, 2900 (1953).

[28] R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956).

[29] C. Reid and R. S. Mulliken, This Journal, **76**, 3869 (1954); S. Nagakura, *ibid.*, **80**, 524 (1958).

ters are energy degenerate. The GO's embracing the skeleton and those of the $C^-$ system are symmetrically disposed energy-wise with respect to the group theoretic species (in $D_{3h}$ only) and energy. Interaction will then be to a first approximation also symmetric.

Efforts were made to take account of the inductive effect due to the difference in field of $NO_2$ as compared to $C^-$ and of the resonance effect due to the $\pi$-orbital extension. Constants involved were evaluated from a *postulated* spectroscopic assignment of the electronic transitions of TNB and an ionization potential. This assignment was itself tenuous, and the value of 1.1 e.v. for the electron affinity of TNB can be questioned.

The ground configurations of TNB and $TNB^-$ are believed accurately given by

$$\ldots\ldots (a''_2)^2\,(e'')^4\,(a''_2)^2\,(e'')^4,\ {}^1A_1 \text{ and}$$

$$\ldots\ldots (a''_2)^2\,(e'')^4\,(a''_2)^2\,(e'')^4\,(e'')^1,\ {}^2E'',$$

respectively.

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# The Role of Hydrogen Iodide in the Photoisomerization of *n*-Propyl Iodide[1]

BY CHARLES E. MCCAULEY AND GEORGE J. HILSDORF

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Air-free and air-saturated samples of liquid *n*-propyl iodide have been photolyzed, principally with the 2537 Å. mercury line. Tracer experiments with $I^{131}$ have shown that the isomerization to isopropyl iodide is a slow post-irradiation process and is inhibited if oxygen was present during the photolysis but not if oxygen is admitted after photolysis to a previously air-free sample. The isopropyl iodide is formed from propylene and hydrogen iodide; the presence of the latter intermediate was established by titration. The primary product ratio $HI/I_2$ is 0.53 at 30° and 0.91 at $-60°$ and increased isomerization at Dry Ice temperature follows the increased production of HI. Interpretation of the results favors a diffusion-controlled reaction. Equations are proposed for the various parts of the reaction and quantum yields calculated for each of the successive and competing steps.

When *n*-propyl iodide is decomposed by irradiation with ultraviolet light, the main products are iodine, propane, propylene and isopropyl iodide. It has been proposed[2] that the isopropyl group arises not from any free radical rearrangement, but from the combination of propylene with HI, with the assumption that the latter is produced as an intermediate in the photolysis. The experimental evidence supporting this proposal was somewhat indirect, although it was shown that HI results from the photolysis of ethyl iodide[3]; this latter result was confirmed in an extensive study by Bunbury, Williams and Hamill,[4] and these investigators have shown that the experimental results require a radically new interpretation of the mechanism of photolysis of ethyl iodide. Since there are many correlations between photolysis and radiolysis of alkyl iodides, it was natural to suppose that HI might also be a product of radiolysis, and this has been shown to be true.[4,5]

In order to verify fully the original inference and explore the implications in a more complex system it seemed desirable to demonstrate the presence of HI in photolyzed *n*-propyl iodide in a direct manner. In this connection it was also of interest to examine more carefully the effects on the photoisomerization due to change of wave length, temperature or presence of dissolved air in the material being photolyzed.

## Experimental

**Purification of Alkyl Iodides.**—Five hundred gram batches of Matheson iodides were washed with aqueous thiosulfate, dried and distilled at 100 mm. pressure through a six-foot column packed with glass helices. The central fifth was used for photolysis and the second and fourth fifths, or a little more, were used for carriers.

**Apparatus.**—The mercury lamp was similar to one described previously.[2] However, in order to maximize the 1849 Å. contribution, the lamp helix was specially fabricated from very thin quartz tubing (wall thickness <0.6 mm.).

The cells used for photolysis were 13 × 200 mm. cylinders of thin quartz (wall thickness 0.6 mm.) for transmission of the 1849 Å. radiation, and similar cylindrical cells of 1.0 mm. Vycor (Corning 7910 glass) which has a cutoff at *ca.* 2400 Å. The cells were provided with a quartz-to-Pyrex graded seal for attachment to the vacuum line, and also with a side arm sealed with a break-off through which carriers and other materials could be introduced into the cell after photolysis.

**Procedure for Photolysis.**—Five-ml. or 10-ml. samples of *n*-propyl iodide, frequently containing dissolved elemental $I^{131}$, were dried and degassed on the vacuum line as previously described.[2] For some runs when radioiodine was not used, the sample was merely deaerated by bubbling dry nitrogen or hydrogen through it for 30 minutes and the cell then sealed by a glass joint lightly smeared with silicone grease. The cell, with vapor space screened with black tape, was placed in the center of the lamp helix, and the temperature kept approximately constant at 32 ± 5° by blowing a stream of air through the lamp assembly. For the low temperature runs, the cell and sample were chilled in a Dry Ice–acetone mixture, wiped quickly, irradiated for two minutes, chilled for one minute and the cycle continued. Dummy runs indicated that the temperature of the absorbing layer was *ca.* $-60 \pm 15°$ during the irradiations.

**Analysis of Samples Containing $I^{131}$.**—After photolysis the sealed cell was stored in the dark for periods ranging from 5 minutes to 30 hours, and the contents were then added to a carrier mixture of iodides and inert $I_2$. A 5-ml. aliquot of this mixture was diluted to 50 ml. with $CCl_4$ and its total and organic activity measured in an annular-jacketed GM tube as described elsewhere.[6] The remaining

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[1] Presented at the 131st meeting of the American Chemical Society, Miami, Florida, April, 1957.

[2] C. E. McCauley, W. H. Hamill and R. R. Williams, Jr., THIS JOURNAL, **76**, 6263 (1954).

[3] This possibility had been suggested much earlier by G. Emschwiller, *Compt. rend.*, **192**, 799 (1931), but seems to have passed unnoticed.

[4] D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **78**, 6228 (1956).

[5] (a) E. O. Hornig and J. E. Willard, *ibid.*, **79**, 2429 (1957); (b) R. J. Hanrahan and J. E. Willard, *ibid.*, **79**, 2434 (1957).

[6] C. E. McCauley, G. J. Hilsdorf, R. J. Geissler and R. H. Schuler, *ibid.*, **78**, 3246 (1956).