

111. Electronic Structure and Photophysical Properties of Isoindole and its Benzo[f]- and Dibenzo[e, g]-Derivatives¹⁾

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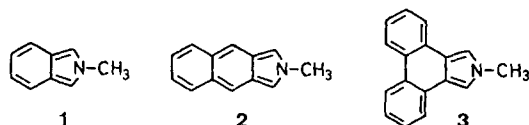
Summary. The synthesis of N-methyl-benz[f]isoindole (**2**) and N-methyl-dibenz[e, g]isoindole (**3**) is reported. The NMR. spectra of N-methyl-isoindole (**1**) and of **2** have been analysed and the implications concerning the alternation of bond lengths are discussed. The photophysical properties of **1** to **3** have been investigated by the following methods: HeI photoelectron (PE.) spectroscopy, UV./VIS. absorption (polarization measurements by the stretched-foil technique) and emission spectroscopy (fluorescence spectra, lifetimes and quantum yields, phosphorescence spectra), and flash spectroscopy (triplet-triplet absorption spectra). The discussion of the results is based on HMO. and PPP SCF CI. calculations and points to the relationship between the heterocycles **1** to **3** and the corresponding benzenoid hydrocarbons obtained by replacement of the –NMe– subunit by –CH=CH–. Some comments concerning the ground state properties of isoindole and related compounds are derived from the analysis of their electronic structure.

In the resonance theory formalism isoindole is represented by a single unexcited, *o*-quinonoid structure only. Indeed, the parent system is a highly reactive compound which has until recently [2] resisted many attempts to its isolation. The chemistry of isoindoles with a free NH group is complicated by a tautomeric equilibrium with the isoindolenine form and subsequent polymerization [2a]. Hence, alkylation of the nitrogen atom greatly increases the stability of isoindoles. N-Methyl-isoindole (**1**) is stable at room temperature in the absence of acid and oxygen and has been synthesized as the first representative of this heterocycle in 1951 by Wittig *et al.* [3]. Since then, numerous studies concerned with the synthesis and reactivity of isoindole and its derivatives have been reported [4] and several theoretical papers have dealt with the question of its 'aromaticity' [5]. No investigation of the photophysical or photochemical properties of this interesting chromophore has appeared to date, apart from some rather divergent results of semiempirical SCF CI. calculations [5f] [5i] [6] and more recently the UV. spectrum of isoindole [2a] and some of its derivatives [7]. We have chosen **1** as the parent substrate of the present study because it is readily synthesized [8] and purified. The N-methyl substituent may be considered as a minor perturbation to the electronic structure of the π -system which does not effectively reduce the symmetry. The introduction of the methyl blocking-group has further made possible the isolation and investigation of the benzo[f]homologue **2**, prior

1) Taken in part from the Ph. D. thesis of W. R. [1].

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evidence for the existence of this heterocycle being limited to trapping reactions [9] [10]³). The photochemistry of **1** will be the subject of a subsequent paper [11].



Results and discussion. - Table 1 summarizes the photophysical data obtained in the present investigation. Details will be discussed in the following sections.

Table 1. Summary of photophysical data. Symmetry assignments for C_{2v} molecular symmetry, z-axis = C_2 -axis, y-axis in plane

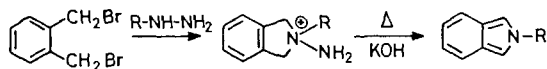
	1	2	3
PE. Spectrum: vertical IP's. [eV], (symmetry assignment).	7.12 ($2a_2$) 8.35 ($3b_2$) 9.42 ($1a_2$) 11. (σ^2)	6.56 ($3a_2$) 8.13 ($4b_2$) 8.5 ⁵ ($2a_2$) 9.7 ⁵ ($1a_2$) 10.2 ⁴ ($3b_1$) 10.7 (σ^1)	7.15 ($4a_2$) 7.61 ($5b_2$) 8.14 ($3a_2$) 9.20 ($2a_2$) 9.3 ⁵ ($4b_1$) 9.8 ⁵ ($3b_1$) 10.4 (σ^1)
$S_0 \rightarrow S_x$ Absorption Spectrum: Energy [cm^{-1}] ⁴ , (symmetry) of excited states S_x	29'300 (B_2) 34'400 (A_2) 45'000 (A_1)	22'200 (B_2) 30'500 (A_2) 39'550 (A_1)	29'250 (A_1) 34'850 (B_2) 38'100 (A_1) 39'550 (B_2)
$T_1 - T_1^X$ Absorption Spectrum: λ_{max} [nm]	620	720	680
Energy ⁴) of T_1 [cm^{-1}]	19'000	>10'250	22'800
Fluorescence Quantum Yield	0.88 ± 0.15	0.70 ± 0.1	0.99 ± 0.15
Triplet Quantum Yield	0.08 ± 0.05		
Phosphorescence lifetime [s]	0.4		8.7
Fluorescence lifetime ⁵) [ns]	12	20	18

³) Prof. Dr. J. Bornstein, Boston College, Chestnut Hill, Massachusetts, informs us that he has very recently succeeded in isolating benz[f]isindole but that it exists mainly in its tautomeric isindolenine form.

⁴) For S_1 : $\{\tilde{\nu}_{00}(\text{abs.}) + \tilde{\nu}_{00}(\text{flu.})\}/2$,
for $S_{>1}$: Energy of first apparent maximum,
for T_1 : Energy of first phosphorescence maximum (limit for **2** from flash photolysis).

⁵) Calculated from $\tau_{F1} = \Phi_{F1}/k_{F1}$; k_{F1} see eq. (2).

1. *Syntheses, ground state properties, and analyses of NMR. spectra.* A convenient synthesis for N-substituted isoindoles was recently described by Zeeh & König [8]:



We have obtained the benzologues **2** and **3** in essentially the same manner starting from 2,3-dimethyl-naphthalene and 9,10-dimethyl-phenanthrene, respectively. The last step and the purification of the products were carried out under exclusion of oxygen. Satisfactory spectral data were obtained for compounds **1** to **3** (Prep. Section). In the absence of acid, oxygen, and light the compounds are stable at room temperature either in substance or in solution. The sensitivity towards acid, oxygen etc. increases in the order **3** < **1** < **2** in qualitative agreement with the predicted [5] resonance energy increases when the isoindole π -systems of *o*-quinonoid topology are converted to derivatives with benzenoid π -systems.

The NMR. splitting patterns of the four strongly coupled 'aromatic' protons of **1** and **2** were analysed as *ABB'A'* systems with the aid of a LAOCOON II computer program. The experimental and calculated subspectra are shown in Fig. 1. The neglect of inter-annular couplings in the calculations is warranted by the fact that the singlet peaks due to the (H_1 , H_3) protons in **1** and (H_4 , H_9) protons in **2** are only broadened to *ca.* 1 Hz width at half-height by unresolved inter-annular couplings. The corresponding broadening of the α -proton signals (H_4 , H_7 in **1** and H_5 , H_8 in **2**) is discernible in Fig. 1 and serves to secure the conventional [12] assignment of the α - and β -protons to the low and high field signals, respectively.

The parameters resulting from the spectral analysis (Table 2) yield some information concerning the aromatic character of **1** and **2** in the electronic ground state. First we note that the chemical shifts of the 'aromatic' protons are only slightly shifted (*ca.* 0.2 ppm) to higher field in comparison with the corresponding protons in naphthalene (**4**) and anthracene (**5**), respectively, suggesting that the ring current in **1** and **2** is comparable to that in **4** and **5**. This statement should, however, be considered with caution since the observed chemical shifts are affected, *inter alia*, by charge distributions [13]. Furthermore, 'ring current shifts' are known [14] not to be directly related to resonance energy and reactivity criteria of aromaticity. Perhaps more useful is the information on bond length alternation which is to be gained from the coupling constants ${}^3J_{AB}$ and ${}^3J_{BB'}$. Vicinal coupling constants in planar benzenoid hydrocarbons show a faithful correlation with experimental bond lengths and hence with calculated π -bond orders [15]. *Crews et al.* have proposed [16] to use the ratio of vicinal coupling constants across formally single and double bonds, respectively, as an index for the delocalization of the nitrogen π -electrons in fused N-heterocycles. Their study includes 1,3-diphenyl-N-methyl-isoindole, the coupling constants of which are nearly identical to those of **1** obtained in this work. Similar data for methyl-substituted 1,3-diphenyl-isoindoles have also been reported by *White et al.* [7]. Both the index ${}^3J_{\text{ratio}}$ and the explicit bond lengths R_a and R_b (Table 2) calculated from the empirical relationship [15]

$${}^3J = -36.40 R_I + 58.46, [R_I] = \text{Å} \quad (1)$$

indicate substantial delocalization in **1** and **2**, the geometry of the benzenoid ring in **2** being identical, within the limits of error, with that in anthracene (**5**). It is interesting to compare the bond lengths calculated by eq. (1) with those predicted by the semiempirical SCF MO. calculations by *Dewar et al.* [5g] for the unsubstituted hetero-

