

Effects of Inductive Substituents on Electronic Spectra Aza Analogs of Fluoranthene

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The conditions under which the Hückel molecular orbital (HMO) treatment of inductive substituent effects can be expected to be reliable are discussed from the viewpoint of the Pariser-Parr-Pople (PPP) model. The HMO theory fails to predict correctly the direction of the shift of the first intense band in the ultraviolet spectrum of fluoranthene ($1 \rightarrow -1$ transition) on 3-aza "substitution". Calculations on the five azafluoranthenes using the simple version of the PPP method suggest that this is due to strong mixing of hydrocarbon states by the effect of the "substituent" and predict significant changes in energies, intensities, and polarizations of fluoranthene electronic transitions on aza "substitution". Transition moment directions derived from dichroic absorption of 3-azafluoranthene in stretched polyethylene sheets are in agreement with PPP predictions. Arguments are given against a previous assignment of the first transition in 1-azafluoranthene as $n - \pi^*$.

Aus der Sicht des Pariser-Parr-Pople-Modells (PPP) werden die Bedingungen diskutiert, unter denen die HMO-Behandlung induktiver Substituenteneffekte als zuverlässig erscheint. Die HMO-Theorie ist nicht in der Lage, die Verschiebung der ersten intensiven Bande im UV-Spektrum des Fluoranthens („ $1 \rightarrow -1$ “-Übergang) bei 3-Aza-Substitution richtig vorauszusagen. Berechnungen an den 5 Azafluoranthenen nach der einfachen PPP-Methode lassen vermuten, daß diese Tatsache durch eine starke Vermischung von Kohlenwasserstoffzuständen – hervorgerufen durch die Wirkung des Substituenten – bedingt ist. Die PPP-Methode sagt ferner beträchtliche Änderungen in den Energien, Intensitäten und Polarisationen der Elektronenübergänge des Fluoranthens voraus, wenn man im Fluoranthen eine Aza-Substitution vornimmt. Die Richtungen des Übergangsmoments, die aus der dichroitischen Absorption des 3-Azafluoranthens in langgestreckten Polyäthylenschichten abgeleitet werden können, stimmen mit den Voraussagen von PPP-Berechnungen überein. Es werden Argumente vorgebracht, die gegen eine Kennzeichnung des ersten Übergangs in 1-Azafluoranthan als $n - \pi^*$ -Übergang sprechen.

On discute à l'aide du modèle de Pariser-Parr-Pople (PPP) les conditions de validité du traitement par la méthode de Hückel (HMO) des effets de substituants inductifs. La méthode de Hückel ne peut prédire correctement la direction du déplacement de la première bande intense du spectre UV du fluoranthène (dite transition « $1 \rightarrow -1$ ») dans les substitutions aza en 3. Les calculs sur 5 azafluoranthènes à l'aide de la méthode PPP ordinaire suggèrent que cet échec est dû à un fort mélange des états de l'hydrocarbure sous l'effet du substituant, et prédit des changements importants dans les énergies, les intensités et les polarisations des transitions du fluoranthène par les substitutions aza. Les directions des moments de transition déduits de l'absorption dichroïque du 3 aza fluoranthène dans des feuilles de polyéthylène étiré sont en accord avec le calcul PPP. On apporte des objections à la caractérisation antérieure de la 1^{ère} bande du 2 azafluoranthène comme une bande $n - \pi^*$.

Introduction

The HMO theory [1] has been used successfully by many authors to rationalize small changes in the energy of the singlet $1 \rightarrow -1$ state of conjugated hydrocarbons due to perturbations (e.g., Refs. [1–10]). Here and in the following $1 \rightarrow -1$ is a

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shorthand notation for the state obtained on transferring an electron from the highest occupied molecular orbital ψ_1 to the lowest free molecular orbital ψ_{-1} . This is the usual interpretation of the L_a state of benzenoid hydrocarbons [11]. In the HMO model, the excitation energy $\Delta E_{1,-1}^{\text{HMO}}$ is equal to the difference of orbital energies:

$$\Delta E_{1,-1}^{\text{HMO}} = \varepsilon_{-1}^{\text{HMO}} - \varepsilon_1^{\text{HMO}} \quad (1)$$

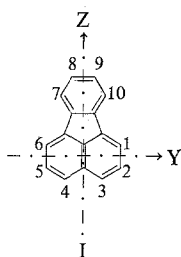
where $\varepsilon_{-1}^{\text{HMO}}$ and $\varepsilon_1^{\text{HMO}}$ are the energies of ψ_{-1} and ψ_1 , respectively, in the HMO approximation. Orbital energies for the perturbed system can be obtained by exactly solving its HMO secular problem, or by means of a first order perturbation calculation. In the latter approximation, the change in the excitation energy $\Delta \Delta E_{1,-1}^{\text{HMO}}$ due to an introduction of a purely inductive substituent into position μ is [4, 5]

$$\Delta \Delta E_{1,-1}^{\text{HMO}} = (c_{-1,\mu}^2 - c_{1,\mu}^2) \cdot \Delta \alpha_\mu \quad (2)$$

Here and in following, $c_{-1\mu}$ and $c_{1\mu}$ are the expansion coefficients of ψ_{-1} and ψ_1 on μ -th atom in the parent system, respectively, and $\Delta \alpha_\mu$ is the change in the Coulomb integral of μ -th atom due to the presence of the inductive substituent. It is self-consistent to use HMO coefficients in Eq. (2). However, sometimes coefficients of better molecular orbitals such as those obtained from Pople's self-consistent-field (SCF) secular equations [12] are used. Expressions for perturbation theory approximations to SCF orbital energy changes are available [13].

Eq. (2) has been used to rationalize spectral effects of various inductive substituents, such as the methyl group (e.g. in azulene [4, 5], fluorenyl anion [6], pyridine [7]; shifts in aceheptylene [14] match the HMO coefficients [15] only imperfectly), and also effects of aza "substitution" (e.g., in azulene [8], aniline [9], indenyl anion [10], indeno [2,1-a]phenalene [16]).

During a discussion [17-19] of the possible lack of significant conjugation across the middle ring of fluoranthene (I), it became of interest to investigate the effect of aza substitution on its



1 → -1 band. The advantages of the aza "substitution" seemed to be first, the absence of the complicating mesomeric effect present with most other substituents, and second, the relatively large electronegativity of nitrogen which should lead to significant shifts even in the case of I, where the values $c_{-1}^2 - c_1^2$ of Eq. (2) are quite small. Since the outcome of the investigations on I so far available is that the effect of conjugation across the five-membered ring on molecular properties is

not negligible, certainly not in the excited states [20] and probably not even in the ground state [17], and since already the simplest version of HMO and PPP [21] methods, which assign the same value of resonance integral β to all C–C bonds including the formally single ones, give good agreement with experiment, it was interesting that the experimental direction of the shift on 3-aza substitution [22] was the opposite of that predicted by the HMO method [23] or the first order perturbation approximation to it. Therefore, an investigation was carried out using the simple version of the PPP method. This rationalized the apparent anomaly and led to some interesting predictions for transition energies, intensities, and polarizations for the five aza fluoranthenes. In the case of the 3-aza isomer, which was available to us, these were found to be in good agreement with experiment.

