

Systematics of the Electronic Absorption Spectra of Fused 5–6 Ring Heterocyclics

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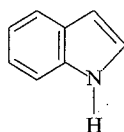
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The electronic absorption spectra of indene, indole, benzofuran isoindole, indolizine, 1- and 2-pyrindine are rationalized using semiempirical SCF-CI calculations. The absorption spectra of these materials are also rationalized using indenyl anion as the common perturbational model. Perturbation theory is also applied to explaining the effect of aza-substitution on the spectra of indolizines.

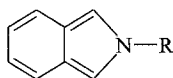
Die elektronischen Absorptionsspektren von Inden, Indol, Benzofuran, Isoindol, Indolizin, 1- und 2-Pyrindin werden an Hand semiempirischer SCF-CI Berechnungen erklärt. Die Absorptionsspektren dieser Verbindungen können auch auf der Grundlage des Indenyl Anion als gemeinsamem Modell für die Störungsrechnung interpretiert werden. Schließlich wird die Störungstheorie zur Erklärung des Einflusses der Aza-Substitution auf die Spektren des Indolizins angewendet.

Les spectres d'absorption électronique de l'indene, de l'indol, du benzofuran, de l'isoindol, de l'indolizine, de 1- et 2-pyrindine sont rationalisés par des calculs SCF-CI sémiempiriques. Les spectres d'absorption de ces matières sont aussi rationalisés se servant de l'anion d'indenyl comme modèle de perturbation commun. La théorie de perturbation est aussi appliquée à expliquer l'effect de l'aza-substitution sur les spectres des indolizenes.

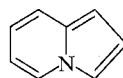
The isomeric 5–6 fused ring nitrogen heterocycles I–V are spectroscopically curious systems. Indole (I) and various azaindoles exhibit π -electronic transitions below 300 $m\mu$ [1]. Isoindoles (II) and indolizines (III) lowest energy transitions are in the 350–400 $m\mu$ region [2–5]. Both 1- and 2-pyrindine (IV and V) absorb weakly in the 400–500 $m\mu$ region [6–9]. Attention has been directed [7–9] to the spectral similarities of IV and V with azulene.



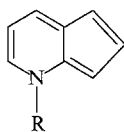
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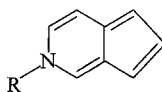
II



III



IV



V

The qualitative reason for the strong dependency of the position of the lowest electronic transition on the position of the nitrogen in the fused ring systems is not readily apparent. The rationalization of the spectral features of I-V will be attempted by i) direct semiempirical SCF-CI calculation of the spectra and ii) application of perturbation theory using indenyl anion as a common perturbational model. Perturbational arguments will also be used to analyze the effect of aza-substitution on the spectra of I-V, particularly III and IV.

Method of Calculation

The semiempirical calculations were obtained using the Bessis-Chalvet SCF-CI program. The standard approximations of Pariser, Parr [10, 11] and Pople [12] were utilized. The coulomb, resonance and one centered electron repulsion parameters incorporated in these calculations (Tables 1 and 2) were the same as previously used on SCF-CI calculations on the structurally related pyridones [13] and dihydropyridines [14]. The geometries were estimated using constant bond distances (Table 2) and varying the internal bond angles of the particular structure under consideration in a regular manner until an accommodation was reached. Configuration interaction was limited to the lowest 10 singly excited states. Calculations were also carried out on indole, indene, and benzofuran using an additional 5 doubly excited configurations.

Table 1. *Coulomb parameters*

Atom	I_p (eV)	Z	$\langle 11 11 \rangle$ (eV)
N	28.16	4.25	15.92
C	11.22	3.25	10.53
O	35.50	4.90	21.55

I_p = valence state ionization potential, Z = Slater Z value, $\langle 11|11 \rangle$ = one centered electron repulsion integral.

Table 2. *Resonance parameters*

Bond type	Bond distance (Å)	Resonance integral (eV)
C=C (aromatic)	1.400	-2.30
C=C (ethylenic)	1.350	-2.40
C-C	1.450	-2.20
C-N	1.390	-2.45

The experimental oscillator strength for indene, benzofuran, indole, and indolizine were measured by graphical integration of spectral data taken in *n*-hexane. This integration proved difficult in the case of indole because of the large degree of overlap between the 1st and 2nd electronic transitions. The integration was accomplished assuming a gaussian distribution for the vibronic components of these transitions. The oscillator strengths of II, IV and V were estimated from the published molar extinction coefficients using the approximation of Sandorfy [15]. A band width of 5000 cm^{-1} was assumed at one half the extinction value of the Franck-Condon maximum. The energy of a particular transition was

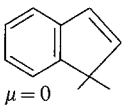
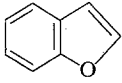
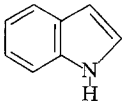
estimated from the position of the maximum or the approximate center of the Franck-Condon envelope. Finally, the following discussion will be limited to singlet-singlet transitions.

