phenylene curves of Fig. 2 and the transient curves of Fig. 5 do.

Despite the large uncertainties in the curves, their time-variation and especially their shapes lead us to assume that the two absorptions are due to the same species. In all, the weight of the evidence supports the assignment of this absorption to benzyne.

V. **Acknowledgments.**—We would like to thank Professor Georg Wittig for suggesting that *o*-iodophenylmercuric iodide and di-*o*-iodophenylmercury be studied by flash photolysis, and for supplying us with samples of these compounds. We would also like to thank Mr. Roy Miller for supplying the benzenediazonium-2-carboxylate and Mr. Wayne Warren for his part in the construction of the apparatus. We are grateful to the Bridgeport Brass Co. for the use of their recording microdensitometer. Finally, we would like to express our gratitude to the U. S. Air Force Office of Scientific Research for the grant under which this work was performed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK, LONG ISLAND CENTER, STONY BROOK, N. Y.]

π-Complex Interactions between Trinitrofluorenone and Polycyclic Aromatic Hydrocarbons[1]

BY ARTHUR R. LEPLEY

RECEIVED APRIL 30, 1962

The charge-transfer spectra of the π-complexes formed by trinitrofluorenone with a number of polycyclic hydrocarbons have been measured. The application of molecular orbital theory to π-complexes is supported by these data. A relationship between charge-transfer bands and donor π–π^*-transitions is proposed and used in evaluation of molecular orbital parameters for fluoranthene and fluorene analogs of the polycyclic aromatics.

A simple molecular orbital treatment has been developed[2,3] which describes the weak attractions between aromatic compounds and such materials as trinitrobenzene, tetracyanoethylene, bromoanil or tetrachlorophthalic anhydride. The forces between these molecules observed through charge-transfer transitions were considered to be intramolecular orbital interactions. Molecular compounds of this type, π-complexes, have been observed in the solid state and in solution.

In general, π-complex formation results in little perturbation of the molecular orbital energy levels of the donor molecule (A) or of the acceptor (B). The weakness of the perturbational influence has been demonstrated by the invariance of transition energies for the principal component electronic energy absorptions.[4] The solid state absorption spectrum is composed of the bands characteristic of pure A and B as well as charge-transfer bands.

The energy, ΔE_{ij}, for an electronic transition is given in simple molecular orbital theory[5,6] by the difference in orbital energies, m (eq. 1)

$$\Delta E_{ij} = m_j - m_i \qquad (1)$$

where the subscripts j and i denote the *j*th and *i*th orbitals, respectively. The energy, E_π for the new charge-transfer band which occurs on excitation of the π-complex similarly requires the transfer from the *i*th orbital of the donor to the *j*th orbital of the acceptor

$$E_\pi = B_j - A_i \qquad (2)$$

where A_i and B_j are the respective orbital energies for the donor A and the acceptor B. The energy of a filled orbital for polycyclic aromatics, as given by the Hückel molecular orbital treatment, is $\alpha + x_i\beta$. Here α is the coulomb integral for carbon, x_i is a quantity calculated theoretically for the *i*th orbital, and β is the carbon–carbon resonance integral. When a value of x_i corresponding to the highest filled orbital of a donor hydrocarbon is used, the transition energy for the first π-complex charge-transfer band should be

$$E_\pi = B_j - \alpha - x_i\beta \qquad (3)$$

If the same acceptor is used with a number of donors, the energy of the lowest unoccupied acceptor orbital will be constant. Under these conditions a linear relationship should exist between the theoretical quantity x_i and the transition energy E_π. The values of β and $B_j - \alpha$ will then be given, respectively, by the slope and the intercept x_i times β at $E_\pi = 0$ of this line.