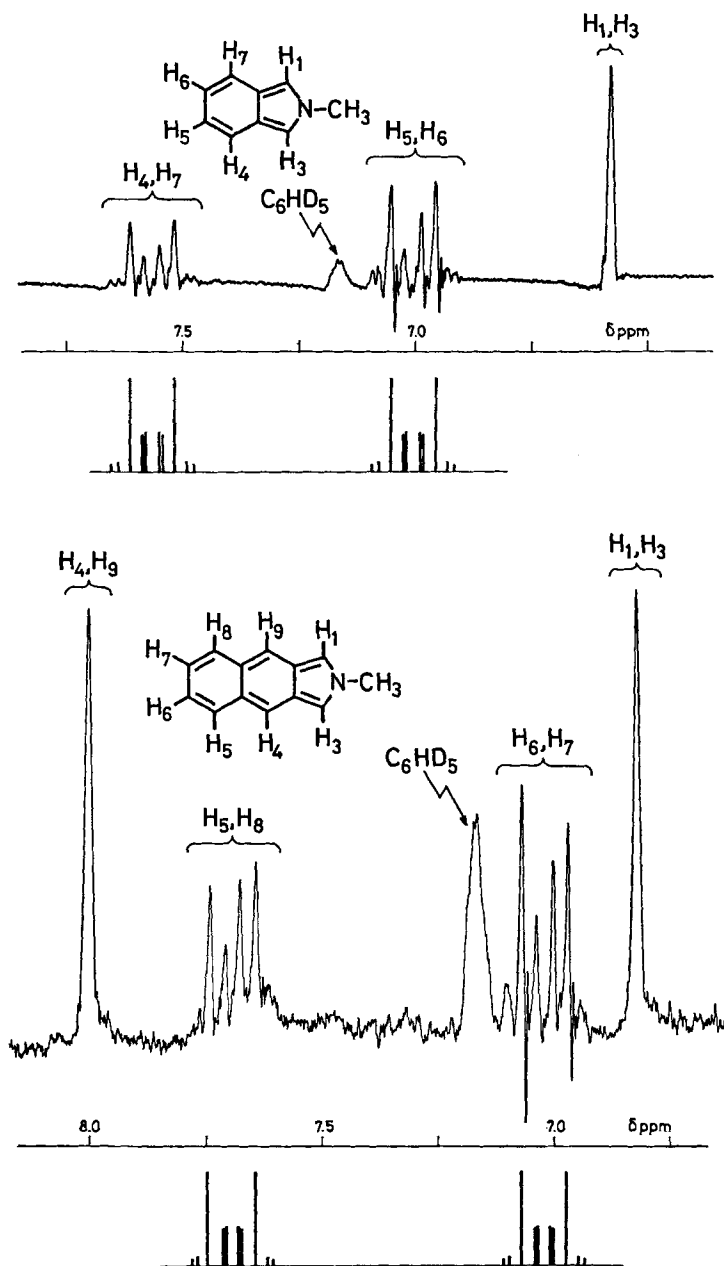
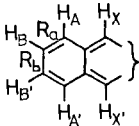

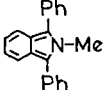

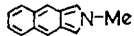



Fig. 1. Analysis of the $^1\text{H-NMR}$ spectra of **1** and **2**

Table 2. *H-NMR. Chemical shifts and coupling constants*

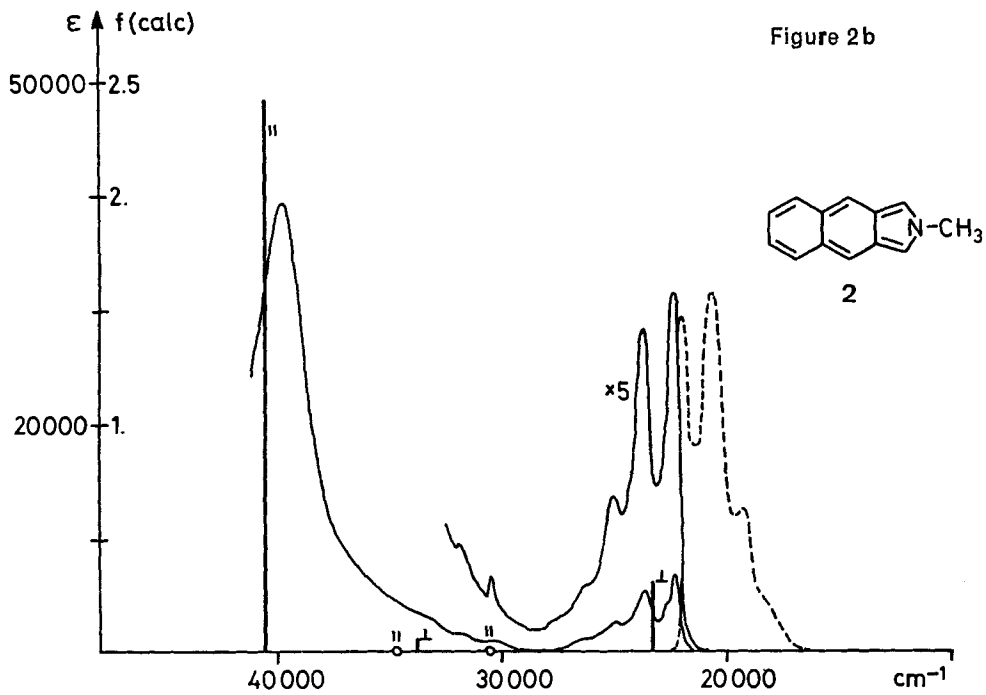
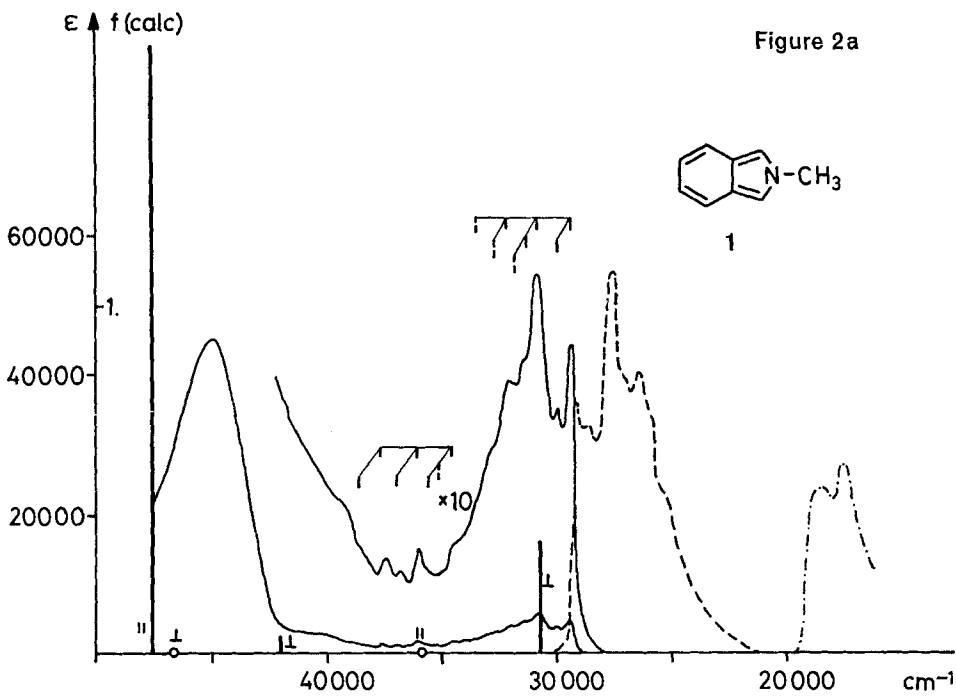
	 1	 [16]	 4 [15]	 2	 5 [15]
${}^3J_{AB} = {}^3J_{A'B'}$ [Hz]	8.60	8.63	8.30	8.51	8.54
${}^3J_{BB'}$ [Hz]	6.28	6.39	6.83	6.49	6.60
${}^4J_{AB'} = {}^4J_{A'B}$ [Hz]	0.86	0.98	1.20	1.29	1.14
${}^5J_{AA'}$ [Hz]	0.98	1.02	0.70	0.72	0.70
$({}^3J_{AB} + {}^3J_{BB'})/2$ [Hz]	7.44	7.51	7.57	7.50	7.57
${}^3J_{BB'}/{}^3J_{AB} = {}^3J_{ratio}$	0.73	0.74	0.92	0.76	0.77
$\delta_A = \delta_{A'}$ [ppm]	7.56	7.58	7.67	7.78	7.99
$\delta_B = \delta_{B'}$ [ppm]	6.96	6.93	7.32	7.10	7.44
$\delta_x = \delta_{x'}$ [ppm]	6.60	-	-	8.02	8.30
R_x^a [Å]	(1.37), [1.36]	(1.37)	1.37 (1.38)	(1.37), [1.36]	1.38 (1.37)
R_x^b [Å]	(1.43), [1.45]	(1.43)	1.41 (1.42)	(1.43), [1.45]	1.42 (1.42)

cycles (Table 2). The agreement with our estimates is fair, the bond length alternation calculated by *Dewar* being somewhat larger for both **1** and **2** which suggests that the calculated resonance energies of 11.6 and 14.6 kcal/mol, respectively, are rather too low. However, the difference may be ascribed to the N-methyl substituent which is expected to increase the availability of the nitrogen 'lone pair' for delocalization.