Results and Discussion

Indene, Benzofuran, and Indole

Although several theoretical calculations [17, 18] have been carried out on these materials some additional comment is necessary. A comparison of the assigned and computed transitions for indene, benzofuran, and indole is shown in Table 3. The observed spectra of these materials are shown in Fig. 1. Indene is classified as an alternate hydrocarbon so that some of the transitions are theoretically forbidden under the restrictions imposed by the pairing rule [19, 20]. The lowest electronic transition in indene is computationally forbidden and perturbationally related to the forbidden ${}^1L_b \leftarrow {}^1A$ transition in benzene [21]. The measured oscillator strength (Table 2) of this transition in indene (0.003) is approximately the same as the L_b transitions in benzene (0.0017) and naphthalene (0.0022) [22]. The 2nd band of indene is clearly a perturbed L_a transition [21]. The theoretical origin of the 3rd observed band in indene is not clear. Allinger and Stuart [23] have shown that the intensity of the 3rd transition in styrene is extremely sensitive to the number and type of configurations used in the CI treatment. The calculated oscillator strength of this 3rd transition varies from very strong to very weak [23]. Fig. 1 shows that the strong maximum in the

Table 3. Comparison of the computed and experimental spectra for indene, benzofuran, and indole (I)

Structure	Computed transitions					Experimental	
	Single and double CI		Single CI		$\hat{\mu}^0$	E_t	f
	E_t	f	E_t	f			
 $\mu = 0$	4.49	0.000	4.49	0.000	—	4.4	0.003
	4.69	0.25	4.59	0.23	- 2	5.0	0.19
	5.61	0.16	5.55	0.17	+26	5.6?	—
	6.10	0.000	6.28	0.95	-35	5.9	0.5
	6.21	0.79	7.04	1.00	+60		
 $\mu = 1.58$	4.64	0.004	4.53	0.006	+68	4.5	0.023
	4.81	0.11	4.74	0.11	-54	5.1	0.18
	6.15	0.59	6.10	0.59	+17	6.1	0.6
	6.41	0.12	6.60	0.71	+78		
	6.65	0.73	6.65	1.13	-14		
 $\mu = 1.95$	4.61	0.008	4.49	0.013	-88	4.4	0.016
	4.79	0.108	4.67	0.10	-59	4.6	0.13
	6.30	0.49	5.96	0.50	+11	5.8	0.7
	6.30	0.11	6.42	0.74	+44	6.2?	
	6.53	0.89	6.55	1.00	-31		

E_t = transition energy in electron volts, f = measured oscillator strength, $\hat{\mu}^0$ = transition moment with respect to the x axis of the structure for single CI calculation, μ = calculated dipole moment.