Internal transitions have been thoroughly treated and summarized.[7,8] These transitions take place between filled and unfilled orbitals in a single molecule. When the donor hydrocarbon A is considered, the transition energy E_A should be

$$E_A = A_j - A_i \qquad (4)$$

where A_i and A_j are, respectively, filled and unfilled orbitals of molecule A. If the donor is a polycyclic aromatic hydrocarbon, the x_i for unfilled orbitals have the same values but are opposite in sign to those of the filled orbitals. The energy of the lowest unfilled orbital is then

$$A_j = \alpha - x_i\beta \qquad (5)$$

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[1] This work was supported by a grant from the Research Foundation of the State University of New York.

[2] M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961).

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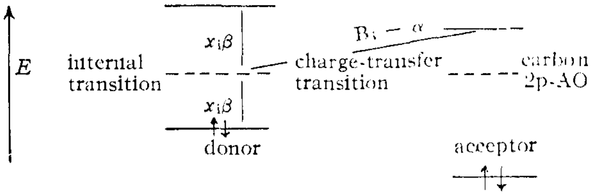


Fig. 1.—Orbital energies for the lowest energy transitions in a complex formed by an alternate hydrocarbon and an acceptor.

where x_i is theoretically calculated for the highest filled orbital. The internal transition energy from the highest filled orbital i to the lowest unfilled orbital, $j = i + 1$, is given by

$$E_A = -2x_i\beta \qquad (6)$$

Since the theoretical quantities $x_i\beta$ are identical in equations 3 and 5, a simple relationship should exist between the charge-transfer band of the π-complex and the lowest energy internal transition of the uncomplexed donor, Fig. 1. The charge-transfer band energy E_π and the internal transition band energy E_A are related by

$$E_\pi = B_j - \alpha + (E_A/2) \qquad (7)$$

where $B_j - \alpha$ is constant for the acceptor B. The relationship between the energies should thus be linear and have a slope of one-half regardless of the values for the parameters α, β, x_i at a constant B_j.

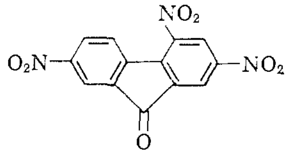
The theory has been applied to the π-complexes of trinitrobenzene[2] and tetracyanoethylene[3] with aromatic hydrocarbons, and to the $\pi-\pi^*$ transitions of polycyclic aromatic hydrocarbons.[7] In each of these cases, the agreement between experimental results and theoretical calculations has been most reasonable.

The π-complex experiments have given values for the lowest unfilled orbitals, B_j's, of both trinitrobenzene and tetracyanoethylene which were consistent with the expected ordering for these acceptors. Resonance integral, β, determinations were consistent and in agreement with other spectroscopic values. The π-complex results have also been employed very neatly for semi-empirical evaluation of the parameters for the heteroatoms boron and nitrogen.[2,3]

The success of molecular orbital theory with the alternant aromatic hydrocarbons suggests application to other compounds, a possibility supported by analogy with the thoroughly reviewed[9] case of valence bond treatment using ionization potentials. The current work is an initial attempt to extend this application of the molecular orbital theory. Here the theory is applied to compounds closely related to the alternant polycyclic aromatics.

It was desired to increase the studied range of calculated coefficients to lower values than previously observed since none of the compounds included in simple extensions of the theory could be expected to have values as high as that of benzene. Trinitrobenzene was not suitable since its normal $\pi-\pi^*$ transitions lie close to the π-complex charge-transfer bands, a condition which becomes worse as the value of x_i decreases. This is certainly not the case with tetracyanoethylene which generally gives an excellent band separation. However, the band separation and Diels–Alder additivity of tetracyanoethylene parallel one another. Thus low x_i compounds such as the polyacenes react very rapidly with this acceptor.

Reactivity or insufficient peak separation eliminated many other common acceptors, *i.e.*, iodine, quinones such as chloranil or bromanil, and maleic anhydride or its halogen derivatives. A more powerful acceptor containing nitro groups, trinitrofluorenone (I), was more successful. This compound met most of the requirements, although weak complexes were poorly defined because of the acceptor absorption shoulder at 340 mμ. Also, several cases of π-complex dissociation into components on crystallization necessitated the use of solution studies in addition to solid state measurements.