2. *UV-Vis. Absorption and emission spectra.* The first absorption band of **1** (Fig. 2, 0-0 transition at 29400 cm^{-1}) exhibits two dominant vibrational progressions of 1400 ± 50 and $550 \pm 50 \text{ cm}^{-1}$ which are revealed more distinctly by a spectrum taken at 77 K in a rigid hydrocarbon matrix. The first absorption band of unsubstituted isoindole [1a] has a very similar fine structure with progressions of 1390 ± 50 and $750 \pm 50 \text{ cm}^{-1}$, the 0-0 transition being blue shifted by 450 cm^{-1} . The vibrational features starting at 34600 cm^{-1} in **1** and at 34900 cm^{-1} in isoindole do not fit into the pattern at lower energies and are absent in the fluorescence spectrum of **1** which otherwise is close to the mirror image of the first absorption band. These findings are readily explained by regarding the above features as the onset of a second electronic transition which again is composed by two dominant progressions of 1500 ± 100 and *ca.* 900 cm^{-1} in both **1** and isoindole.

The presence of a weakly allowed, second electronic transition in **1** near 35000 cm^{-1} is indeed predicted by standard semiempirical π -electron SCF CI. calculations by the method of *Pariser, Parr & Pople* (PPP.) [17]. All calculations were carried out for idealized standard geometries (all bond lengths equal 1.4 Å, rings as regular polygons) using the *Mataga*-approximation for the two-center repulsion integrals. The nitrogen heteroparameters used ($I_N - I_C = -15.9 \text{ eV}$, $Z_N^c = 2$, $\gamma_{NN} = 18.0 \text{ eV}$, $\beta_{CN} = 0.9 \cdot \beta_{CC} = -2.09 \text{ eV}$) are those proposed by *Zahradnik* [18] for pyrrolic nitrogen. All singly excited configurations up to a maximum of 49 were included in the CI. calculations. A test calculation on **1** including doubly excited configurations

⁶⁾ Experimental, (calculated by eq. 1), [SCF calculation by *Dewar et al.* [5g]].



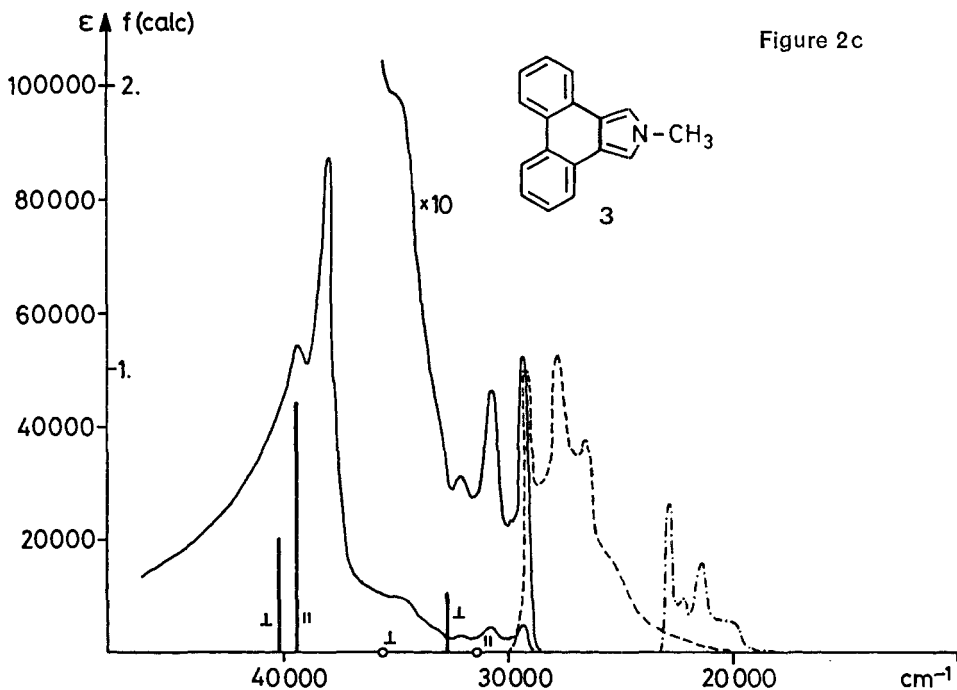


Figure 2c

Fig. 2 a-b-c. Absorption and emission spectra of **1** to **3**. — Absorption spectrum (*n*-hexane, room temperature); --- corrected fluorescence spectrum (*n*-hexane, room temperature, arbitrary scale in quanta per cm^{-1}); - . - . - uncorrected phosphorescence spectrum (EPA, 77 K). Vertical bars indicate calculated oscillator strengths f (o for very weak transitions); calculated polarizations \parallel and \perp refer to C_2 -axis

kindly performed upon request by Prof. *J. Michl* did not result in significant changes of the calculated spectrum in the near UV.

The first and second electronic transitions in **1** and **2** are predicted to be short and long axis polarized, respectively, by the PPP calculations. This was verified by measuring the linear dichroism spectra of these compounds in stretched polyethylene sheets [19]. In Fig. 3, a set of reduced spectra with different reduction factors d_{\parallel} and d_{\perp} is shown for **1** and **2**, where the long-axis polarized features of the second electronic transition beginning at 34400 and 30500 cm^{-1} , respectively, can clearly be discerned. For **2**, the intense band at 39500 cm^{-1} was measured in a separate experiment and found to be long-axis polarized (dichroic ratio about 75%). The higher energy vibronic peaks of the short axis polarized first absorption band show mixed polarization due to vibrational intensity borrowing. *Michl et al.* [20] have recently demonstrated that the analogous behaviour of the first (${}^1\text{L}_a$) absorption band of anthracene is also due to vibronic mixing with the intense ${}^1\text{B}_b$ band and does not provide evidence for the expected presence of a weak ${}^1\text{L}_b$ band in the region of the ${}^1\text{L}_a$ absorption.

As shown in Fig. 2, the transition energies, oscillator strengths, and polarizations predicted by the PPP calculations for **1** to **3** are in very good agreement with experiment. Comparison of the calculated SCF MO's. of **1** to **3** with those of the related hydrocarbons naphthalene (**4**), anthracene (**5**), and triphenylene (**6**), obtained by