Experimental Transition Moment Directions

The angles φ by which transition moment directions in 3-aza-I (assumed to lie in the molecular plane) deviate from its effective orientation axis in stretched polyethylene were determined by the method of Eggers and collaborators [24–27]. 3-aza-I (m.p. 101°) was a kind gift of Professor C. F. Koelsch, School of Chemistry, University of Minnesota, Minneapolis, USA. Commercial I was zone melted, m.p. 110.5°.

Details of the experimental technique are given in Ref. [25]. Precautions were taken to have the same number of molecules in the lightpath during measurements of optical density for light with electric vector parallel to stretching direction, $E_{\parallel}(\lambda)$, and those for light oppositely polarized, $E_{\perp}(\lambda)$. The measurements were repeated several times using different numbers of polyethylene sheets to obtain optimum optical densities in various wavelength regions. The method used for evaluation of the angles φ from E_{\parallel} and E_{\perp} is described in Ref. [27]. A brief summary follows.

Let $A_i(\lambda)$ be the contribution of i -th transition to total optical density which would be observed if all molecules were aligned with the i -th transition moment direction along the light electric vector. Assuming the number of molecules in the lightpath during the measurements of E_{\parallel} and E_{\perp} to be equal, one can write [26]

$$\begin{pmatrix} E_{\parallel}(\lambda) \\ E_{\perp}(\lambda) \end{pmatrix} = \begin{pmatrix} K_1 & K_2 \\ K_3 & K_4 \end{pmatrix} \left[\sum_i \begin{pmatrix} \cos^2 \varphi_i \\ \sin^2 \varphi_i \end{pmatrix} A_i(\lambda) \right], \quad (3)$$

where $K_1 - K_4$ are wavelength-independent orientation factors characterizing the orientation distribution of the solute molecules in the stretched sheet. There is good evidence that they depend primarily on molecular shape, at least in the non-polar polyethylene medium [26]. If the ratios $K_1 : K_2 : K_3 : K_4$ are known, and if one can find the value c_i for which the spectral features due to the i -th transition are just absent in the curve $E_{\parallel}(\lambda) - c_i \cdot E_{\perp}(\lambda)$, Eq. (3) gives $K_1 \cos^2 \varphi_i + K_2 \sin^2 \varphi_i - c_i K_3 \cos^2 \varphi_i - c_i K_4 \sin^2 \varphi_i = 0$, and $\cos^2 \varphi_i$ can be calculated:

$$\cos^2 \varphi_i = (c_i - K_2/K_4) / [c_i(1 - K_3/K_4) + K_1/K_4 - K_2/K_4]. \quad (4)$$

For symmetrical molecules in which only two in-plane transition moment directions are possible the ratios $K_1 : K_2 : K_3 : K_4$ can be determined from experimental

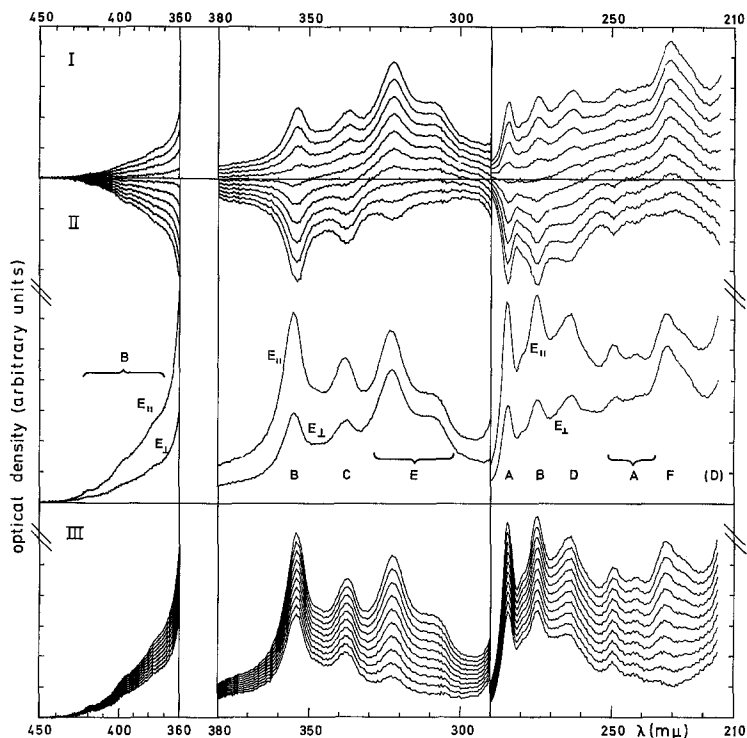


Fig. 1. Dichroic absorption spectra of 3-azafluoranthene in a stretched polyethylene sheet (II) and derived sets of reduced curves (I: $E_{\parallel}(\lambda) - c'E_{\parallel}(\lambda)$, $c' = 0.1$ in the top curve and increasing by steps of 0.1 up to $c' = 1.0$ in the bottom curve, III: $E_{\parallel} - cE_{\perp}$, $c = 0.1$ in the top curve and increasing by steps of 0.1 up to $c = 1.0$ in the bottom curve)

dichroic curves in various ways [24, 25]. Thulstrup and Eggers found $K_3/K_1 = 0.48$, $K_2/K_4 = 0.67$ [24] for I. In our experiments we have used polyethylene sheet of somewhat better orienting properties; we find $K_3/K_1 = 0.40$, $K_2/K_4 = 0.80$, $K_3/K_4 = 0.68$ (all ± 0.03) for I. Since the shapes of I and 3-aza-I should be rather similar, these values can be used as approximations to the values appropriate for 3-aza-I.