I

Trinitrofluorenone was first used as a complexing agent by Orchin and Woolfolk.[10] They observed the visible color in crystals but noted no new bands in the spectrum of dilute solutions. Subsequently, the reagent has been widely used in the preparation of derivative molecular compounds by π-complexing. A number of others have reported visible colors for trinitrofluorenone complexes. These color changes have been incorporated as analytical methods in mixed fusion analysis[11] and spot test identifications.[12] Actual measurements[4,13,14] of charge-transfer spectra with trinitrofluorenone have been exceedingly meager.

Where possible, current measurements and related values have been compared with earlier visual and spectral work.

Experimental

Materials.—2,4,7-Trinitro-9-fluorenone was purified by recrystallization from a 3:1 nitric acid–water mixture, washed with water and dried *in vacuo* over phosphorus pentoxide.

Phenanthrene was purified by treatment with maleic anhydride in hot xylene,[15] followed by sublimation and zone melting. Chrysene, fluoranthene, fluorene, pyrene and triphenylene were zone melted. All other hydrocarbons were used in the form obtained from the Aldrich Chemical Co. The spectra and melting points of these compounds agreed with literature values.

Spectra.—Measurements were made with a Beckman DK-2 spectrophotometer. Solution spectra were measured from 350 to 900 mμ on equal volume mixtures of 0.01 M trinitrofluorenone and 0.02 M donor in chloroform.[3] Satu-

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rated solutions of known concentration were used where the donor solubility was less than 0.02 *M*. Potassium bromide disks containing weighed equimolar (about 10^{-5} mole) amounts of trinitrofluorenone and donor were prepared by standard infrared techniques.[2] The disks were scanned over the range 250–900 mμ in a laminated quartz windowed cell. Paraffin oil decreased light scatter. Since only charge-transfer band maxima were relevant to the present work, no attempt was made to determine the equilibrium constants, extinction coefficients or heats of formation for the complexes.

Results

Table I lists the wave lengths, λ_π, found for the twenty-three π-complexes of calculated donor orbital energy. The wave length maxima, λ_A, for the first singlet π–π* transitions are as previously reported.[16–18] The highest filled orbital energies are those calculated by the Hückel method which neglects overlap. These values were taken from a recent compilation.[19]

The energies of the observed charge-transfer transitions are plotted against the values of the molecular orbital coefficient x_i in Fig. 2. The location of points is seen to agree with the linear relationship in eq. 3; the line in Fig. 2 was fitted by the method of least squares.

TABLE I

CHARGE-TRANSFER BANDS OF π-COMPLEXES FORMED BY TRINITROFLUORENONE WITH POLYCYCLIC HYDROCARBONS; FIRST SINGLET ABSORPTION BAND AND HÜCKEL ENERGIES OF THE HIGHEST FILLED MO'S OF THE DONOR HYDROCARBONS

Compound	Designation	λ_π, mμ	λ_A,[a] mμ	x_1[b]
Acenaphthalene	1	415 ± 15	324[c]	0.637
Anthracene	2	541 ± 4	374.5	.414
Azulene	3	535 ± 10	353[d]	.477
1,2-Benzanthracene	4	522 ± 5	359	.452
1,12-Benzoperylene	5	570 ± 5	387.5	.439
1,2-Benzopyrene	6	510 ± 10	331.5	.497
3,4-Benzopyrene	7	590 ± 5	384.5	.371
3,4-Benzotetraphene	8	561 ± 5	367	.405
Chrysene	9	482 ± 10	319	.520
Coronene	10	512 ± 5	341.5	.539
1,2,3,4-Dibenzanthracene	11	505 ± 5	349	.499
1,2,5,6-Dibenzanthracene	12	525 ± 15	351	.473
1,2,3,4-Dibenzopyrene	13	548 ± 7	402	.398
1,2,4,5-Dibenzopyrene	14	562 ± 2	378	.442
Fluoranthene	15	430 ± 15	358.5	.618
Naphthacene	16	654 ± 2	471	.294
Naphthalene	17	430 ± 15	285	.616
Pentacene	18	745 ± 15	575.5	.220
Perylene	19	620 ± 5	434	.347
Phenanthrene	20	435 ± 15	292.5	.605
Picene	21	470 ± 10	328.5	.501
Pyrene	22	520 ± 5	333.5	.445
Triphenylene	23	425 ± 15	284	.684