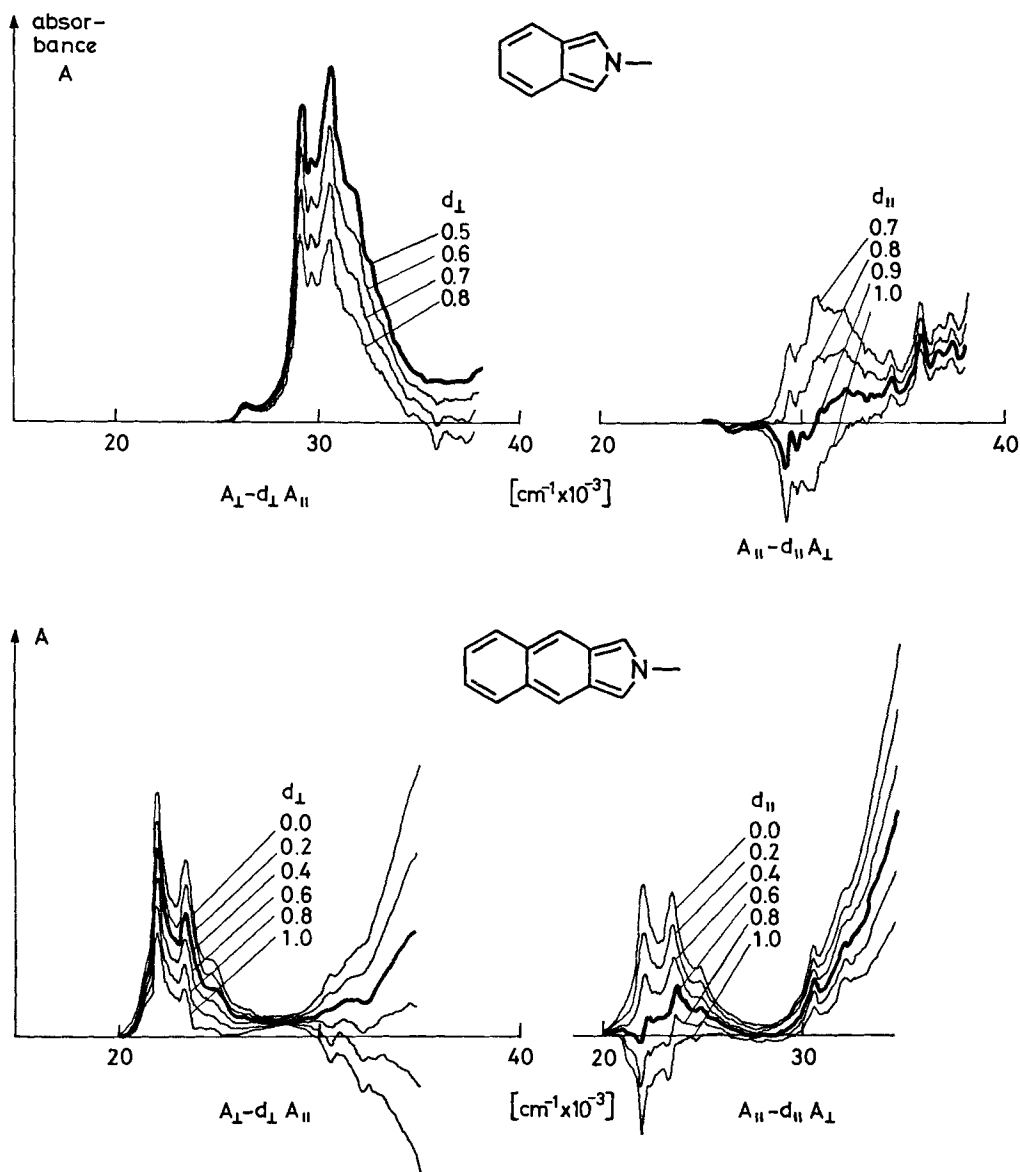


Fig. 3. Reduced dichroic absorption spectra of **1** and **2**

replacement of $-\text{NCH}_3-$ by $-\text{CH}=\text{CH}-$, reveals striking similarities in the orbital shapes and energies. In particular, the pairing properties of the hydrocarbon orbitals are retained to a good approximation in the isoindoles, although the latter as well as their isoconjugate hydrocarbons (indenyl anion *etc.*) are of course nonalternant. As a result of this, the mixing of configurations in the calculations for **1** to **3** closely mimics that in **4** to **6**, respectively, and the corresponding absorption bands are readily correlated as shown in Fig. 4. The empirical relationships between *Clar's* [21]

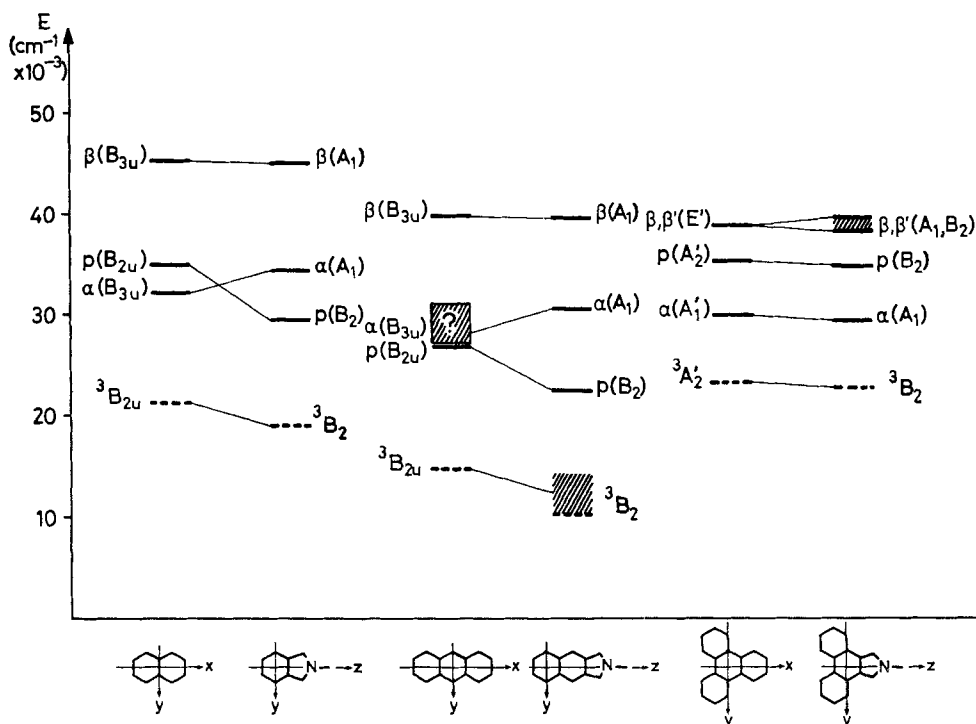


Fig. 4. Relationships between the α , p , and β excited states (—) and the lowest excited triplet state (---) of **1** to **3** and **4** to **6**

α , p , β , and β' bands of benzenoid hydrocarbons as well as the theoretical interpretation of these regularities by Dewar & Longuet-Higgins [22] using first-order CI. are thus qualitatively carried over to the nonalternant heterocycles **1** to **3**.

The replacement of a $-\text{CH}=\text{CH}-$ subunit by $-\text{NCH}_3-$ may be expected to affect the electronic spectra to a lesser extent, the larger the parent hydrocarbon. Indeed, the spectra of **3** and **6** are nearly superimposable. It should be noted that the UV. spectrum reported [23] for unsubstituted dibenz[e,g]isoindole differs significantly from our spectrum of **3**. We believe that some of the differences (intensity near 250 nm, absence of 385 nm band in **3**) cannot be due to the methyl substituent.

The charge distributions and bond orders obtained by the PPP. calculations for the ground and lowest excited singlet states of **1** to **3** are shown in Diagram 1. These indices may be useful to predict the thermal and photochemical reactivity of these compounds at various sites.

An intriguing problem is posed by the shift of the p -band along the isoelectronic series of indenyl systems with heteroatoms $X = \text{CH}^-$, S, NMe, NH, O at position 2 (Fig. 5). According to the results of PPP SCF CI. calculations the lowest excited state giving rise to the p -band is well represented ($> 85\%$) by the single configuration corresponding to the HOMO. \rightarrow LUMO. transition (Diagram 2) throughout the series. It may thus be anticipated that the observed shifts should be reproduced qualitatively within the framework of simple Hückel theory. Since charge is transferred to the heteroatom upon excitation, a strong red shift is predicted by first-order perturbation theory for increasing electronegativity of the heteroatom X. We note in passing that a red shift

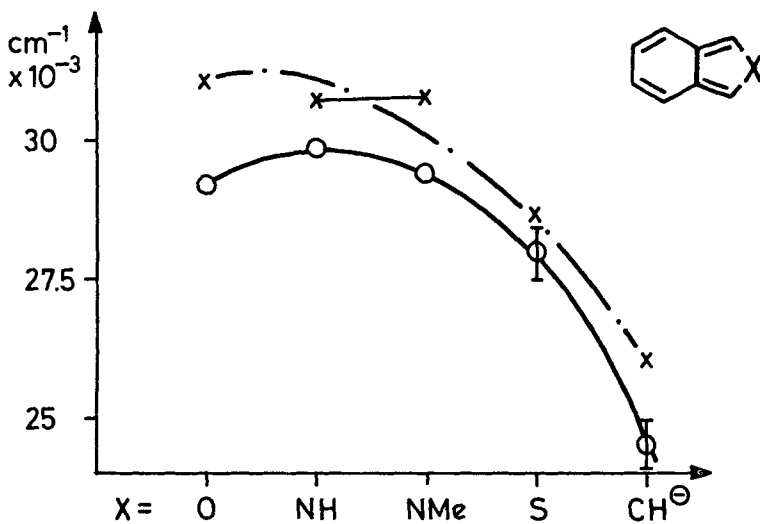
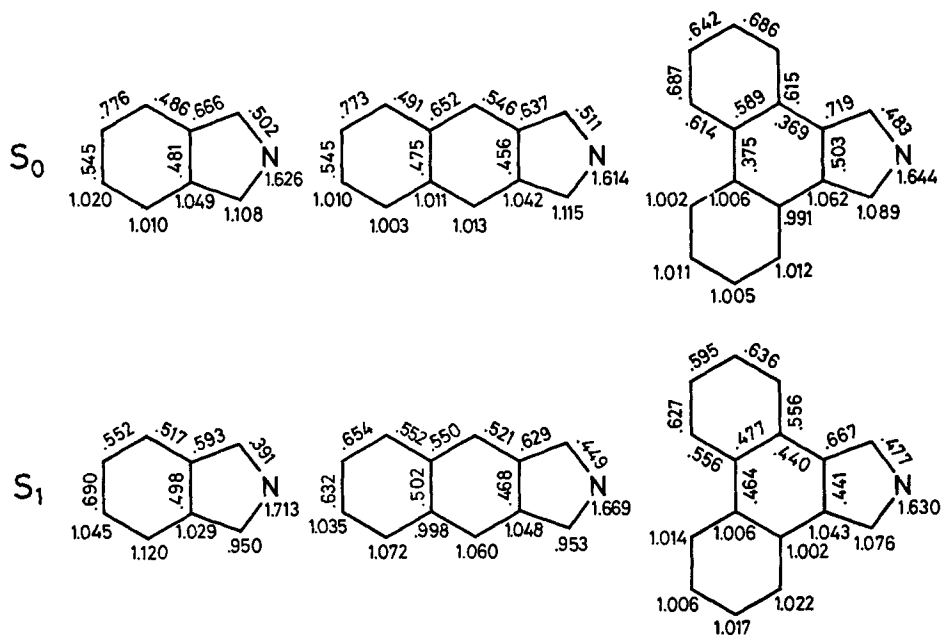
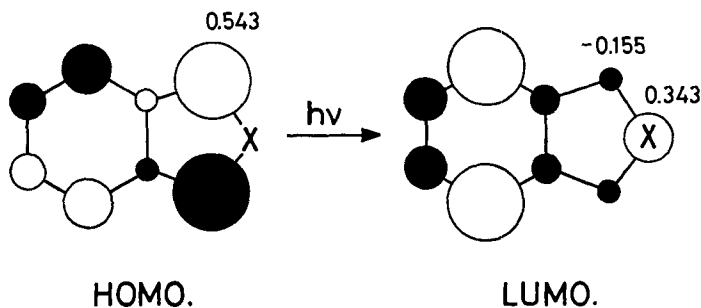
Diagram 1. Charge densities and bond orders of **1** to **3** in the ground (S_0) and lowest excited (S_1) singlet state