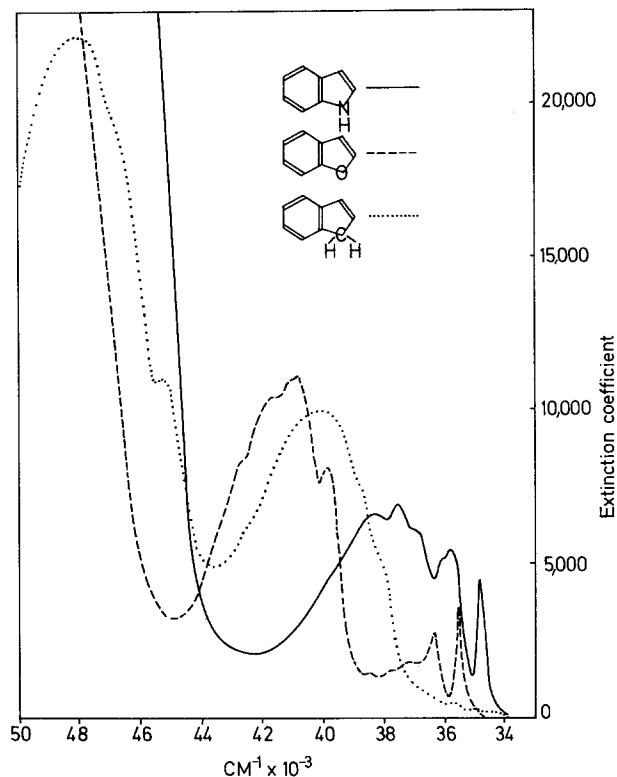


Fig. 1. Ultraviolet absorption spectra of indene, indole, and benzofuran

48,000 cm^{-1} region is accompanied by a weaker maximum at 44,000 cm^{-1} . At this time it is not possible to determine if these maxima are part of the same or different Franck-Condon envelopes. Thus there is some doubt as to the assignment of the 3rd and higher transitions in indene.

In benzofuran and indole the pairing rule no longer applies and the major observed effect of the inclusion of heteroatoms in the indene structure is to increase the intensity of the lowest transition. Visual comparison of the spectra of these three materials (Fig. 1) also shows that the two lowest transitions in indole overlap to a larger degree than with indene and benzofuran. This makes it difficult to reliably estimate the individual integrated intensities of these two transitions in indole. The vibronic components in the region of 35,000 and 36,500 cm^{-1} are assigned to the lowest electronic transition on the basis of their approximate mirror image relationship to the vibronic components in the fluorescence spectrum of indole in *n*-hexane [24].

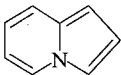
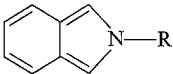
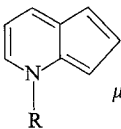
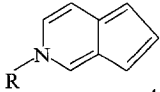
With the exception of the intensity of the lowest electronic transition the computed spectral features of benzofuran and indole are nearly the same. Thus the calculations do not reflect the fact that the separation between the first and second electronic states in indole is smaller than in benzofuran. However the calculation is parameter dependent. A calculation (single CI only) in which I_p , $\langle 11|11 \rangle$ and Z for nitrogen were changed to 25.0 eV, 15.0 eV, and 4.00, respectively,

produced transition energies and oscillator strengths in the following order: 4.39 eV (0.096), 4.53 (0.039), 5.95 (0.072), 6.25 (1.21). Examination of the configuration wave function for the two lowest energy transitions in this calculation and the one presented in Table 3 showed that the stronger transition was perturbationally L_a and the weaker was L_b . Thus, a moderate change in the nitrogen parameters produced an inversion in the predicted assignment of the lowest energy transition. Obviously some intermediate parameter values would produce agreement between the experimental and computed positions of these two lowest energy transitions. Of further importance is that parameter variation generates some question on just how many transitions occur in the 200–300 m μ region. As with indene the theoretical origins of the 3rd observed strong transition in indole is still obscure.

Isoindole, Indolizine, 1- and 2-Pyridine

Comparison of the computed and observed spectral features of compounds II–V is shown in Table 4. Experimentally, lowest energy transitions of III, IV, and V are relatively weak ($f = 0.02$ – 0.04) [7–9], similar to benzofuran and indole. The 2nd electronic transition in these materials is stronger than the 1st. Finally the strongest observed transition ($f = 0.4$ – 0.6) is in the 4.5–6.1 eV region. Although

Table 4. Comparison of the computed and experimental spectra of compounds II, III, IV, and V

Structure	Calculated transitions ^a			Experimental	
	E_t	f	Sym. λ_a	E_t	f
 $\mu = 1.80$	3.84	0.098	+70	3.7	0.039 ^b
	4.57	0.095	–3	4.3	0.049
	5.94	1.11	–25	5.4	0.7
	6.09	0.35	+39		
 $\mu = 2.66$	4.26	0.31	B_1		
	4.81	0.001	A_1		
	5.41	0.011	B_1		
	6.39	0.000	B_1		
	6.44	1.85	A_1		
 $\mu = 3.7$	2.65	0.050	+57	2.6	0.02 ^c
	3.74	0.11	+2	3.9	0.2
	5.38	0.72	–15	4.8	0.5
	5.61	0.41	+14		
 $\mu = 4.6$	2.76	0.073	–37	2.9	0.03 ^d
	3.66	0.017	–71	3.7	?, sh.
	5.15	0.59	+31	4.5	0.4
	5.73	0.62	+4		

^a Symbols the same as in Table 3.

^b Measured in *n*-hexane.

