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ELECTRONIC STRUCTURE AND SPECTRA OF FUSED n/m RING SYSTEMS WITH ONE OR TWO BRIDGEHEAD NITROGEN ATOMS—IV[1]

THE PYRAZOLO[1.2*a*]PYRIDAZINIUM CATION, THE BENZO(c)PYRAZOLO[1.2*a*]CINNOLINIUM CATION AND PYRROLO[1.2*f*]PHENANTHRIDINE

V. GALASSO and G. DE ALTI

Istituto di Chimica, Università di Trieste, 34127-Trieste, Italy

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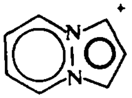
Abstract—The π-electronic structures and absorption spectra of the pyrazolo[1,2-*a*]pyridazinium cation, the benzo(c)pyrazolo[1,2-*a*]cinnolinium cation and pyrrolo[1,2-*f*]phenanthridine were investigated by means of the semiempirical SCFMO-CI method of Pariser–Parr–Pople. Discussions are given on the π-bonding situation, chemical reactivity, location and origin of the lowest excited states.

THE pyrazolo[1.2*a*]pyridazinium cation (I) is to be regarded as the first member of the fused 6/5 azaaromatic ring systems with two bridgehead nitrogen atoms and a ten π-electron structure and is, therefore, closely related to the iso-π-electronic molecule of indolizine (II), (i.e. the prototype of the fused 6/5 azaaromatic ring systems with one bridgehead nitrogen atom), which was the subject of a previous study.[2] Up to date, as far as we know, this heterocyclic system has not been synthesized. Recently, however, Farnum *et al.*[3] started an investigation of possible routes to a synthesis of this cation and, preliminarily, reported the preparation and the properties of one of its benzoderivatives, namely the benzo(c)pyrazolo[1.2-*a*]cinnolinium cation (III). At about this time, the synthesis and the properties of the corresponding derivative of indolizine, i.e. pyrrolo[1.2-*f*]phenanthridine (IV), were described in the literature.[4] However, compounds I, III and IV have never been studied theoretically. Thus, within the framework of this series of papers, it seemed of special interest to undertake a theoretical investigation in order to gather some insight into the π-bonding structure and the excited π-electronic states of these closely related molecules.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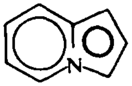
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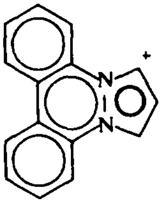
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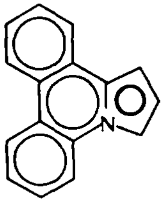

IV

COMPUTATION DETAILS

The electronic structures were determined by the SCFMO method of Roothaan using the semi-empirical scheme developed by Pariser–Parr[5] and Pople.[6] The transition energies and oscillator strengths were evaluated by means of a CI calculation taking into account all the singlet mono-excited electronic configurations in the case of the pyrazolo[1.2-*a*]pyridazinium cation and only the 16 configurations, (among 72 singly-excited configurations), formed from the four highest occupied and the four lowest unoccupied molecular orbitals in the case of the compounds III and IV.

The one-centre repulsion integrals and the valence state ionization potentials were given the same values as those used for indolizine,[2] viz. $\gamma(C^{+}C^{+}) = 9{\cdot}87$, $\gamma(N^{2+}N^{2+}) = 11{\cdot}07$ eV, and $I(C^{+}) = 11{\cdot}54$, $I(N^{2+}) = 11{\cdot}95$ eV. The C—C, C—N and N—N core resonance integrals were assigned the standard values of $-2{\cdot}39$,[5] $-2{\cdot}576$,[5] and $-2{\cdot}35$[7] eV respectively. Ohno's[8] refined approximation was used to evaluate two-centre electron repulsion integrals.

The molecules were assumed to be planar with regular polygonal angles and with bond lengths of 1·39 Å.

The calculations were carried out by means of a Fortran IV program coded for an IBM 7044 digital computer.

RESULTS

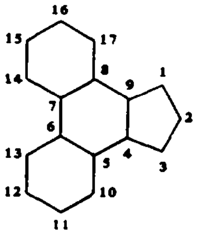
The distribution of the π-electron densities and the bond orders in the ground electronic state is given in Tables 1 and 2, along with the relevant data on indolizine.[2]

TABLE 1. π-ELECTRON DENSITIES*

Atom	1	2	3	4	5	6	7	8	9
Compound I	1·058	0·974	1·058	1·476	1·064	0·913	0·913	1·064	1·476
Compound II	1·134	1·016	1·238	1·387	1·120	0·981	1·049	0·949	1·124
Compound III	1·021	1·021	1·021	1·489	1·149	1·012	1·012	1·149	1·489
Compound IV	1·087	1·054	1·180	1·453	1·066	1·008	1·037	0·982	1·143

Atom	10	11	12	13	14	15	16	17
Compound III	0·989	0·943	0·923	0·963	0·963	0·923	0·943	0·989
Compound IV	1·025	0·987	0·996	0·988	0·993	1·010	0·988	1·002

* Atom numbering is assumed as follows:



Energies of the first excited states, oscillator strengths and wavelengths of transitions of the benzo(c)pyrazolo(1,2-a)cinnolinium cation and pyrrolo(1,2-f)phenanthridine are given in Tables 3 and 4, together with the available experimental spectral data.[3,4]

The lower transition energies, oscillator strengths and contributions to each excited state from the most important electronic configurations of the pyrazolo[1.2-*a*]-pyridazinium cation are summarized in Table 5.