 Fig. 5. Experimental and calculated position of p-band in compounds isoelectronic to **1**. \circ Energy of 0-0 transition (X = CH^\ominus [57], X = S [58], X = O [51]). \times Calculated by standard version of PPP SCF CI. [17] [58]

Diagram 2. Highest occupied and lowest unoccupied Hückel orbitals of indenyl anion [47 a][48]



of 0.3 eV in changing $X=\text{CH}^-$ to $X=\text{NH}$ at position 2 was indeed predicted by *Evleth* [6] in his perturbational rationalization of the UV. spectra of various isomeric N-heterocycles isoelectronic with indenyl anion. However, these predictions flatly contradict the observed strong blue shift along the series $X=\text{CH}^-$, S, NMe, NH. The inclusion of electron interaction terms in the SCF. calculations results in a weakening of the strong red shift predicted by *Hückel* theory but does not reverse the trend. The fact that explicit PPP. calculations for each compound of the series are in reasonable agreement with the experimental data (Fig. 5) is due to the simultaneous change of several parameters upon changing the heteroatom X (valence state ionization potential I_X , one-center electron repulsion integral γ_{XX} , core charge Z_c , resonance integral β_{C-X}) and is of no general illustrative value.

A simple explanation of the observed trend (Fig. 5) can be given on the basis of the *Hückel* model if the inductive effect of heteroatom substitution on the adjacent carbon atoms is included in the treatment. The importance of this effect is obvious from photoelectron spectroscopic data (cf. [24] and Section 3) which suggest that an inductive perturbation $\delta\alpha_X$ at the heteroatom induces a perturbation of $m \cdot \delta\alpha_X$ ($m \cong 1/3$) at the adjacent carbon atoms. As is evident from Diagram 2, the HOMO. \rightarrow LUMO. excitation not only increases the charge density of X, but strongly decreases the charge density at the adjacent positions. Using the well-known formula [25] for first-order inductive perturbation of a one-electron excitation $\psi_J \rightarrow \psi_K$ it is readily seen that a blue shift is correctly predicted for heteroatom substitution of indenyl anion at position 2 for values of m greater than 0.22. Furthermore, if second-order perturbation terms are included, an inversion of this trend is predicted for highly electronegative substituents X in complete agreement with experiment.

The fluorescence spectra of **1** to **3** have been displayed in Fig. 2 and the fluorescence quantum yields Φ_{FI} are given in Table 1. Details of the procedure for correction of the spectra and determination of Φ_{FI} by comparison with fluorescence standards are given in the Exper. Section. No excimer fluorescence from **1** could be detected by increasing the concentration in *n*-hexane solution up to 10^{-2}M . As the fluorescence spectra closely resemble the mirror image of the first absorption bands, integration of the latter should yield a fairly accurate estimate of the radiative rate constants k_{FI} [26].

$$k_{\text{FI}} = 2900 \cdot n^2 \int_{\text{1st abs. band}} \frac{(2\tilde{\nu}_0 - \tilde{\nu})^3}{\tilde{\nu}} \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (2)$$

where $\tilde{\nu}_0$ = wavenumber of mirror symmetry point between the absorption and fluorescence bands in μm^{-1} ; n = refractive index of solvent

The high values of Φ_{FI} of **1** to **3** imply that the rates of intersystem crossing to the triplet state are relatively slow ($k_{\text{ISC}} \lesssim 10^9 \text{ s}^{-1}$) in these compounds. It has been noted by *Huber* [27], *Kasha* [28], and *Lim* [29] and their coworkers that intersystem crossing in aromatic amines becomes rapid with increasing deviations from planarity around the N atom.

The phosphorescence of **1** in an EPA. matrix at 77 K was very weak but was considerably intensified upon addition of benzophenone. The identification of this weak, long-lived emission with the phosphorescence of **1** is corroborated by the results of flash photolysis experiments (Section 4) which allow to bracket the triplet energy of **1** between 20000 and 18000 cm^{-1} . The phosphorescence spectrum of **3** resembles that of triphenylene (**6**) and its excitation spectrum is in good agreement with the absorption spectrum of **3**. Our inability to detect phosphorescent emission from **2** is presumably due to the lack of sensitivity of our instrument above 700 nm.

3. *Photoelectron (PE.) spectra.* The PE. spectra of **1** to **3** are shown in Fig. 6 and the energies of the observed band maxima, referred to as vertical ionization potentials (IP's.), are listed in Table 1. As demonstrated by numerous examples [30], the interpretation of PE. spectra is greatly facilitated when the spectra can be compared with those of related molecules, particularly, if the correlation of observed IP's. can be interpreted with the aid of simple quantum mechanical models on the basis of *Koopmans'* theorem. It was noted in Sect. 2 that the π molecular orbitals of the isoindoles are closely related to those of the corresponding benzenoid hydrocarbons obtained by replacement of $-\text{NMe}-$ with $-\text{CH}=\text{CH}-$. Choosing the pattern traced by the PE. spectra of the acenes [31] as a guideline to interpret the spectra of the series N-methyl-pyrrole [32], **1** and **2**, the correlation shown in Fig. 7a suggests itself on purely empirical grounds.

The pattern of SCF. orbital energies predicted by the PPP. calculations described in Sect. 2 is depicted in Fig. 7b. The value of the valence state IP. of carbon – which need not be fixed for the calculation of electronic spectra – was chosen as 9.8 eV, the value determined by *Heilbronner et al.* [31] from a linear regression between PPP. eigenvalues and experimental IP's. of the acenes. The agreement between Fig. 7a and 7b is fair, the discrepancies arising largely from the fact that the energies calculated for the symmetric (b_1) orbitals are too low throughout. This may be attributed to our particular choice of N-heteroparameters which were originally proposed [18] to reproduce electronic spectra of heterocycles with a pyrrolic NH (and not NMe) group. Instead of varying PPP. parameters we preferred to use the more lucid *Hückel* model which yields accurate predictions of IP's. for a variety of conjugated hydrocarbons if allowance is made for the bond lengths changes upon ionization by a perturbative treatment [31] [33] [34]. Taking the parameters of this model from [34] and assuming $\beta_{\text{CN}} = \beta_{\text{CC}}$, we are left to choose a value for the basis energy of the $-\text{NMe}-$ group, $\alpha_{\text{N}} = \alpha_{\text{C}} + h_{\text{N}}\beta$, and a value for the inductive effect of the heteroatom on the adjacent carbon atoms, $\delta\alpha_{\text{adj.}} = m \cdot h_{\text{N}}$. The necessity to include an inductive effect in a *Hückel* treatment is demonstrated by the fact that the band shifts in going from pyrrole to N-methyl-pyrrole [32] or from **1** to isobenzothiophene [35] are of the same order of magnitude for ionizations from symmetric (b_1) or antisymmetric (a_2) orbitals, although the latter have a node at the position of the heteroatom. The value of $m = 1/3$ was chosen in agreement with previous experience [24]. Two calculations