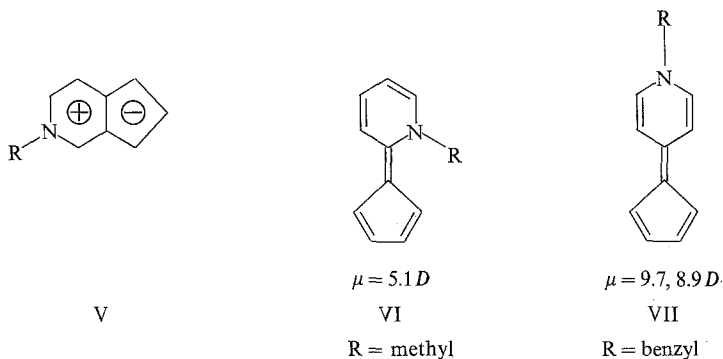
^c Refs. [7] and [8], R = methyl.

^d Ref. [9], R = phenyl, calculation done on R = H.

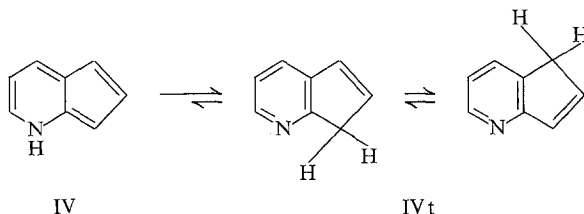
the spectral features of II are unknown the reported [2] data on 1-phenyl-2H-isindole shows a strong transition ($f \sim 0.3$) at 3.5 eV. Thus the calculations shown in Table 4 reasonably correlate with the observed spectral features of III-V with II still open to question. The calculations especially reflect the strong bathochromic shift in the position of the 1st transition on transferring the nitrogen from the 5 to the 6 member ring.

Ground State Properties of I-V

The computed dipole moments of I-V (Tables 2 and 3) range from 1.8 to 4.5D. Since the hybridization effects will not contribute extensively to the σ moments of these materials the calculations predict a fair degree of charge separation in 1- and 2-pyrindine. Structurally IV and V are fused-ring analogs of the cyclopentadienyldidinedihydropyridines VI and VII. These latter materials are known to have high computed [25, 26] and measured dipole moments [27, 28]. The qualitative resonance arguments of the high dipole moments of these materials, as with azulene, require the invocation of zwitterionic structures of the type shown.



The calculations I-V were done using the same coulombic parameters, the same average resonance parameters (-2.30 eV) and nearly the same average geometries. This allows for a direct comparison of the electronic stabilization energies of I-V. In comparison to indole, compounds II, III, IV, and V were less stable by 0.20, 0.19, 0.97, and 1.07 eV respectively. Although the absolute magnitude of these quantities should not be taken seriously, the values indicate that II and III are close to I in stability and that IV and V are considerably destabilized with respect to I. This lack of resonance energy in IV is reflected experimentally by the preference of the tautomers IVt over the pyridine IV in an approximate ratio of 10^3 to 1 [7].



In the case of isoindoles the preference for the tautomeric form is substituent dependent [2]. In the case of 1-phenyl-2H-isoindole the fully aromatized structure is preferred over the tautomer. These results indicate that the resonance energy of isoindole is higher than 1-pyridine but lower than indole.

Perturbational Rationalization of the Spectral Features of I-V and Azaindolizines

A systematic but non-quantitative interpretation of the spectral features of I, III, and IV has been formulated by Mason [1] using indenyl anion as the perturbational model. A quantitative estimate using the same model and the wavefunctions obtained from the perimeter MO's has also been formulated for the same materials [16]. This treatment is adapted here using the SCF-CI calculation on indenyl anion. The SCF-CI electronic transitions, intensities, symmetries and ground and excited state electron densities are shown for indenyl anion in Table 5. Experimentally only the lowest energy transition is reported [29, 30]. The experimental transition energy and intensity (3.3 eV, $f_{\text{est}} = 0.03$) approximates the computed values (3.4 eV, 0.09). The assignment of this transition is ${}^1B_1 \leftarrow {}^1A_1$. This is in agreement with the perimeter MO assignment [16].

The first order shift in the position of a particular electronic transition is approximated by the following equation [16, 31].

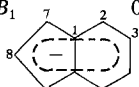
$$\Delta E_{g \rightarrow e} = (q_e - q_g) \Delta H_{rr}$$

where q_e and q_g are the excited and ground state electron densities at position r and ΔH_{rr} is the change in the coulomb parameter at position r .