The values of c_i were determined by "stepwise reduction". An example is given in Fig. 1. The order of these values, preferably obtained from one spectrum over the whole range of wavelengths to eliminate errors due to imperfect reproducibility, immediately gives the order of the deviations, independent of assumptions about the ratios of $K_1 - K_4$: $|\varphi_A| \leq |\varphi_B| < |\varphi_C| < |\varphi_D| < |\varphi_E| < |\varphi_F|$ (for band labelling see Fig. 1). Assuming that the ratios of $K_1 - K_4$ are the same for 3-aza-I as for I, Eq. (4) gives $|\varphi_A| = 25^\circ$, $|\varphi_B| = 28^\circ$, $|\varphi_C| = 31^\circ$, $|\varphi_D| = 39^\circ$, $|\varphi_E| = 54^\circ$, $|\varphi_F| = 66^\circ$. For $|\varphi|$ both near 0° and near 90° the accuracy is poor since $\cos^2 \varphi$ is a slowly changing function of φ . Further, the degree of orientation is probably slightly worse than for I (cf. Ref. [27]); it cannot be much worse in view of the c_i values found (lowest 1.0, highest 2.1) because of the condition $0 \leq \cos^2 \varphi \leq 1$. An examination of the possible deviations gives the more realistic ranges for the $|\varphi_i|$'s quoted in Fig. 2.

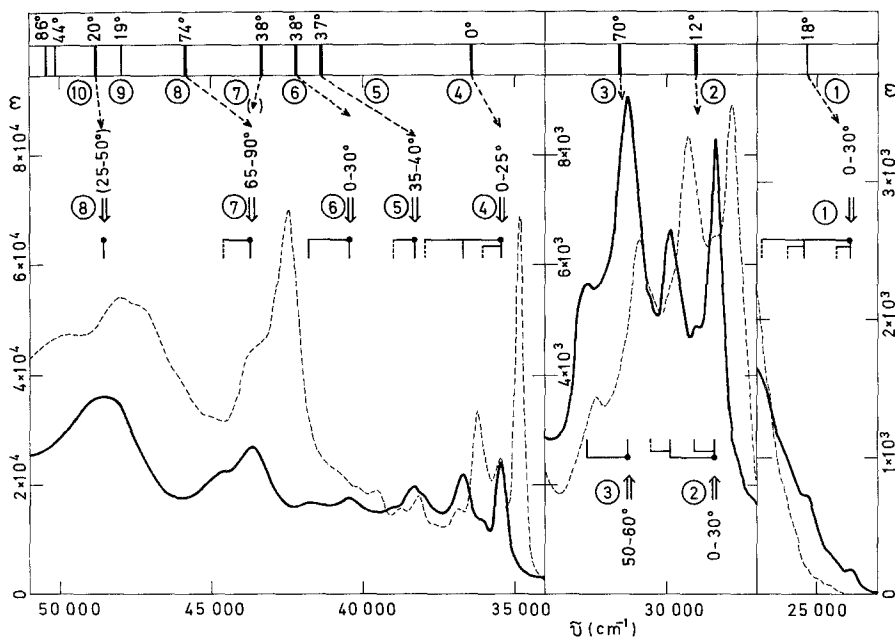


Fig. 2. Room temperature absorption spectrum of 3-aza fluoranthene in 3-methylpentane (3-MP) solution (solid line). Double arrows indicate the origins of 8 observed electronic transitions [22] and nearby numbers give the values of ϕ . On top calculated (PPP) frequencies of vertical transitions 1-12. Thick lines: oscillator strength above 0.2, thin lines: below 0.2. Dashed arrows indicate assignment to observed transitions. Numbers above give calculated values of ϕ . The dashed line is the absorption curve of fluoranthene (3-MP, room temp.)

Spectral Effects of Inductive Substituents

It is known that already the simplest version of the PPP model (configuration interaction only with singly excited states, constant resonance integrals β between neighbours, neglect of β 's between non-neighbours, neglect of penetration integrals) gives a rather good account of many features of the low-lying excited states of conjugated hydrocarbons without pronounced bond length alternation [21, 28-33]. Some parts of this apparently successful interpretation are likely to change as better methods become available (cf. the drastic decrease in energies of some states when doubly and higher excited configurations are taken into account [34-36], as well as the gradually accumulating experimental and theoretical evidence for possible importance of σ -electrons for spectral properties of π -electron molecules [37-41]). Nevertheless, at present it seems appropriate to assume the validity of the PPP model when one wishes to examine when the above-discussed HMO model is likely to fail. We shall limit our attention to non-polyenic molecules without strong bond length alternation where the usual version of the HMO method with its assumption of equal β integrals for all bonds has some chances to be successful. Few data are available for polyenic systems; the effect of methyl substitution on the spectra of fulvene and 6-vinylfulvene is not described

correctly by the HMO method and has been rationalized in terms of the molecules-in-molecules [MIM] method [42]. The simple version of the PPP theory gives poor results for spectra of polyenic hydrocarbons but versions in which β is varied with bond length to self-consistency are successful. Unfortunately, it seems that small hydrocarbons (e.g., butadiene, fulvene) require a steeper dependence of β on bond length than large ones (e.g., perylene, pentacene), and none of the methods proposed fits all perfectly [43–48 and references therein]. This could be due to inherent limitations of the π -electron approximation [38].

It was pointed out some time ago [30, cf. 32, 46, 49–52] that from the viewpoint of the PPP model the correlation of excitation energies of $1 \rightarrow -1$ excited states of benzenoid hydrocarbons with HMO orbital energy differences (Eq. (1)) succeeds because (i) the $1 \rightarrow -1$ configurations practically never mix strongly with other configurations in the PPP model, (ii) for benzenoid hydrocarbons the contribution of electron repulsion terms to the excitation energy, as calculated by the PPP method, is almost constant. No satisfactory theoretical explanation of these observations seems to have been offered so far. Under fairly reasonable assumptions, the contributions of the Coulomb and exchange integrals to the excitation energies can be estimated from experimental data [52]; they are indeed almost constant for benzenoid hydrocarbons and have quite a different value for azulene, which along with many other non-alternants deviates badly in the HMO plot.

By a similar reasoning (cf. Ref. [16]), the HMO treatment of the effect of inductive substituents on the $1 \rightarrow -1$ transition, even in molecules without a strong bond length alternation, is unreliable unless the following conditions are fulfilled.

1. The parent molecule must have a relatively pure $1 \rightarrow -1$ state in the PPP model. Here we are using the fact that Hückel MO's and SCF MO's generally differ very little; the $1 \rightarrow -1$ configurations constructed from one and the other are also almost identical. As mentioned above, the $1 \rightarrow -1$ configuration of hydrocarbons is only rarely found to mix strongly with others. A typical example is a PPP study of 45 non-alternant hydrocarbons, using HMO's for starting orbitals, of which only two did not have any excited states that could be unequivocally called $1 \rightarrow -1$ and only two or three others had their $1 \rightarrow -1$ configurations mixed to any significant extent [32]. A priori predictions of when this will happen do not seem possible at present.