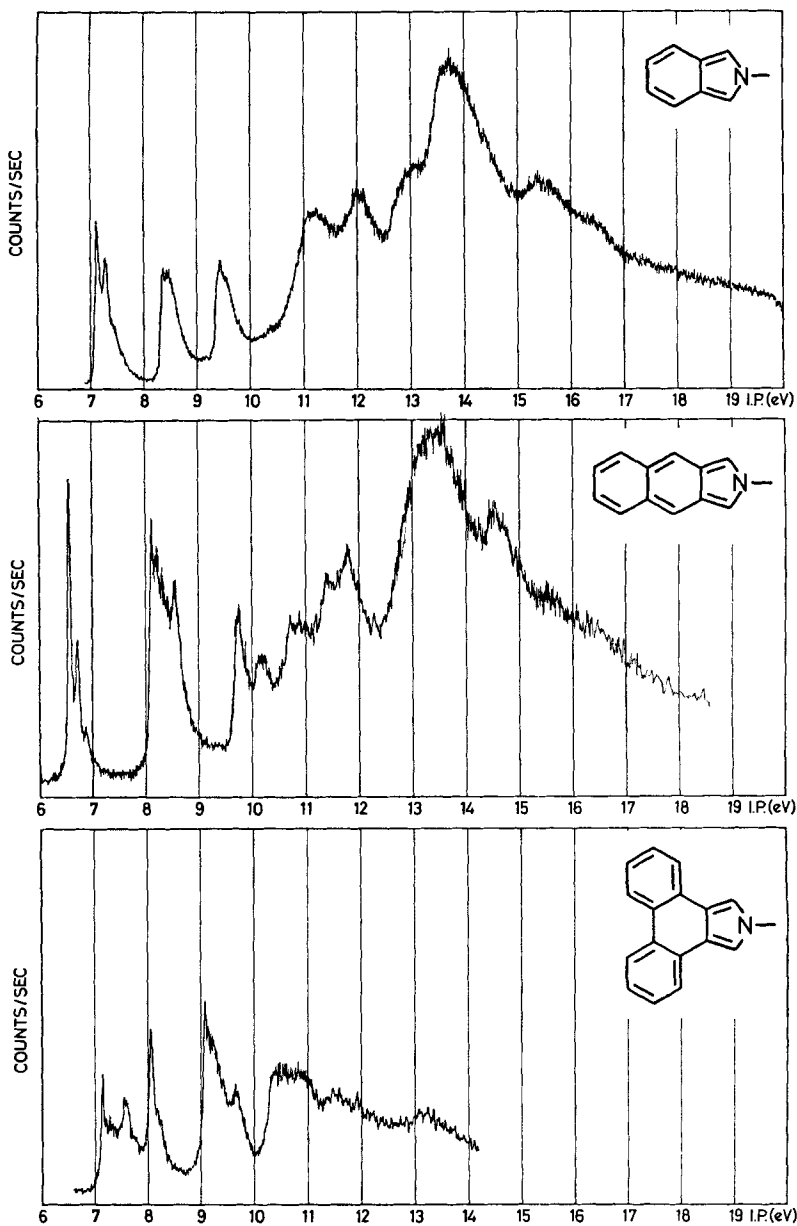


Fig. 6. Photoelectron spectra of **1** to **3**

were then performed with $h_N = 1$ and 0.5 , respectively, where the results of the latter (Fig. 7c) were in better agreement with experiment. The same calculation ($h_N = 0.5$) predicts the following sequence of IP's. for **3** in good agreement with the observed data (Table 1): 7.47 ($4a_2$), 7.66 ($5b_1$), 8.42 ($3a_2$), 9.51 ($2a_2$), 9.55 ($4b_1$), 9.86 eV ($3b_1$).

The *Hückel* calculations described above reproduce the observed spectra of **1** to **3** with sufficient accuracy, albeit at the cost of six adjustable parameters. It is thus

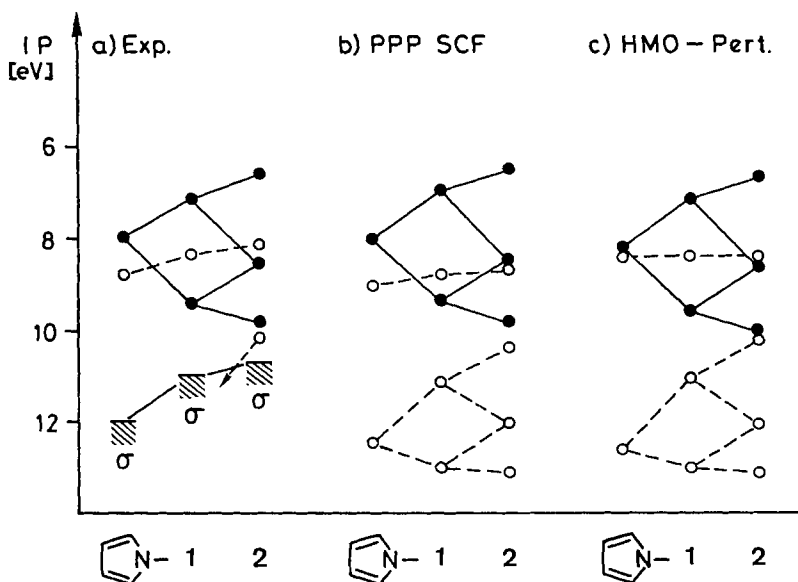
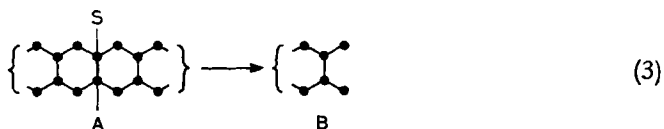


Fig. 7. Correlation diagram of orbital energies ●—● a_2 orbitals ○---○ b_1 orbitals

desirable to use a simpler scheme which draws in a more direct manner from experimental data of related molecules. A well-known approach is the formal union of molecular fragments making use of perturbation theory. *Turner & Maier* have interpreted the PE. spectra of anilines [36] and naphthylamines [37] by considering the union of benzene or naphthalene with the corresponding amino groups. Now, the PE. spectra of the highly reactive, *o*-quinonoid hydrocarbons obtained by removal of nitrogen from the isoindoles are of course unknown. However, an even better model for these hydrocarbon backbones is provided by the acenes: It has been shown by *Heilbronner* [38] that the symmetry factorized secular determinant constructed from graph A (3) contains the secular determinant of graph B as a subdeterminant. Hence, the spectrum spanned by those *Hückel* orbitals of A which are antisymmetric with



respect to the symmetry plane S is identical with the spectrum of B, *i.e.* the a_u and b_{3g} orbitals of naphthalene, tetracene, and hexacene are identical in shape and energy with the orbitals of butadiene, *o*-xylylene, and 2,3-naphthoquinodimethane, respectively. We can now proceed to construct the eigenvalue spectra of the isoindoles by coupling of the *o*-quinonoid hydrocarbon backbone with the nitrogen lone pair. Invoking *Koopmans'* theorem, we choose as basis energies A_1 of the decoupled hydrocarbon moieties those observed IP's. of the corresponding acenes which are associated with ionization from a_u and b_{3g} orbitals [31] [39]. The basis energy A_N of $-NMe-$ may be located near -9.6 eV in line with previous experience [37]. If we assume that the inductive effect due to the substitution of the central C=C group in the acene by the

-NMe- may be ignored then only the IP's. correlated with the acene b_{3g} orbitals will be perturbed by conjugative interaction with -NMe- for reasons of symmetry. Since the spacing of the acene b_{3g} orbitals is rather large, the conjugative interaction is well approximated by considering only the mixing of the highest occupied b_{3g} orbital with the nitrogen lone pair. We thus predict the ionization energies (4) corresponding to orbitals of b symmetry while those of a symmetry remain unchanged (Fig. 8, $B_{CN} = 2c_{j,\mu}/\sqrt{2} \cdot \beta_{CN}$, $\beta_{CN} = \langle \Phi_{\mu} | \mathbf{H} | \Phi_N \rangle = -2.4$ eV [37]). In view of the simplicity of this model, the accuracy of its predictions is gratifying.

$$IP(b_1) = (A_J + A_N \pm \sqrt{(A_J - A_N)^2 + 4B_{CN}^2})/2 \quad (4)$$

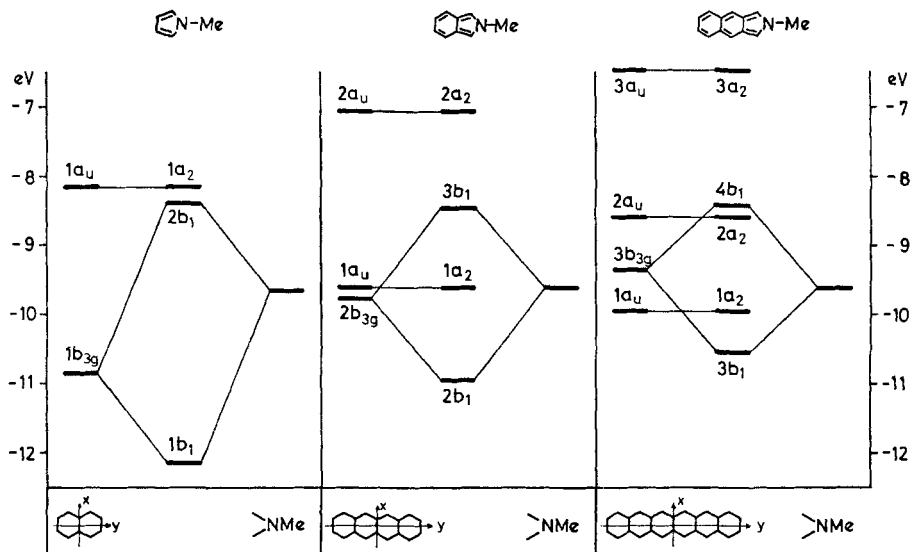


Fig. 8. Interaction scheme

4. *Flash photolysis: Properties of the triplet state.* Direct excitation of **1** or **2** in dilute deaerated solutions by a conventional μ s flash source gave rise to very weak, diffuse transient absorptions in the visible region (λ_{\max} (**1**) 620 nm, λ_{\max} (**2**) 720 nm, lifetimes in benzene *ca.* 0.2 ms). The identification of these transients as the triplet states T_1 (**1**) and T_1 (**2**), respectively, was achieved by a number of energy transfer experiments using aromatic hydrocarbons with well characterized triplet spectra [40] and energies [41] as sensitizers and quenchers. Near diffusion controlled energy transfer from triplet excited picene (E_T 20100 cm^{-1}) and chrysene (E_T 20000 cm^{-1}) to **1**, from **1** to pyrene (E_T 16900 cm^{-1}) and to 1,2,3,4-dibenzanthracene (E_T 17800 cm^{-1}), and from 1,2,5,6-dibenzanthracene (E_T 18300 cm^{-1}) to **2** was directly observed by kinetic flash spectroscopy in deaerated benzene solutions. The tetracene triplet (E_T 10300 cm^{-1}) was not quenched in the presence of **2** ($k_Q < 10^8$ s^{-1}). These experiments allow us to bracket the triplet energies within the ranges

$$E_T(\mathbf{1}) = 19000 \pm 1000 \text{ cm}^{-1}; E_T(\mathbf{2}) = 14000 \pm 4000 \text{ cm}^{-1}.$$