[a] Ref. 16. [b] Ref. 19. [c] Ref. 17. [d] Ref. 18.

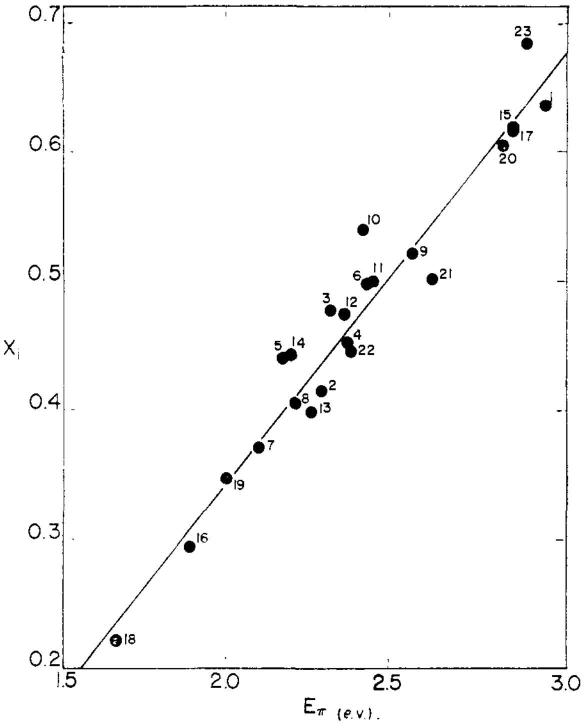

Fig. 2.—Plot of the charge-transfer transition energies, E_π, for the π-complexes of hydrocarbons with trinitrofluorenone against the molecular orbital coefficient, x_1, for the highest filled orbital of the hydrocarbon; the numerical designations are those given in Table I.

The wave length maxima for the π-complex and first singlet transitions[16,20–25] of fifteen donors are given in Table II. The values for the theoretical quantity x_i of the highest occupied donor molecular orbital were determined from Fig. 2.

The energies of the observed first π–π* singlet transition for the donor hydrocarbon are plotted against the observed first π-complex charge-transfer transition energies in Fig. 3; the points are seen to lie close to a straight line as required by eq. 7. The points 1, 15, 25–27, 31, 32 and 35 were not included in the least squares fit of the straight line for Fig. 3.

Discussion

The requirements of eq. 3 are met in Fig. 2, where the points lie close to a straight line. The deviation of individual points from the line may originate in the oversimplification of the orbital evaluation by the Hückel method and in the measurement uncertainties. Coronene (10) and triphenylene (23) are considerably above the line in agreement with earlier π-complex studies.[2,3] In the Hückel treatment, the two highest occupied orbitals of these compounds are identical in energy. Such a degeneracy should give a splitting of states,

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[16] E. Clar, "Aromatische Kohlenwasserstoffe," 2nd ed., Springer Verlag, Berlin, 1952.