2. The inductive substituent must not cause such a mixing. For derivatives of alternant hydrocarbons, approximate rules are available by means of which a simple inspection of the form of the molecular orbitals allows a prediction whether this condition will be fulfilled [34]. No such guidelines have been derived for the case of non-alternant hydrocarbons. In general, if the inductive effect of the substituent is weak, if the $1 \rightarrow -1$ state is far removed in energy from other excited states, and if at least some of the coefficients at the atom in question of molecular orbitals ψ_1, ψ_{-1} , and those involved in the nearest-lying configurations are small, the HMO approach should have the best chances to succeed.

3. If the above conditions are fulfilled and CI is of no importance, it still has to be required that the substituent effect on the HMO $1 \rightarrow -1$ excitation energy $\Delta E_{1,-1}^{\text{HMO}}$ defined in Eq. (1) should resemble its effect on the SCF MO $1 \rightarrow -1$ singlet excitation energy $\Delta E_{1,-1}^{\text{SCF}}$ (the diagonal element of the PPP Hamiltonian in

the representation of singlets constructed from Pople's SCF orbitals):

$$\Delta E_{1,-1}^{\text{SCF}} = \varepsilon_{-1}^{\text{SCF}} - \varepsilon_1^{\text{SCF}} - J_{1,-1} + 2K_{1,-1} \quad (5)$$

where $\varepsilon_{-1}^{\text{SCF}}$ and $\varepsilon_1^{\text{SCF}}$ are the energies of ψ_{-1} and ψ_1 in the SCF approximation, respectively, and $J_{1,-1}$ and $K_{1,-1}$ are the Coulomb and exchange integrals between ψ_{-1} and ψ_1 (real):

$$J_{1,-1} = \int \psi_1^2(1) \frac{e^2}{r_{12}} \psi_{-1}^2(2) d\tau_1 d\tau_2, \quad (6)$$

$$K_{1,-1} = \int \psi_1(1) \psi_{-1}(1) \frac{e^2}{r_{12}} \psi_1(2) \psi_{-1}(2) d\tau_1 d\tau_2. \quad (7)$$

The orbital energies ε^{HMO} and ε^{SCF} are eigenvalues of the Hückel and SCF Hamiltonians, respectively. The electron-repulsion terms of the SCF method enter both the ε 's and the J and K integrals. If the effect of a substituent is purely inductive, i.e., if it only affects the electronegativity of say the μ -th site in the conjugated system, to which it is attached, then, in the representation of atomic orbitals, the substituent will affect only the μ -th diagonal element of the former and to the first order also only the μ -th diagonal element of the latter. To a reasonable approximation, the effect of inductive substituents on orbital energies will thus be qualitatively similar in both methods as required if the HMO approach is to give correct signs of spectral shifts. Quantitative agreement is hardly to be expected. Moreover, it is possible that in some cases even the qualitative agreement will not be obtained, particularly if the substituent affects both ψ_1 and ψ_{-1} strongly (cf. 3-aza-I in Table 1). Finally, a comparison of Eqs. (1) and (5) shows that the electron repulsion terms $-J_{1,-1} + 2K_{1,-1}$, which amount typically to -3 – 5 eV [52], must not be affected significantly by substitution. For small perturbations such as methyl or even aza substitution, it is usually tacitly assumed that this condition is satisfied. It is shown below that in I it is satisfied rather poorly. However, if substituent effects on ionization potential and electron affinities are not required to be reproduced correctly in the HMO approximation, it is not necessary to require separately that the term $-J_{1,-1} + 2K_{1,-1}$ should remain strictly constant and that the HMO and SCF orbital energies should change in exactly the same way under the effect of substitution, as long as the deviations are in opposite sense and compensate. This actually happens in the azafluor-anthenes (Table 1) so that in spite of fairly large variations in the value of $-J_{1,-1} + 2K_{1,-1}$ the substituent effects on $\Delta E_{1,-1}^{\text{HMO}}$ and $\Delta E_{1,-1}^{\text{SCF}}$ are similar.

To summarize, the most likely source of trouble for the simple qualitative HMO prediction of effects of inductive substituents on the energy of the $1 \rightarrow -1$ singlet state (Eqs. (1) or (2)) is the violation of the second and perhaps the third of the above conditions. To minimize the danger, one should preferably apply the HMO approach to substituents with a weak inductive effect such as methyl rather than to aza substitution. Therefore, Eq. (2) should be intirely sufficient and an exact solution of the HMO secular problem is not needed. However, the mesomeric effect of groups such as methyl may be a complicating feature; in molecules calculated to be little sensitive to inductive effects the mesomeric effect may prevail completely and lead to red shifts for every position of substitution. This is known to happen in I [18].

PPP Calculations on the Azafluoranthenes and Discussion

1. *Method.* The calculations constituted a part of an extensive study of amines and aza heterocycles [54]. They were done in the usual manner [21] using all singly excited configurations (constructed from SCF orbitals) with diagonal matrix elements of the PPP Hamiltonian smaller than 8 eV, using the Mataga-Nishimoto [55] approximation for two-center repulsion integrals $\gamma_{\mu\nu}$, all bond lengths equal to 1.40 Å, regular geometry, parameters for carbon as in previous work of the Prague group [30–33, 56]: valence state ionization potential $I_C = 11.42$ eV, $\beta_{CC} = -2.318$ eV, one-center $\gamma_C = 10.840$ eV; the parameters for nitrogen were those recommended in Ref. [34]: $I_N = 16.55$ eV, $\gamma_N = 14.77$ eV, $\beta_{CN} = -2.70$ eV. They give the best overall agreement for the large number of aza compounds examined but they seem to exaggerate the spectral shifts on aza substitution in azulene and fluoranthene. Table 1 gives a summary of the results and a comparison with fluoranthene.

The method of selection of the singly excited configurations to be used in CI according to the size of their diagonal elements is quite arbitrary and so is the limit used (8 eV). It is based on the assumption that if a large enough number of low-energy configurations are used, all of those with appreciable weight in the several low-lying excited states will automatically be included along with a good many unnecessary ones. Energies and wave functions of low-lying excited states should then be little sensitive to the exact number of the singly excited configurations used (cf. Ref. [54]). Judging by the well-known success of the PPP method, such an assumption is reasonable, although it has only rarely been tested by numerical calculations.

However, we were interested in rather small differences in excitation energies of two similar molecules, comparable to those induced by a change in the extent of configuration interaction. Therefore, we considered it necessary to compare the excitation energies, oscillator strengths and polarization directions of the first eight excited states of I and 3-aza-I calculated using different numbers of configurations and different methods for their selection (Table 2). The differences are small, except for polarization directions for the sixth and seventh excited states. In particular, the calculations with CI limits 8 and 9 eV lead to virtually identical results, showing that the limit of 8 eV used in our calculations is sufficient within the framework of singly excited configurations.