An estimate of the molar absorptivity ϵ of T_1 (**1**) at 620 nm was obtained as follows: Liquid paraffin solutions of picene both with and without **1** were flash ex-

cited with filtered light absorbed only by picene. Conditions (concentrations, flash energy) were chosen such that the decay of T_1 (picene) was first order in the absence of **1** and faster than 10^6 s^{-1} in the presence of **1**. Given a reproducible flash intensity we may then assume that the concentration of T_1 (picene) immediately after the flash in the solution without **1** is the same as that of T_1 (**1**) in the solution containing **1**. Extrapolation to the initial transient absorbances A^0 making use of the first order decay constants then allows a relative determination of ε_T (**1**) from:

$$\varepsilon_T(\mathbf{1}) = \varepsilon_T(\text{picene}) \cdot A^0(\mathbf{1}) / A^0(\text{picene}) \quad (5)$$

Using a mean of the literature values [40] for ε_T (picene, 620 nm) of 50000 ± 10000 we obtained

$$\varepsilon_T(\mathbf{1}, 620 \text{ nm}) = 3500 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}.$$

Application of the above procedure to determine ε_T (pyrene, 520 nm) yielded a value of 15000 ± 5000 in satisfactory agreement with available data [40].

The knowledge of ε_T (**1**) allows us to determine the concentration c_T^0 of T_1 (**1**) generated by direct excitation and - given the number of quanta absorbed - the quantum yield of intersystem crossing Φ_T . As an actinometer we used the absorbance A_{corr}^0 of triplet picene generated under the same conditions where the dependence of A^0 on the respective absorption spectrum and its overlap with the spectrum of the light flash was corrected for by graphical integration [1] [42]. Note that any error introduced by ε_T (picene) will cancel if ε_T (**1**) is inserted according to (5).

$$\Phi_T(\mathbf{1}) = \frac{A^0(\mathbf{1}) \cdot \varepsilon_T(\text{picene}) \cdot \Phi_T(\text{picene})}{A_{\text{corr}}^0(\text{picene}) \cdot \varepsilon_T(\mathbf{1})} \quad (6)$$

Using the value $\Phi_T(\text{picene}) = 0.36$ determined by *Windsor & Dawson* [41] [43] and considering the errors involved we estimate

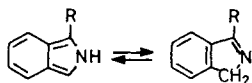
$$\Phi_T = 0.08 \pm 0.05.$$

The quantum yields $\Phi_{FI}(\mathbf{1})$ and $\Phi_T(\mathbf{1})$ in highly dilute, deaerated solution thus add up to unity within the limits of error. Slow photochemical decomposition of the isoindoles **1** to **3** is nevertheless observed upon prolonged direct irradiation while they appear to be quite stable to sensitized excitation to the triplet state [11].

Flash photolysis of **3** in degassed benzene solution also yielded a rather weak transient absorption of *ca.* 0.2 ms lifetime extending from 500 to 720 nm (λ_{max} 680 nm) with little fine structure. The transient was completely quenched upon admission of air and by analogy is attributed to T_1 (**3**) without further evidence. The only notable feature in the triplet absorption spectra of **1** to **3** is the absence of an intense transition in the visible region. *Panciř & Zahradnik* [44] have been able to predict the energies of the intense triplet absorption bands in benzenoid hydrocarbons by standard PPP calculations with modified parameters. We have calculated the triplet absorption spectra by the same procedure using the following heteroparameters: $I_N - I_C = -18 \text{ eV}$, $\gamma_{NN} = 14.33 \text{ eV}$, $\beta_{CN} = -2.62 \text{ eV}$, $Z_N^c = 2$. The results are in qualitative agreement with the experimental findings, predicting numerous weak transitions in the visible region while the first intense absorption bands are calculated to lie at 28500 cm^{-1} (**1**), 25400 cm^{-1} (**2**), and 26500 cm^{-1} (**3**).

Concluding remarks. - The spectroscopic information relating to the electronic structure of the excited states and radical cations of the isoindoles has been

discussed in Sections 2 to 4. We wish to add a number of comments concerning the ground state properties of these and related heterocycles. The numerous molecular orbital (MO.) calculations [5] unanimously predict a considerable stabilization of the *o*-quinonoid hydrocarbon backbones due to the conjugative interaction with the nitrogen lone pair although the quantitative estimates of 'resonance energy' differ considerably. This stabilization manifests itself by the fact that both **1** and **2** are isolable as crystalline compounds stable up to 100° in sharp contrast to the corresponding hydrocarbons *o*-xylylene (**7**) [45] and 2,3-naphthoquinodimethane (**8**) [46]. More quantitative evidence comes from measurements of the equilibrium constants between substituted isoindoles and their tautomeric isoindolenine form [5d]. Although the latter tautomer incorporates benzenoid resonance structures, the equilibrium



constants are near unity depending on minor structural variations. Further support comes from our analysis of the H-NMR. spectra of **1** and **2** (Sect. 1) which indicates that the C–C bond lengths in the hydrocarbon rings are quite similar to those in naphthalene and anthracene, respectively, and certainly different from those expected for the polyenes **7** and **8**.

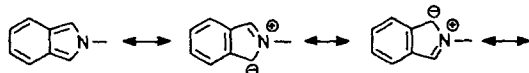
The stabilization predicted by MO. theory for the union of a heteroatom lone pair with **7** or **8** is best visualized by perturbation theory [47]. This approach was successfully used in this work for the interpretation of the PE. spectra (Fig. 8). However, the interaction between occupied MO's. considered there makes little contribution to the total π energy of the united system since within the zero differential overlap approximation the mutual stabilization and destabilization of occupied MO's. is exactly cancelled. Considering interactions between occupied and unoccupied orbitals it is immediately obvious that the predominant stabilization predicted by second order perturbation theory arises from the mixing of the heteroatom lone pair with the lowest unoccupied MO. of **7** or **8**. These orbitals have the proper symmetry (b_1), an unusually low energy, and large coefficients at the positions μ adjacent to the heteroatom X ($c_{\text{LUMO},\mu} = 0.543$ and 0.487 in **7** and **8**, respectively [48]). It is seen from the second order perturbation formula (7) that the resonance stabilization

$$\Delta E^{(2)} = \frac{4c_{\text{LUMO},\mu}^2 \cdot \beta_{\text{CX}}^2}{|\epsilon_{\text{LUMO}} - \alpha_{\text{X}}|} \quad (7)$$

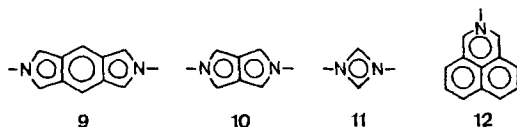
will decrease with increasing electronegativity (*i.e.* decreasing basis energy α_{X}) of X. This simple argument readily accounts for a number of peculiarities of isoindole and related compounds. Since the predominant mesomeric stabilization $\Delta E^{(2)}$ affects the subjacent [49], *i.e.* second highest occupied orbital and since $\Delta E^{(2)}$ shows the opposite dependence on α_{X} than the inductive effect on the HOMO., it is clear that a discussion of the reactivity of such systems based on frontier orbitals [50] is bound to fail. *E.g.*, the reactivity of isobenzofuran towards dienophiles [51] appears to be considerably greater than that of **1** although the first IP. of isobenzofuran is doubtless higher than that of **1**. The same argument applies to the pair furan/pyrrole. A consequence of the strong mixing between the hydrocarbon LUMO. and the heteroatom lone pair orbital is that the charge distributions in the combined systems (*e.g.* **1** and **2**,

see diagrams Sect. 2) are qualitatively those of the radical anions of the hydrocarbon backbones, *i.e.* ($q_\mu - 1$) is proportional to $c_{LUMO, \mu}^2$. The high charge density at the positions adjacent to the heteroatom is destabilized by electron donors such as *p*-dimethylaminophenyl [5d] and stabilized by aza substitution as demonstrated by the chemical stability of 2H-benzotriazole derivatives.