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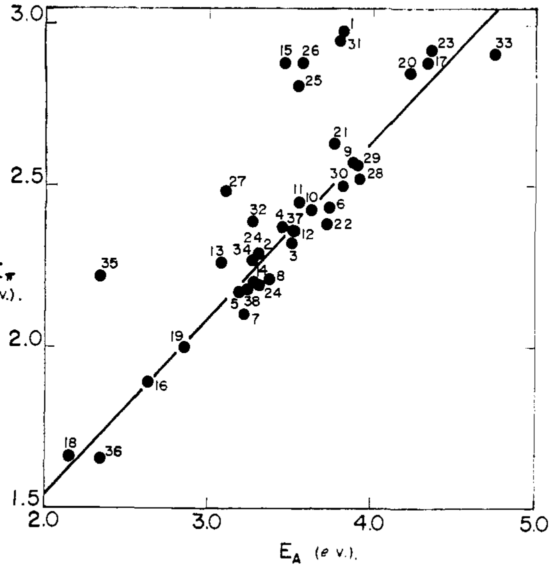

Fig. 3.—Plot of the transition energy, E_π, for the first charge-transfer bands of hydrocarbon–trinitrofluorenone complex against the energy, E_A, for the first π–π^* singlet transition of the donor hydrocarbon; the points are numbered according to the designations in Tables I and II.

the two new states normally lying above and below the original energy level. Since the π-complex interaction of eq. 3 considers only the highest orbital (*i.e.*, that with lowest orbital energy), the x_i values for these compounds probably should be slightly lower, improving the agreement with the predicted line.

The deviations in assignment of wave length maxima were of greater importance in the empirical evaluation of parameters for eq. 3. The estimated limits, Table I, increase with decreasing solubility and with decreasing separation of the charge-transfer band from parent compound peaks. Pentacene (18), for example, did not form a complex on grinding with acceptor and was very slightly soluble even in hot chloroform. Its charge-transfer band was distinct but diffuse. At lower wave lengths the increase in peak definition normally observed was not apparent because of acceptor absorption; *cf.* naphthalene (17) and phenanthrene (20). The breadth and low extinction coefficients for charge-transfer bands and the solution molar absorbance concentration product dependence were used in minimizing assignment errors.

Figure 2 does give a reasonably straight line; therefore, the parameters of eq. 3 may be evaluated. Equation 3 required that the slope of the line be equal to β; from the slope in Fig. 2, one finds $\beta = -3.12$ e.v. The corresponding values found[2,3] for trinitrobenzene and tetracyanoethylene complexes were -3.0 e.v. and -3.06 e.v., respectively, while the spectrum of benzene gave -3.1 e.v. The current estimate is in good agreement with these values, deviation being well within the limits of experimental error.

The energy for the lowest unoccupied orbital of trinitrofluorenone in eq. 3 should be given by the intercept of the plotted line with the x_i axis.

TABLE II

CHARGE-TRANSFER SPECTRA OF COMPLEXES FORMED BY POLYCYCLIC HYDROCARBONS WITH TRINITROFLUORENONE: THE FIRST SINGLET ABSORPTION BAND AND ESTIMATED HIGHEST FILLED MO ENERGIES FOR THESE HYDROCARBONS

Compound	Designation	λ_π, mμ	λ_A, mμ	x_i from Fig. 2
Benzocoronene	24	540 ± 5	374	0.44
3,4-Benzofluoranthene	25	440 ± 10	350[a]	.60
Benzo[m,n,o]fluoranthene	26	430 ± 15	347[b]	.63
11,12-Benzofluoranthene	27	500 ± 5	400[a]	.50
1,2-Benzofluorene	28	492 ± 5	316[c]	.51
2,3-Benzofluorene	29	485 ± 5	317[c]	.52
3,4-Benzofluorene	30	495 ± 5	324[c]	.505
9-Benzylidenefluorene	31	420 ± 15	326[d]	.65
Decacyclene	32	518 ± 10	379	.47
Fluorene	33	425 ± 10	261[a]	.635
o-Phenylenepyrene	34	545 ± 5	379	.43
Rubicene	35	555 ± 10	530[e]	.41
Rubrene	36	750 ± 10	528.5[f]	.23
1,2,3,4,5,6,7,8-Tetrabenzonaphthalene	37	525 ± 7	352[g]	.46
1,2,4,5,8,9-Tribenzopyrene	38	567 ± 5	382[a]	.405

[a] Ref. 16. [b] Ref. 20. [c] Ref. 21. [d] Ref. 22. [e] Ref. 23. [f] Ref. 24. [g] Ref. 25.