2. *Nature of the Excited States.* In fluoranthene itself, the first four long-wavelength electronic transitions have been well characterized in the absorption spectrum [22, 57] and in the simple PPP description (Table 1) they correspond to quite pure $2 \rightarrow -1$, quite pure $1 \rightarrow -1$, a mixture of $3 \rightarrow -1$ and $1 \rightarrow -3$ and a mixture of $4 \rightarrow -1$ with $2 \rightarrow -2$ configurations, respectively [20, 32]. This interpretation is the same regardless of whether HMO's or SCF MO's are the starting orbitals for CI; compare Table 1 and Ref. [32], (see also Ref. [56] for a comparison of CI calculations starting with HMO's and SCF's). Directions of polarization for transitions 2–4 are known [20, 24] to agree with PPP calculations (Table 1). Transition 1 presented experimental problems. According to polarized emission spectra [20] it is probably y -axis polarized as predicted by PPP calculations [32]

but the evidence is not quite conclusive. Measurements of dichroism in a stretched polyethylene sheet [24] were inconclusive because of the weak intensity of absorption in this region. We have now repeated the latter measurements using a larger number of sheets and are able to confirm the *y*-axis polarization of the 0–0 vibrational component of transition 1.

Measurements of dichroism [24] and substituent effects [22] make it likely that two weak oppositely polarized transitions 5 and 6 are present in the region 37000–41000 cm^{-1} in fair agreement with PPP calculations, according to which they are predominately of $2 \rightarrow -3$ and $1 \rightarrow -2$ character, respectively. Further, according to dichroic measurements [24] the seventh observed transition of Ref. [22], a strong band at 42500 cm^{-1} , should be assigned to calculated transition 8, described by the $1 \rightarrow -3$ and $3 \rightarrow -1$ configurations. Thus, it is related to transition 3 similarly as the L_b and B_b states are related to each other in benzenoid hydrocarbons. The dichroic spectra do not exclude the possibility that transition 7, calculated to be weaker and of opposite polarization, is hidden under transition 8, whose energy should be only a little higher. No further calculated transitions are listed in Table 1 since the use of the PPP method is questionable at these and higher energies. Up to 52000 cm^{-1} only one additional intense transition is predicted (47800 cm^{-1} , osc. str. 0.72, *z*-axis polarized). It could correspond to the observed intense transition 9 of Ref. [22] at 48000 cm^{-1} which has been shown [24] to be polarized along the *z*-axis. Although the simple PPP calculation thus seems to match the experimental data up to surprisingly high energies we think that this may be fortuitous, particularly in case of the weak transitions 5 and 6.

Studies of I using more elaborate versions of the PPP theory have been reported recently. A calculation using orthogonalized MO's and bond length dependent β integrals [58] gave results virtually identical with those of Table 1 for energies, intensities, and polarizations of all transitions up to 50000 cm^{-1} (only the order of our almost degenerate transitions 5 and 6 is reversed, the intensity of transition 5 increased strongly and the calculated energies are all shifted a little too high). As mentioned above, larger effects could be expected from consideration of doubly excited configurations or perhaps introduction of $\sigma - \pi$ interactions. In another calculation using orthogonalized MO's [59] and including penetration integrals the results for the lowest two excited states were similar to those of Table 1. CI was limited to 5 excited configurations so that no meaningful discussion of other states is possible.

A calculation [60] by the MIM method gave excited state energies and symmetries which are again almost the same as those of Table 1 for the first four transitions but suggest a more straightforward interpretation of the higher energy region: the fifth calculated transition is at 38560 cm^{-1} ($f = 0.04$, *z*-axis polarized), corresponding to the observed fifth transition (38170 cm^{-1} , weak, *z*-axis pol.), the sixth calculated transition is at 40660 cm^{-1} ($f = 0.42$, *y*-axis pol.), corresponding to the sixth observed transition (39530 cm^{-1} , weak, *y*-axis pol.), the seventh calculated transition is at 42600 cm^{-1} ($f = 1.13$, *y*-axis pol.), assigned to the seventh observed transition (42460 cm^{-1} , strong, *y*-axis pol.); higher transitions were not calculated. Then, it need not be assumed that the observed strong transition 7 corresponds to two overlapping bands. The fact that the calculated intensity of transition 6 seems much too high is perhaps less disturbing

Table 1. PPP Calculations on excited

Molecule		Excited states ^a - CI SCF				
		1	2	3	4	5
I	ΔE^{PPP}	3.32	3.51	3.93	4.48	5.08
	f	0.014	0.52	0.076	0.22	0.010
	pol.	0°	90°	0°	90°	90°
		2-1 (83 pct.)	1-1 (92 pct.)	3-1 (55 pct.)	4-1 (48 pct.)	2-3 (60 pct.)
		3-1 (15 pct.)	2-2 (4 pct.)	1-3 (28 pct.)	2-2 (33 pct.)	3-2 (7 pct.)
1-AZA-I	ΔE^{PPP}	3.17	3.44	4.16	4.41	5.16
	f	0.0093	0.56	0.013	0.15	0.096
	pol.	172°	83°	151°	93°	96°
		2-1 (92 pct.)	1-1 (90 pct.)	1-3 (32 pct.)	3-1 (29 pct.)	1-2 (51 pct.)
		3-1 (4 pct.)	2-2 (4 pct.)	4-1 (26 pct.)	4-1 (28 pct.)	2-2 (20 pct.)
2-AZA-I	ΔE^{PPP}	3.38	3.50	4.06	4.57	5.08
	f	0.044	0.51	0.024	0.29	0.064
	pol.	26°	97°	175°	94°	26°
		2-1 (89 pct.)	1-1 (91 pct.)	3-1 (49 pct.)	4-1 (34 pct.)	2-2 (59 pct.)
		3-1 (6 pct.)	2-3 (3 pct.)	1-2 (28 pct.)	2-3 (28 pct.)	2-3 (8 pct.)
3-AZA-I	ΔE^{PPP}	3.15	3.60	3.91	4.51	5.13
	f	0.057	0.40	0.23	0.25	0.44
	pol.	72°	78°	160°	90°	127°
		1-1 (47 pct.)	1-1 (45 pct.)	3-1 (54 pct.)	4-1 (50 pct.)	1-2 (35 pct.)
		2-1 (35 pct.)	2-1 (34 pct.)	2-1 (23 pct.)	2-2 (25 pct.)	4-1 (20 pct.)
7-AZA-I	ΔE^{PPP}	3.30	3.73	3.94	4.56	5.06
	f	0.023	0.45	0.099	0.50	0.0013
	pol.	142°	90°	8°	90°	141°
		2-1 (61 pct.)	1-1 (71 pct.)	3-1 (56 pct.)	2-2 (61 pct.)	2-3 (38 pct.)
		1-1 (22 pct.)	2-1 (21 pct.)	1-3 (25 pct.)	4-1 (15 pct.)	1-2 (22 pct.)
8-AZA-I	ΔE^{PPP}	3.34	3.59	3.94	4.63	5.10
	f	0.17	0.42	0.096	0.079	0.20
	pol.	74°	84°	155°	112°	137°
		1-1 (48 pct.)	1-1 (46 pct.)	3-1 (45 pct.)	4-1 (62 pct.)	1-2 (64 pct.)
		2-1 (36 pct.)	2-1 (33 pct.)	2-1 (24 pct.)	2-2 (17 pct.)	2-3 (10 pct.)