From the above discussion it is clear that the description of **1** or **2** by a single *o*-quinonoid valence structure is inadequate. A better qualitative picture is provided by including zwitterionic structures where those having the negative charge in the six-membered ring are considered less important following the empirical *Fries* rule [52].



While such zwitterionic structures with charged carbon atoms are thought to be useful for the prediction of charge distributions and reactive positions, they are usually not assumed to contribute significantly to the overall resonance energy. This may be due to the eminent success of simple resonance theory in predicting relative stabilities, bond lengths *etc.* of benzenoid hydrocarbons by ignoring contributions from zwitterionic or biradical valence structures [53]. It is, however, well-known [47b] [54] that the success of these methods is limited to a restricted class of compounds for which there is an intimate mathematical connection with MO. theory. In nonbenzenoid systems resonance theory is an unreliable guide to predict resonance energies. Most chemists would agree that compounds **9** to **12** which have no covalent valence structure should be extremely reactive [55]. Simple MO. models predict closed shell electronic structures with considerable resonance stabilization. Recent preliminary results obtained in this laboratory [56] indicate that **9** and **12** are indeed isolable at room temperature.



Preparative part. - *N*-Methyl-benz[*f*]isoindole (**2**). A solution of 5 g methyl-hydrazine in 10 ml of dry diethyl ether was added dropwise over a period of 30 min to a stirred suspension of 12 g 2,3-bis(bromomethyl)naphthalene [10] in 160 ml of dry ether whereby the product separated as an amorphous white precipitate. After standing overnight the solvent was decanted and the precipitate was washed with ether and dried *in vacuo* (yield of raw product 15 g). A 5 g portion of this product was thoroughly pounded in a mortar together with 13 g of pulverized sodium hydroxide pellets under an atmosphere of argon. The deep yellow mixture was heated in an evacuated sublimator (0.1 Torr). A yellow amorphous product was collected on the cold finger as a first fraction above 130°. Upon further heating to 150° the product began to deposit on the cold finger as orange needles (overall yield *ca.* 600 mg). The last fraction of orange needles (50 mg) isolated by heating the reaction mixture up to 170° was found to be pure **2** which decomposed without melting above 110°. Attempts to isolate further **2** from the first fractions containing an unidentified yellow compound by fractional crystallization or resublimation were not satisfactory. - H-NMR. (5% **2** in C₆D₆, internal TMS.): δ 8.10 (s, 2H), 7.8 (m, 2H), 7.1 (m, 2H), 6.83 (s, 2H), and 3.14 ppm (s, 3H). An analysis of the aromatic multiplets in the NMR. spectrum as well as the UV./VIS. absorption and fluorescence spectra are shown in Figs. 1 and 2b. - MS. (relative intensity): *m/e* 182 (14), 181 (100), 180 (26), 167 (5), 166 (39), 152 (6), 140 (18), 139 (23), 90.5 (17).

C₁₃H₁₁N (181.24) Calc. C 86.16% H 6.12% Found C 85.17% H 6.52%

In solution **2** is highly sensitive to oxygen (half-life in 10^{-5} M aerated *n*-hexane *ca.* 1 min).

N-Methyl-dibenz[*e,g*]isoindole (**3**) was prepared as **2** from 9,10-bis(bromomethyl)phenanthrene [59]. The raw sublimate (overall yield 400 mg from 1.6 g of the dibromide) was purified by preparative TLC. under argon in the dark whereby **3** (160 mg) was eluted as the front product (R_F 0.5 with petroleum ether/benzene 1:1 on SiO_2). Recrystallization from hexane at -78° and sublimation *in vacuo* (160°, 0.1 Torr) yielded **3** as colourless crystals, m.p. 161–162°. – H-NMR. (in $CDCl_3$, internal TMS.): δ 8.4 (*m*, 2H), 7.95 (*m*, 2H), 7.4 (*m*, 6H), and 3.86 ppm (*s*, 3H). The UV./VIS. absorption and emission spectra are shown in Fig. 2. – MS. (relative intensity): *m/e* 232 (17), 231 (100), 230 (29), 216 (16), 202 (7), 190 (7), 189 (25), 115.5 (18).

Spectrophotometric part. – UV./VIS. absorption spectra were recorded on a *Cary* 14 spectrophotometer and the molar absorptivities were determined by at least two independent measurements. Special care was taken to avoid oxidative degradation of the samples and a small amount of triethylamine was added to the solvents to eliminate traces of acid.

Linear dichroic spectra were determined at room temperature by the stretched-foil method [19] on the *Cary* 14 spectrophotometer. Polyethylene sheets were stretched by 600% and subsequently doped with the sample by vacuum sublimation in the case of **1** and by soaking in a deaerated chloroform solution of **2** containing a trace of triethylamine. The films were not rinsed with ethanol to prevent degradation of the samples, so microcrystals on the surface of the film are presumed responsible for the long-wavelength tail of the first absorption band (Fig. 5) which is not observed in solution spectra [20].

Fluorescence spectra were measured at room temperature with a *Zeiss* PMQII/ZFM4 spectrophotometer equipped with a RCA 1P28 photomultiplier tube. Slit widths were set at ≤ 0.2 mm corresponding to a resolution of 200 cm^{-1} or better at 25000 cm^{-1} . The samples were irradiated at right angles to the detection system with 313 and 365 nm light isolated with *Zeiss* glass filters from a medium pressure mercury lamp *Hanau* St. 41. Highly dilute solutions ($\leq 10^{-5}$ M, optical density ≤ 0.02) were used to avoid reabsorption effects. Luminescent intensities were corrected for stray light and back ground luminescence ($\leq 2\%$ of sample intensity) with a solvent blank. Spectrograde solvents (*Merck* Uvasol) were used as provided. The relative spectral sensitivity of the instrument was calibrated in order to correct the apparent fluorescence spectra in the range of 17000 to 30000 cm^{-1} using standard fluorescent solutions ($2 \cdot 10^{-6}$ M quinine sulfate in $0.1\text{ N H}_2\text{SO}_4$ [60] [61] and 10^{-5} M β -naphthol in 0.020 N acetate buffer solution (*Merck*) at 24.0° [60]) of known spectral distribution. Comparative fluorescence intensity measurements for quantum yield determinations were carried out repeatedly within short time periods and with identical instrument settings on a minimum of two reference and sample solutions prepared independently. The fluorescence quantum yield of α -naphthylamine ($3 \cdot 10^{-6}$ M in cyclohexane) was determined as 0.38 by reference to quinine sulfate (10^{-5} M in 0.1 N sulfuric acid, $\Phi_{F1} = 0.55$ [62]) with excitation at 313 nm in addition to previous [63] tests for satisfactory performance of the experimental set-up. The fluorescence quantum yields given in Table 1 were determined at room temp. by comparison of the sample fluorescence intensity for **1** and **3** with α -naphthylamine ($\lambda(\text{exc.}) = 313\text{ nm}$) and for **2** with quinine sulfate ($\lambda(\text{exc.}) = 365\text{ nm}$) as quantum yield standards (eq. 8).

$$\Phi_{F1}(\text{sample}) = \frac{I(\text{sample}) A(\text{ref.})}{I(\text{ref.}) A(\text{sample})} \cdot \frac{n^2(\text{sample})}{n^2(\text{ref.})} \cdot \Phi_{F1}(\text{ref.}) \quad (8)$$

I = integrated fluorescence intensity using corrected spectra

A = absorbance at excitation wavelength

n = index of refraction of solvent.

The fluorescence quantum yield of quinine sulfate was taken as 0.55 [62] and that of α -naphthylamine as 0.46 [64] where the correction factor proposed by *Birks* [41] was not applied [65]. Phosphorescence spectra were recorded⁷⁾ on a *Perkin-Elmer* MPF-2A fluorescence spectrophotometer equipped with a rotating can attachment and a R 136 photomultiplier tube and are reported without correction.

The HeI photoelectron spectra were recorded on a modified *Perkin-Elmer* PS 16 instrument. The samples were inserted directly in the vicinity of the ionization region which was heated to

⁷⁾ We wish to thank Dr. *Stadelmann*, *Ciba-Geigy* AG, for the permission to use his instrument.

temperatures of 60 to 120° in order to increase the sample pressure. The ionization energies were determined by an *in situ* calibration with rare gases.

The flash photolysis equipment was of conventional design [66]. Solutions were degassed by the freeze-pump-thaw technique until the pressure remained below 10^{-3} Torr upon thawing and refreezing.

Note added in proof: A related study of *o*-quinonoid heterocycles including N-methyl-isoindole (1) has appeared [67] since we submitted our manuscript. We have some doubts concerning the significance of the H-NMR. transannular coupling constants (quoted down to 10^{-3} Hz) and of the analysis of the PE. spectrum beyond 11 eV given in [67]. The general appearance of the PE. spectrum and the assignment of the π -ionization bands agree with ours while calibrated values for the experimental IP's. are not given explicitly.

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