The energy level is thus: $B_j = \alpha - 0.30\beta$. As expected, this value lies between those previously determined for trinitrobenzene and tetracyanoethylene.

The close agreement observed between the theoretical and experimental quantities lends strength to the simple hypothesis on the nature of the π-complex. First, the π-complex spectrum retains the bands of the unassociated donor and acceptor but has at least one new diffuse band of lower energy than the principal transitions of either pure compound. Second, this new band has an energy directly related to the highest occupied molecular orbital of the donor. Thus there is no evidence for appreciable perturbation of molecular energy levels.

The Hückel molecular orbital picture assumes that all interacting atomic orbitals have the same basic repulsion and attraction parameters, *i.e.*, α and β are constants. The same result is obtained when the sum of all atomic orbital α's and β's for more than one element is equal to the sum of atomic orbital parameters in an equivalent system of a single element. This perturbation approach[26] has been employed successfully for the borazaro compounds[2,3] where π-complexes were used to obtain the highest occupied orbital energy of the perturbed (boron–nitrogen containing) system.

It would seem much less of an extension of the π-complex-molecular orbital relationship to apply the method to the evaluation of highest occupied molecular orbitals in other hydrocarbon systems. In the hydrocarbons every atom involved in the π-electronic network has the required identity of atomic orbitals. Since only the donor ground state is important in the semi-empirical π-complex treat-

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[26] 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).

ment, the presence of other hybridized carbon orbitals such as sp^3 may be assumed to have no more than a weak polarizing influence on the conjugated sp^2 system. Compounds which may exhibit an appreciable effect of this nature are being studied and will be covered in a later paper. The effect of saturated carbon atoms on the present π-systems appears to be negligible.

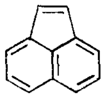
The principal difference between the new compounds and those previously considered is that these compounds include systems in which the atomic p-orbital spin does not reverse at each adjacent atom, *i.e.*, non-alternant hydrocarbons. It should be noted that even in these compounds, occupied orbitals are those with the smallest number of uncoupled spins. The energy necessary for charge-transfer excitation should still be proportional to the highest occupied donor molecular orbital and the lowest unoccupied acceptor orbital. Furthermore, the values of α and β in the simplified treatment remain the same.

π-Complexes of nine non-alternant hydrocarbons were measured. Appropriate theoretical calculations have been reported[18] for only three of these: acenaphthalene (1), azulene (3) and fluoranthrene (15). The values for these compounds are in excellent agreement with eq. 3 as shown by Fig. 2. Equation 3 with the empirical values for β and $\alpha - B_j$ has therefore been used to calculate a semi-empirical value of the quantity x_i for the six other non-alternant hydrocarbons. The x_i-values for these compounds, related fluorenes, and several alternant polycyclic hydrocarbons not previously studied are given in Table II. At this point, the inclusion of the fluorenes is rather tenuous, being based only on the valence bond relationship between ionization potential and the energy of the π-complex charge-transfer transition. Although no directly applicable calculated values are available, an empirical argument may be used to justify this extension of the theory.

As pointed out before, the π-complex charge-transfer transition should be directly related to any other donor spectroscopic transition involving the ground state. The first excited state in particular was treated in eq. 4 through 7. Unfortunately, the Hückel method when applied to transition energies gives the average of the first singlet–singlet and first singlet–triplet π–π^* transition energies. Since relatively few of the singlet–triplet π–π^* transition energies have been measured, the exact application of eq. 7 cannot be made. However, reasonable consistency and not absolute values are of interest in establishing the general theory. The readily measured singlet–singlet transition suffices for this purpose.