^a The excitation energy in eV (ΔE^{PPP}), the oscillator strength (f), and the angle of the transition moment direction measured anticlockwise from the positive direction of the y -axis in formula I, in the SCF PPP approximation. For each excited state wavefunction, two leading configurations and their per cent weights are listed. The symbol $i-j$ represents a singly excited configuration in which one electron is missing in the i -th bonding molecular orbital and an extra electron is present in the j -th antibonding molecular orbital; the bonding orbitals are numbered in the direction of decreasing energy, the antibonding in the direction of increasing energy, starting with the frontier orbitals.

^b For fluoranthene, energies of the highest occupied (ϵ_1) and lowest virtual (ϵ_{-1}) molecular orbitals, energy of the 1-1 excited configuration (ΔE_1^{-1} , no CI) and the two electron term ($-J_1^{-1} + 2K_1^{-1}$, see

singlet states of azafluoranthenes

			The 1-1 excited configuration ^b		
6	7	8		SCF (eV)	HMO ^c (-β)
5.13	5.26	5.39	ϵ_1	-9.406	-0.618
0.053	0.60	1.3	ϵ_{-1}	-3.258	0.371
0°	90°	0°			
1-2 (90 pct.)	4-1 (40 pct.)	1-3 (66 pct.)	$\Delta E_{1,-1}$	3.666	0.989
2-4 (5 pct.)	2-2 (36 pct.)	3-1 (27 pct.)	$-J_{1,-1} + 2K_{1,-1}$	-2.482	
5.17	5.32	5.48	$\Delta \epsilon_1$	-0.098	-0.017
0.37	0.37	1.3	$\Delta \epsilon_{-1}$	-0.162	-0.064
94°	68°	171°			
2-2 (36 pct.)	2-3 (34 pct.)	1-3 (45 pct.)	$\Delta \Delta E_{1,-1}$	-0.050	-0.047
1-2 (27 pct.)	4-1 (18 pct.)	3-1 (21 pct.)	$\Delta(-J_{1,-1} + 2K_{1,-1})$	0.014	$c_{-11}^2 - c_{11}^2: 0.075$
5.13	5.26	5.45	$\Delta \epsilon_1$	-0.081	-0.018
0.13	0.54	0.86	$\Delta \epsilon_{-1}$	-0.067	-0.013
9°	57°	164°			
1-3 (55 pct.)	2-3 (35 pct.)	4-1 (35 pct.)	$\Delta \Delta E_{1,-1}$	0.002	0.005
1-2 (17 pct.)	3-1 (27 pct.)	1-2 (27 pct.)	$\Delta(-J_{1,-1} + 2K_{1,-1})$	-0.012	$c_{-12}^2 - c_{12}^2: -0.024$
5.23	5.38	5.68	$\Delta \epsilon_1$	-0.225	-0.045
0.33	0.22	0.78	$\Delta \epsilon_{-1}$	-0.214	-0.080
52°	52°	164°			
1-3 (30 pct.)	2-2 (42 pct.)	2-3 (39 pct.)	$\Delta \Delta E_{1,-1}$	-0.131	-0.035
1-2 (29 pct.)	1-2 (20 pct.)	1-3 (30 pct.)	$\Delta(-J_{1,-1} + 2K_{1,-1})$	-0.142	$c_{-13}^2 - c_{13}^2: 0.043$
5.07	5.48	5.57	$\Delta \epsilon_1$	-0.230	-0.051
0.072	1.3	0.67	$\Delta \epsilon_{-1}$	-0.020	-0.009
14°	173°	66°			
1-2 (60 pct.)	1-3 (51 pct.)	4-1 (68 pct.)	$\Delta \Delta E_{1,-1}$	0.108	0.041
2-3 (14 pct.)	3-1 (23 pct.)	2-2 (14 pct.)	$\Delta(-J_{1,-1} + 2K_{1,-1})$	-0.101	$c_{-17}^2 - c_{17}^2: -0.105$
5.15	5.36	5.46	$\Delta \epsilon_1$	-0.073	-0.015
0.067	0.73	0.92	$\Delta \epsilon_{-1}$	-0.115	-0.021
36°	30°	147°			
2-3 (34 pct.)	2-2 (30 pct.)	2-3 (25 pct.)	$\Delta \Delta E_{1,-1}$	-0.064	-0.007
1-3 (20 pct.)	1-3 (26 pct.)	2-2 (22 pct.)	$\Delta(-J_{1,-1} + 2K_{1,-1})$	-0.021	$c_{-18}^2 - c_{18}^2: -0.007$

text). For aza fluoranthenes, changes of these quantities relative to fluoranthene. For the parameters used, and from the measured photoionization potential (*IP*) of benzene (9.245 eV [53], calculated $\epsilon_1 = -10.66$ eV): $IP = -(\epsilon_1 + 1.41)$; from the measured gas-phase electron affinities (*EA*) and calculated ϵ_{-1} values for eight hydrocarbons of Ref. [52]: $EA = -(\epsilon_{-1} + 2.41) \pm 0.2$, both in eV. Experimental *EA* of fluoranthene is 0.63 eV [22], the value predicted from ϵ_{-1} is 0.85 eV.

^c From Ref. [23]; $c_{1\mu}$ and $c_{-1\mu}$ are the expansion coefficients at atom μ of the highest filled and lowest empty molecular orbital, respectively.