Using the above equation, the electron densities listed in Table 5, and the experimental energies for the 1st and 2nd transitions for compounds I-V the average empirical change in the coulomb parameter in going from carbon to nitrogen is 4.0 eV. Conversely, using this value the calculated values of the 1st and 2nd electronic transitions for I-V are: I, 4.5, 4.7 eV; II, 3.1, 4.6; III, 3.4, 4.4; IV, 2.6, 3.7; and V, 3.4, 3.8 eV. These values are in reasonable agreement with the experimental ones. Thus, perturbationally, the relative high energy for the lowest transitions in indole and low energy in II-V is related to the redistribution of electronic charge in indenyl anion on excitation. Conversely, these results support the idea

Table 5. Calculated energies and electron densities of the ground and excited states of indenyl anion

Calculated transitions ^{a, b}			Electron densities at atoms				
E_t	f	Sym	1	2	3	7	8
Ground	State	1A_1	1.04	1.04	1.12	1.26	1.09
3.43	0.089	1B_1	1.05	1.24	1.14	0.98	1.18
4.16	0.006	1A_1	0.99	1.17	1.22	1.13	0.98
5.58	0.034	1B_1	0.97	1.07	1.23	1.24	0.97

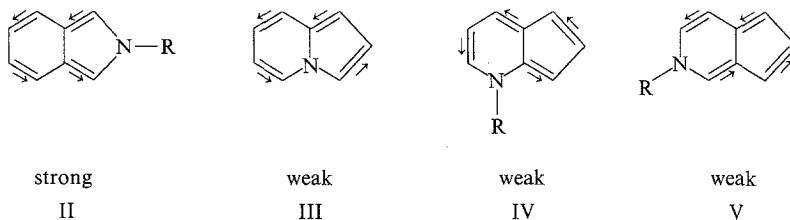


^a See Table 2 for Symbols.

^b A strong ($f = 1.38$) ${}^1A_1 \leftarrow {}^1A_1$ transition is calculated at 5.78 eV.

that there is a high degree of electronic charge redistribution in the lowest excited states of indenyl anion.

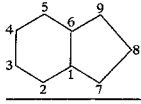
This simple first order perturbation treatment assigns the symmetries of the 1st and 2nd transitions of I-V as being derived from the ${}^1B_1 \leftarrow {}^1A_1$ and ${}^1A_1 \leftarrow {}^1A_1$ transitions, respectively, in indenyl anion. However, the perimeter MO treatment of Feitelson [16] does predict an inversion of states for indole. Since there is a breakdown of symmetry ($C_{2v} \rightarrow C_{1h}$) in going from indenyl anion to I, III, IV, and V the direction of actual transition moments will not be symmetry determined for these latter materials. The actual SCF-CI moments are shown in Tables 3 and 4. Examination of the direction of these moments in III and IV indicates a correlation with the symmetry of the 1st and 2nd transitions in indenyl anion. This is not the case of I and V. Both II and the indenyl anion as well as azulene [32, 33] have the same symmetry 1st and 2nd excited states. Since the lowest two transitions in indenyl anion are weak the expectation is that this would be passed on to I-V. This is true for the lowest energy transitions for I, III, IV, and V but not II. However, a qualitative rationalization of relative high intensity of the lowest energy transition in II and low values in III-V can be found using a simple dipole model based on adding up ethylenic transition moments [14]. In this model the ethylenic transition dipoles are lined up in a minimum energy configuration, head to tail, along the perimeter of the system. As seen below this affords a strong intensity for II, and weak for III-V. In addition the correct symmetry is predicted for the lowest energy transition for II.



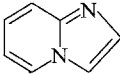
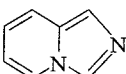
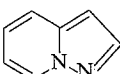
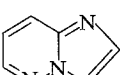
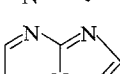
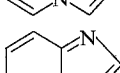
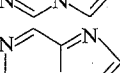
The moments in the 5 and 6 member rings of III and IV largely cancel one another. The 6 member ring would make no contribution to the total moment of V. Since nitrogen contributes to all these systems there would be additional diminution of intensity [34] resulting from the inclusion of charge transfer terms.