The first π–π^* singlet transitions of interest have been classified by Clar[16] as "para bands" and by Platt[6] as ^1L_a transitions. The proportionality of the calculated and measured transitions has also been reviewed.[7] Tables I and II include the wave length maxima for the initial peak in the first singlet–singlet transition. When the energy of the π-complex charge-transfer band is plotted against the energy of the respective donor π–π^* band, a straight line is generated, Fig. 3. This linear relationship is required for agreement between the measured values and eq. 7. The slope of the line should then give the proportionality of the transition energies; from Fig. 3, one finds slope = 0.54. The agreement is very good between this value and the slope of 0.5 predicted in eq. 7. The actual deviation in slope and spread of polycyclic aromatic compounds is somewhat less than expected from Fig. 2. This improvement may arise from the use of empirical values for both energies in Fig. 3, and the fact that the observed bands are both singlet transitions.

All but eight of the points in Fig. 3 lie well within the estimated limits of error. The several compounds which deviate markedly from the line are acenapthylene (1), fluoranthene (15), 3,4-benzofluoranthene (25), benzo[m,n,o]fluoranthene (26), 11,12-benzofluoranthene (27), 9-benzylidenefluorene (31), decacyclene (32) and rubicene (35).



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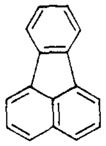

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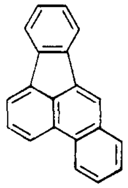

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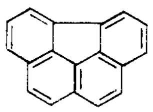

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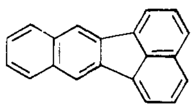

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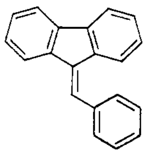

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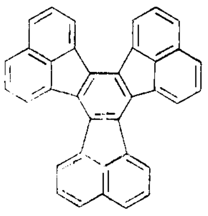

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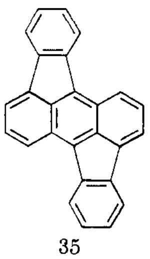

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These compounds which contain the five-membered conjugated ring common to the fulvenes are non-alternant benzenoid hydrocarbons. Thus, as expected, a change is observed in going from the alternant to non-alternant aromatic hydrocarbons. These compounds do seem to form a consistent class since their points all lie above the line. They also appear to parallel the line even though the number of compounds is not large enough to confirm this point. Thus, the relationship in eq. 7 is obeyed, but the singlet–triplet excited state separation for alternant and non-alternant compounds differs. The point for the single pseudo-aromatic compound azulene (3) lies within the estimated margin of error for the alternant hydrocarbons in Fig. 3.

Compounds included in the other small class contain one saturated carbon atom. These are fluorene (33) and its benzo analogs (28–30), all of which fit the curve. The maximum deviation here is for fluorene itself which has the highest proportion of saturated atoms to conjugated rings. However, this single example is within the limits for the polycyclic aromatics, a fact which seems to confirm the prediction based on other spectroscopic evidence that the interaction of the sp^2- and sp^3-hybridized orbitals in the highest occupied orbital and first excited state is limited. Thus, the hypothesis of weak polarization of the aromatic ring in most states by saturated groups is supported rather than hyperconjugation. The latter effect would be expected to make an appreciable shift in the excited states.

The work described in this paper seems to provide some justification for the extension of the simple molecular orbital treatment of π-complexes to several cases of hydrocarbons related to the polycyclic aromatic compounds. The comparison of empirical values for complex and donor transitions furnishes further support for the basic theoretical approach. The values determined by the molecular orbital treatment for an additional acceptor, trinitrofluorenone, should further aid in the application of π-complex theory; a number of studies on applications are being carried on at the present time.

Acknowledgment.—The author wishes to thank Professor M. J. S. Dewar for helpful discussions.