Table 2. Bond orders*

Bond	1–2	2–3	3–4	4–5	5–6	6–7	7–8	8–9	1–9	4–9
Compound I	0·682	0·682	0·568	0·414	0·800	0·504	0·800	0·414	0·568	0·344
Compound II	0·678	0·674	0·532	0·446	0·778	0·543	0·772	0·496	0·609	0·457
Compound III	0·680	0·680	0·589	0·312	0·584	0·356	0·584	0·312	0·589	0·381
Compound IV	0·639	0·708	0·523	0·345	0·597	0·362	0·594	0·363	0·666	0·485

Bond	5–10	10–11	11–12	12–13	6–13	7–14	14–15	15–16	16–17	8–17
Compound III	0·617	0·641	0·679	0·624	0·685	0·685	0·624	0·679	0·641	0·617
Compound IV	0·615	0·688	0·641	0·689	0·613	0·613	0·689	0·640	0·689	0·613

* For atom numbering see Table 1.

Table 3. Electronic transitions in the benzo(c)pyrazolo[1.2-*a*]cinnolinium cation (III)

Calculation				Experiment [Ref. 3]
Transition energy (eV)		f	λ (mμ)	λ (log ε) (mμ)
${}^1A_1 \rightarrow {}^1A_1$	4·05	0·0002	306	333 (3·72), 319 (3·72), 293 (3·81)
${}^1A_1 \rightarrow {}^1B_1$	4·09	0·288	303	
${}^1A_1 \rightarrow {}^1B_1$	4·83	0·375	257	259 (4·74)
${}^1A_1 \rightarrow {}^1A_1$	4·94	0·809	351	
${}^1A_1 \rightarrow {}^1B_1$	5·25	0·491	236	218 (4·11)
${}^1A_1 \rightarrow {}^1B_1$	5·31	0·135	233	
${}^1A_1 \rightarrow {}^1A_1$	5·98	0·0004	207	
${}^1A_1 \rightarrow {}^1B_1$	6·01	0·004	206	

Table 4. Electronic transitions in Pyrrolo[1.2-*f*]phenanthridine (IV)

Calculation				Experiment [Ref. 4]
Transition energy (eV)		f	λ (mμ)	λ log ε) (mμ)
${}^1A' \rightarrow {}^1A'$	4·09	0·038	303	326 (3·83)
	4·32	0·073	287	298 (4·08), 280 (4·26)
	5·08	0·536	244	255 (4·60), 248 (4·52) sh
	5·14	0·357	241	
	5·43	1·239	228	237 (4·42)
	5·65	0·184	219	
	5·81	0·666	213	
	6·15	0·491	201	

TABLE 5. ELECTRONIC TRANSITIONS IN THE PYRAZOLO[1.2-*a*]PYRIDAZINIUM CATION (I)

Transition energy (eV)		f	Weight (%) of configurations
$^1A_1 \rightarrow {}^1B_1$	3·72	0·070	5 → 6 (81), 4 → 7 (17)
$^1A_1 \rightarrow {}^1A_1$	4·11	0·212	5 → 7 (80), 4 → 6 (15)
$^1A_1 \rightarrow {}^1B_1$	5·67	0·469	4 → 7 (68), 5 → 6 (14), 5 → 8 (13)
$^1A_1 \rightarrow {}^1A_1$	6·05	1·092	4 → 6 (66), 5 → 7 (14), 3 → 6 (11)
$^1A_1 \rightarrow {}^1A_1$	6·85	0·342	4 → 8 (35), 3 → 6 (25), 2 → 7 (15), 4 → 6 (11)
$^1A_1 \rightarrow {}^1B_1$	6·88	0·308	5 → 8 (62), 2 → 6 (10), 4 → 7 (10)

DISCUSSION

Electronic structures

An inspection of the results collected in Tables 1 and 2 shows some marked differences in the π-bonding situation between compounds I and II. Worthy of mention are the opposite variations displayed by the π-charge on the nitrogen atom, on the one hand, and by the bond order of the bridge-bond, on the other. In both compounds, however, the largest π-population, apart from that on the nitrogens, is on the carbon atoms directly linked to the nitrogen atoms. The smallest π-population is carried by the carbons "meta" with respect to nitrogen.