There are a large number of possible aza-derivatives of compounds I-V. Although it is possible to obtain direct SCF-CI calculations of the π -electronic spectra of these materials it is probable that perturbation theory will furnish sufficient information for the purposes of rationalizing a large amount of experimental data. Table 6 contains the calculated electron densities for the ground and two lowest excited states of I-V. Detailed examination of these densities shows that the redistribution of electronic charge on excitation is quite extensive for III, IV and V but only moderate for I and II. Only in the case of II does the nitrogen atom undergo significant change in electron density. The significance of this large change in electron densities at particular carbon atoms for III, IV, and V is the

Table 6. Calculated electron densities for the ground, first and second excited states in compounds I-V

Structure	State	Electron densities at atoms								
		1	2	3	4	5	6	7	8	9
	G^a	1.05	0.97	1.03	0.99	1.06	1.05	1.09	1.07	1.69
	1	1.02	1.04	1.01	1.01	1.09	1.05	1.04	1.07	1.67
	2	1.06	1.02	1.02	1.03	1.07	1.07	1.00	1.09	1.64
II, 8-N	G	1.05	1.00	1.02	—	—	—	1.14	1.59	—
	1	1.04	1.00	1.01	—	—	—	1.10	1.70	—
	2	1.03	1.00	1.02	—	—	—	1.14	1.59	—
III, 1-N	G	1.53	1.08	1.00	1.02	0.97	1.10	1.17	1.02	1.11
	1	1.55	1.23	1.08	1.02	1.13	1.04	1.01	1.04	0.90
	2	1.56	1.08	1.10	1.08	0.97	1.15	1.11	0.96	0.99
V, 3-N	G	1.05	0.94	1.67	1.11	0.97	1.04	1.11	1.00	1.10
	1	1.05	1.30	1.72	1.06	0.97	1.01	0.96	1.07	0.85
	2	1.04	1.10	1.68	1.23	1.11	1.00	0.97	0.88	0.98
IV, 2-N	G	1.08	1.66	0.98	1.10	0.88	1.03	1.17	0.98	1.12
	1	1.02	1.69	1.20	1.02	1.16	1.08	0.88	1.06	0.89
	2	1.08	1.72	1.12	1.14	1.04	1.01	1.06	0.82	1.01

^a Ground state.Table 7. Comparison of the calculated and observed^a spectral shifts in substituted indolizines

Structures	0-Band	ΔE_t (obs.) ^c	ΔE_t (calcd.) ^d
IIIa 	3360 ^a	+0.43 eV	standard
IIIb 	3785 ^a	+0.02 eV	-0.04
IIIc 	3400 ^a	+0.40 eV	+0.33
III d 	3660 ^b	+0.14 eV	+0.12
III f 	3690 ^b	+0.11 eV	-0.10
III g 	3390 ^b	+0.41 eV	+0.27
III h 	3270 ^b	+0.54 eV	+0.43

^a Ref. [4], in cyclohexane.^b Ref. [5], in water.^c Observed shift from the 3815 Å band in indolizine.^d Using $\Delta H_{rr} = +2.05$ eV, calculated from standard.

same as was shown with indenyl anion. Indolizine is an important case [35]. Although the calculated ground state dipole moment ($1.8D$) is not high the redistribution of charge on excitation is large. In Table 7 are listed a number of azaindolizines in which the position of the $0 \rightarrow 0$ band of the lowest electronic transition could be identified from reported spectra [4,5]. For IIIa (Table 7) the position of the $0 \rightarrow 0$ band at $336 m\mu$ is strongly shifted from III itself at $382 m\mu$ [4]. However, IIIb exhibits a negligible shift while IIIc is strong. The strong shift in IIIa and IIIc is matched by a large decrease in electron density at the location of aza-substitution on excitation. This is not the case for IIIb. Using IIIa as a standard, and the 1st order perturbational equation, the coulomb parameter for aza-substitution, ΔH_{rr} , is 2.05 eV. Using this value a set of $\Delta E_{g \rightarrow e}$ for the other indolizines were calculated and are listed in Table 7. In the case of multiple aza-substitution the terms were simply summed up position by position. The calculated shifts approximate the observed shifts and lend support to the idea that the calculated change in the electron density in III on excitation is quantitatively correct. The observed (7, 36, 37) spectral shifts on aza-substitution in derivatives of IV is also rationalized by the data presented in Table 6. However, the indole derivatives [1] are not adequately rationalized and the data presented in Table 6 indicate that the calculations should not be sensitive to nitrogen parameter changes when in fact actual calculations are.

Conclusion

It can be stated that the theoretical origins of the two lowest transitions in I-V, indenyl anion, benzofuran and indene are adequately understood. Higher transitions are still open to question. Radiative and radiationless processes in I-V are presently under study and will be reported at a later date along with an analysis of the triplet manifold of these materials.

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