Table 2. 3-aza-I: Effect of the extent of configuration interaction^a (CI-SCF)

Exc. state	16 conf. ^b			18 conf. ^c			25 conf. ^d			26 conf. ^e			36 conf. ^f		
	$\Delta\Delta E$	f	pol.	$\Delta\Delta E$	f	pol.	$\Delta\Delta E$	f	pol.	$\Delta\Delta E$	f	pol.	$\Delta\Delta E$	f	pol.
1	-0.18	0.083	72°	-0.20	0.057	72°	-0.19	0.070	71°	-0.18	0.057	72°	-0.18	0.058	71°
2	+0.11	0.39	77°	+0.10	0.41	77°	+0.11	0.36	78°	+0.09	0.40	78°	+0.11	0.40	78°
3	-0.01	0.24	159°	-0.03	0.24	156°	-0.02	0.23	159°	-0.02	0.23	160°	-0.01	0.23	160°
4	0.00	0.29	87°	+0.04	0.25	89°	+0.03	0.26	90°	+0.03	0.25	90°	+0.04	0.25	91°
5	+0.05	0.55	107°	+0.04	0.55	110°	+0.02	0.52	113°	+0.05	0.44	127°	+0.04	0.41	127°
6	+0.10	0.12	119°	+0.10	0.27	174°	+0.12	0.31	30°	+0.11	0.33	52°	+0.12	0.28	54°
7	+0.06	0.71	16°	+0.09	0.54	39°	+0.12	0.28	54°	+0.11	0.22	52°	+0.12	0.24	45°
8	+0.36	0.47	154°	+0.35	0.56	154°	+0.30	0.77	161°	+0.29	0.78	164°	+0.29	0.75	161°

^a $\Delta\Delta E$ is the change in the excitation energy with respect to I calculated using the same rule for the choice of configurations (16, 18, 25, 26, 34 confs., respectively).

^b Excitations from the four highest occupied to the four lowest virtual MO's.

^c All configurations with diagonal elements of the Hamiltonian up to 7 eV.

^d Excitations from the five highest occupied to the five lowest virtual MO's.

^e All configurations with diagonal elements up to 8 eV.

^f All configurations with diagonal elements up to 9 eV.

when one notices that the relative intensities predicted by this calculation for the first four transitions are also quite incorrect (transition 1 much stronger than 3 and even 4). Unfortunately, it seems impossible to decide between the two possible interpretations for observed transition 7 on basis of the experimental data available.

For the time being, we prefer to continue to use the simple original PPP model as the basis of our discussion; first, because it is very simple and yet provides just as good or better an interpretation of the experimental data in comparison with others, second, because it seems possible that the incorrect intensities in the MIM calculation signal a more serious trouble: the calculated fairly strong transition 1 should perhaps be assigned to the fairly strong observed transition 3 and the very weak calculated transition 3 to the very weak experimental transition 1. Our doubts are strengthened by an inspection of the MIM results for the related dibenzo [*a, g*]pyracyclene (D-7 of Ref. [60]) where the observed weak first band starting at about 500 m μ is calculated to be second and lie as high as 360 m μ ; our unpublished PPP calculation gives the correct order of states. (However, more detailed experimental data are needed for this molecule). Moreover, the MIM calculations [60] encountered similar problems with some other molecules (biphenylene).

3. *Applicability of the HMO Approach to Shifts of the First Intense Band (Transition 2 in Fluoranthene, Corresponding to 1 \rightarrow -1).* Table 1 shows that the first condition of those listed above for the applicability of the HMO approach is fulfilled well and the third one fairly well. Table 1 does not show clearly how well the second condition is fulfilled, because the configurations were constructed from different starting MO's in each molecule, namely its own SCF MO's. Therefore, the 1 \rightarrow -1 configuration say in 1-aza-I is not the same as in I. However, for molecules of this size and as closely related one could assume that the SCF MO's are similar. Then, the composition of the CI wavefunction given in Table 1 would

suggest that in 1-, 2-, and 7-aza-I the second excited state is still predominantly of $1 \rightarrow -1$ character as in I itself, while in the 3- and 8-isomers mixing is strong and no state can be classified $1 \rightarrow -1$.

More direct information is obtained by repeating the calculations for the aza-I's using the SCF MO's of I to construct configurations, and otherwise using the same parameters as before. The results are similar: the second excited state is of predominantly $1 \rightarrow -1$ character in 1-aza-I (weight 68 pct.), 2-aza-I (60 pct.), and 7-aza-I (74 pct.), while no state can be classified as $1 \rightarrow -1$ in the other isomers. In 3-aza-I, the weight of the $1 \rightarrow -1$ configuration is almost the same in the first three excited states (22 pct., 31 pct., 23 pct.), in 8-aza-I, it is shared between the first two excited states (46 pct., 35 pct.).

Thus, while our second condition is satisfied fairly well but not perfectly in the 1, 2, and 7 isomers, it is not satisfied in the 3 and 8 isomers and HMO predictions should be completely unreliable. Indeed, while for both of these the PPP method predicts a blue shift, HMO calculations predict a red shift (0.10 eV, using $\Delta\alpha = -18750 \text{ cm}^{-1}$ in Eq. (2) [29]) and virtually no shift, respectively. Experimentally, (Fig. 2), the shift in 3-aza-I is by 0.07 eV to the blue (PPP prediction is 0.09 eV). The PPP and HMO methods agree for 1-aza (red shift), 2-aza (virtually no shift), and 7-aza (blue shift) substitution. The experimental shift (room temp., hydrocarbon solvent) in 1-aza-I is by 0.05 eV to the red [61] (PPP prediction is 0.07 eV, HMO prediction 0.17 eV). Thus, if one can base a conclusion on the available results for two compounds, it would seem that the PPP predictions agree well with experiment and that the HMO model fails where it should be unreliable.

To check the reliability of the PPP method in our case further, we have extended the spectral investigations of the one compound available to us (3-aza-I) to obtain information on polarization of transitions. An examination of directions of polarization in an unsymmetrical molecule is quite a severe test of the quality of the calculation.

4. Effect of Aza Substitution on Energy, Intensity, and Polarization of Fluoranthene Transitions. Comparison with Experiment. According to PPP results of Table 1, aza substitution should have quite complicated effects on the spectrum of I. The weak *y*-axis polarized transition 1 should keep its polarization in the 1-aza and 2-aza analogues, should be almost half way between the axes in 7-aza-I, and should lie essentially along the *z* axis in 3- and 8-aza-I. It should be intensified very strongly in 8-aza-I, somewhat less in 2- and 3-aza-I, a little in 7-aza-I, and should have decreased intensity in 1-aza-I; it should be red-shifted in 1- and 3-aza-I (by 0.15 and 0.17 eV, resp.), blue-shifted in 2-aza-I (probably hidden under the strong transition 2), but not shifted in the 7- and 8-isomers. Experimentally (room temp., hydrocarbon solvent) the 0-0 component in 1-aza-I [62] is weaker ($\epsilon = \text{ca. } 20$) than in I ($\epsilon = \text{ca. } 65$) and red shifted (0.08 eV), in 3-aza-I (Figs. 1, 2) it is polarized approximately along the *z*-axis, it is intensified ($\epsilon = 190$) and red-shifted (0.10 eV), all as expected. Also the qualitative observation [61, 63] that 7-aza-I is colorless, like I itself, while 1-aza-I and 3-aza-I are pale yellow, agrees with the expectations.