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Alkaline Hydrolysis of Normal and Pseudo Methyl Esters of *o*-Benzoylbenzoates and of Hindered Alkyl Acetates[1]

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RECEIVED MAY 12, 1962

The rates of alkaline hydrolysis in 70% dioxane–30% water at 30° of a series of normal and pseudo methyl esters of methyl substituted *o*-benzoylbenzoic acids have been measured. The high rate for methyl 2-benzoyl-6-methylbenzoate seems best interpreted by initial attack of hydroxide ion on the ketonic carbonyl followed by intramolecular expulsion of a methoxide ion. Certain secondary alkyl acetates have been shown to undergo hydrolysis at rates slower than that of *t*-butyl acetate.

The fact that *o*-benzoylbenzoic acids form two types of esters, normal and pseudo, has long been known.[2] Usually, the point of interest involved in this area has been the determination of structure of each ester. To our knowledge, no measurements of the relative reactivity of such isomeric esters with any reagent have been made. Because of some qualitative observations concerning the rapidity of conversion of ψ-methyl *o*-benzoylbenzoate to the normal ester under alkaline conditions,[3] we decided to measure the rates of alkaline hydrolysis of several pairs of normal and pseudo esters. Accordingly, the second-order rate constants in 70% dioxane–30% water at 30° for the alkaline hydrolysis of five pairs of methyl *o*-benzoylbenzoates were measured. The results are listed in Table I.

The relative rates of hydrolysis of the pseudo esters are roughly what might be expected from the combined steric and inductive effects of methyl groups. Esters IV, VI, VIII and X would all be expected to hydrolyze at rates slower than that of II. Since the steric effects of the methyl groups in IV and VI are approximately the same (in terms of hindrance to addition of hydroxide ion to the carbonyl group) one might explain the slower rate for VI by noting that in VI the methyl group is attached to the ring containing the carbonyl and hence should exert its rate-retarding inductive effect[4a] whereas in IV this effect would not be expected to be felt.

One might have expected a greater steric effect from the methyl group in VIII.[4b] However, because the carbonyl group in VIII is coplanar with the ring and attack by hydroxide ion is surely from a direction perpendicular to the ring,[5] the steric effect of the methyl group is minimized.[6] Finally, the rate for X reflects the two effects of methyl groups in VI and VIII. The above arguments all assume that the same mechanism for hydrolysis, namely, addition of hydroxide ion to the carbonyl group to yield a tetrahedral transition state,[7] applies.

We believe that the alkaline hydrolysis of the normal methyl esters I, III, V, VII and IX is more complicated than that of the pseudo esters because two different mechanisms for hydrolysis are involved. The rate measured, therefore, is a composite of two rates and hence interpretation is difficult. The main fact which demands this explanation is that ester VII hydrolyzes at a rate so much greater than that of any of the others.

The two mechanisms are: an ester carbonyl addition mechanism (1) similar to that involved in ordinary carboxylic esters,[5] and a ketone carbonyl addition mechanism (2).

The key feature to mechanism 2 is the cyclization of intermediate A to B. In this step, *the preferred geometry would have the plane of the ester group roughly perpendicular to the plane of the ring so that the negatively charged oxygen atom can approach the carbonyl group from a direction per-*

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[1] This research was supported by grant G 10345 of the National Science Foundation.

[2] Probably the first example of an acid which formed normal and pseudo esters was that of opianic acid; H. Wegscheider, *Monatsh.*, **13**, 252 (1892). A list of known isomeric esters (as of 1940) may be found in the Ph.D. thesis of C. D. McCleary, O.S.U., 1940.

[3] See the Ph.D. thesis of C. D. McCleary, Ohio State University, 1940.

[4] (a) Ethyl *m*-toluate hydrolyzes in alkali at a rate about 0.7 that of ethyl benzoate; D. P. Evans, *et al.*, *J. Chem. Soc.*, 1430 (1937). (b) The rate for ethyl *o*-toluate is about 0.13 that of ethyl benzoate.

[5] See M. L. Bender, *Chem. Revs.*, **60**, 60 (1960).

[6] Stated in another way, the transition state for hydrolysis of such a lactone (pseudo ester) is not greatly crowded by an *o*-methyl group.

[7] Reference 5, page 59.