A similar variety of effects is predicted for transitions 2-4. Their polarization should be much less sensitive to aza substitution. Shifts of transition 2 have been

already discussed; its intensity should be remarkably insensitive to aza substitution. In contrast, transition 3 should lose intensity on 1- and 2-aza substitution but gain considerably in the 3-aza case, as is indeed observed (Fig. 2). It should undergo a striking blue shift on 1-aza and a smaller one on 2-aza substitution. Transition 4 should be red-shifted on 1-aza substitution, this seems to be in disagreement with the rather incomplete experimental data available [61]. It should be blue shifted in all other isomers, in agreement with experiment in the only available case (3-aza-I). Its intensity should be increased in 7-aza-I and decreased dramatically in 8-aza-I. The striking decrease of its intensity in 3-aza-I relative to fluoranthene (Fig. 2) is not reproduced by the calculations.

As mentioned above, the higher states of azafluoranthenes are often difficult to relate individually to the excited states of I because of predicted strong mixing. The most striking feature are the predicted strong variations in the calculated intensities. However, not much confidence can be placed in these. On 3-aza substitution the intensity of transitions 5 and 6 should increase strongly but this is not observed (Fig. 2). On the other hand, the decrease of intensity of the observed transition 7 (presumably a superposition of calculated transitions 7 and 8) agrees with the calculation. The observed directions of polarization are in accordance with the assignment of two distinct electronic transitions 5 and 6 in the region $37\,000\text{--}41\,000\text{ cm}^{-1}$ [20, 22, 24]. The calculated energies of transitions 5 and 6 are somewhat too high, just as in I itself [20, 22]. Also the calculated blue shift of transition 8 is exaggerated.

For the first five excited states the calculated transition moment directions correctly represent the trend found experimentally for band origins $|\varphi_4| < |\varphi_1| = |\varphi_2| < |\varphi_5| < |\varphi_3|$ and even the calculated magnitudes agree well, considering experimental uncertainties (Fig. 2). For the sixth excited state, however, $|\varphi_6| = |\varphi_4|$ from experiment, while the calculation gives $|\varphi_6| = |\varphi_5|$. To account for the experimental polarization of the observed transition 7, one has to assume again, as in I itself, that it is due to a superposition of calculated transitions 7 and 8.

The solution spectrum shows an additional intense band at $48\,500\text{ cm}^{-1}$, probably related to the fluoranthene band at $48\,000\text{ cm}^{-1}$. Only the onset of this band is seen in the sheet spectra (Fig. 1) and it is not possible to read off its polarization with accuracy. The probable range for the deviation from the symmetry axis is $25\text{--}50^\circ$. Calculations predict the next intense band of 3-aza-I to be at $48\,800\text{ cm}^{-1}$ (osc. str. 0.74, polarized at 70° , corresponding to a deviation of 20° from the orientation axis).

On the whole, for low-lying excited states the agreement between calculated and experimental results is surprisingly good while the higher states present problems and it could well be that they require a consideration of doubly excited configurations.

In 1-aza-I, our transition 1 (first peak at $416\text{ m}\mu$) has previously been assigned to an $n - \pi^*$ state [62]. The assignment was based on an evaluation of small changes in the shape of the absorption curve when minute amounts of proton-donors were added to cyclohexane solvent. We believe that this assignment was incorrect: (i) PPP calculations for parent I predict the existence of a weak $\pi - \pi^*$ transition in this region; the calculated effects of 1- and 3-aza substitution match

those observed. (ii) The transition energy seems much too low for an $n - \pi^*$ state. According to Ref. [62], lowest $n - \pi^*$ transition energies in mono aza derivatives of conjugated hydrocarbons are determined mostly by the energy of the lowest empty π -orbital, since the energy of the nitrogen lone pair orbital should be only little sensitive to the total charge on nitrogen, which in turn does not vary much from a molecule to another. In spite of the additional neglects involved (e.g. of the J and K terms and of configuration interaction), this seems to be a reasonable first-order approximation. Indeed, the authors show the existence of a nice linear relationship between the $n - \pi^*$ transition energies in four mono aza analogues of alternant hydrocarbons and the HMO energies of their lowest empty π -orbitals. According to this relation, the lowest $n - \pi^*$ transition in 1-aza-I should lie at $365 \text{ m}\mu$ [62]. The authors remark that the large discrepancy is probably due to non-alternant nature of I. However, HMO [23, 64, 65] as well as our present SCF calculations on both 1-aza-I and also I itself show that position 1 should be relatively electron-deficient. Using the parameters of this paper, PPP SCF π -electron-densities on nitrogen in 1, 2, 3, 7, and 8-aza-I are 1.246, 1.263, 1.257, 1.263 and 1.263 respectively, as compared e.g. to 1.265 in quinoline and 1.257 in isoquinoline. In I itself, the SCF π -electron-densities in these positions are 0.968, 1.007, 0.979, 0.999, 1.005, respectively. Experimentally, both the strikingly low basicity of 1-amino-I [17] and a comparison of basicities as well as nucleophilicities of 1- and 7-aza-I [65] lead to a similar conclusion. Thus, in 1-aza-I, electrons in the nitrogen n orbital should be more tightly bound than usual. If this effect is large enough, the $n - \pi^*$ transition energy should indeed deviate from the expected value of $365 \text{ m}\mu$ but towards shorter rather than longer wavelengths. (iii) Finally, not only 1-aza-I and 3-aza-I but also all other derivatives of I that have been investigated in detail, as well as the parent hydrocarbon itself, show a weak transition in this same region. The fine structure observed is rather similar in all cases, including 3-aza-I, and can be easily interpreted in terms of a few vibrational frequencies. It gives no evidence for the presence of more than one distinct electronic transition in this region in 3-aza-I [22].

5. *Conclusions.* In view of its crudeness, the ability of the simple version of the PPP theory to predict correctly intricate changes in energies, intensities, and polarizations of the first three fluoranthene transitions on 3-aza substitution is quite striking. Even for higher lying states the agreement is good. It would be of interest to check experimentally the validity of the variety of predictions made for aza substitution in the other positions.

On the other hand, the use of the simple HMO method for predictions of spectral shifts due to inductive substituents as well as the use of such shifts for estimates of electron density changes on excitation may be less safe than often assumed.

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