On the other side, passing from compound I to its dibenzoderivative III, the following features are apparent: (i) the π-electron density on the bridgehead nitrogen atoms stays constant at the value of ca. 1·48 atomic units; (ii) the π-charge on all the carbon atoms, with the exception of atoms 1 and 3, is increased; (iii) all the bond orders, apart from those of the central bridge-bond and of bonds 1–9 and 3–4, are lowered significantly; (iv) the central bridge-bond is strengthened. As expected, in compound III the carbon atoms not belonging to the parent nucleus have undergone a marked π-electron withdrawal.

Comparing the results obtained for compound II with those for its dibenzoderivative IV, we see that in this case the above-mentioned trends are only partially maintained. In particular, a more pronounced change in the π-population on the nitrogen atom and an opposite variation in the charge of the carbon atom 5 are displayed on going from the parent to the derivative compound.

Finally, the correlations observed between compounds I and II are reflected with no strong differences over compounds III and IV. However, it must be emphasized that the π-electron density on the carbon atoms of the two phenyl rings stays close to unity in compound IV, while it is relatively much farther than 1 in compound III.

As far as the chemical reactivity of the examined compounds is concerned, some qualitative predictions can be provided upon the basis of the calculated ground-state π-charge distribution. So far, out of all the carbon positions the electron density value is lowest for positions 6 and 7 in compound I and for positions 12 and 15 in compound III: hence these positions are predicted to behave as the most reactive ones towards nucleophilic substitution. In compounds II and IV the carbon atom at position 3 bears the largest π-charge: this position should accordingly show great reactivity towards electrophilic attack. This prediction is in full agreement with the experimental findings. Indeed protonation of compound II has been shown by NMR spectroscopy to take place preferentially at carbon 3;[9] and experimental evidence of high electron density at the 3 position in compound IV is provided by the ready loss of the 3-carboxy-group,[4] similar to the preferential loss of carboxy-groups at positions 1 and 3 in II.[10] Finally, since there are no carbon atoms with an unusually low electron charge, nucleophilic substitution is not expected to occur easily for these two molecules.

Following on from the previous discussion on the π-electron structure of the examined compounds, it must be stressed that the comparisons and predictions made are quite reliable insofar as the σ-π separation, invoked in the SCFMO–PPP formalism used here, is valid. In order to provide more complete knowledge of the electronic structure of these systems, a simultaneous treatment of all the valence electrons by means of the CNDO/2 method is now in progress in our laboratory, both for compounds I and II as well as for other representative systems of interest in this research. The relevant results will be discussed in detail in a forthcoming paper.

Electronic spectra

As can be seen from the results reported in Table 3, the observed spectrum of the benzo(c)pyrazolo(1,2-a)cinnolinium cation is fairly well reproduced by the calculation. Indeed, the agreement between the calculated and observed transition energies looks quite satisfactory. The theoretical oscillator strengths are also consistent with the intensities of the observed bands. These results can thus be regarded as a reliable check on the accuracy of the theoretical results obtained for the parent compound I. As far as the origin of the lower calculated one-electron transitions is concerned, an analysis of the CI wave functions shows the following. The $^1A_1 \rightarrow {}^1A_1$ transition of 4·05 eV is derived from an almost equal mixture of excitations 8 → 10 and 9 → 11, (the highest filled molecular orbital and the lowest unfilled one are numbered 9 and 10 respectively). The $^1A_1 \rightarrow {}^1B_1$ transitions of 4·09 and 4·83 eV are due essentially to excitations 9 → 10 and 7 → 10 respectively. The remaining transitions turn out to be originated from a combination of several simple configurations.

The present calculations, (Table 4), predict quite well the location of the bands measured in the absorption spectrum of pyrrolo(1,2-f)phenanthridine.[4] With regard to the nature of the lower estimated transitions, the transition of 4·09 eV mainly originates from the excitation of an electron from the highest occupied molecular orbital to the lowest virtual one, i.e. the excitation 9 → 10, with a minor contribution from excitation 8 → 11. The transition of 4·32 eV is primarily associated with the excitation 9 → 11; there is, however, a little participation of configuration 8 → 10. Finally, a mixing of several simple excitations is ascribed to the remaining transitions.

On the basis of the present results, (Table 5), the UV absorption spectrum of the pyrazolo(1,2-a)pyridazinium cation is expected to correspond closely to that of the iso-π-electronic molecule of indolizine as regards both the energies and intensities of the one-electron transitions. Thus, the spectrum should consist of three bands located in the region 340–200 mμ. A moderately intense band, assigned to a $^1A_1 \rightarrow {}^1B_1$ transition, is predicted to be centred at 333 mμ (3·72 eV), hypsochromically shifted with respect to the corresponding band of indolizine, observed at 346 mμ.[11] The absorption maximum of the second medium-intensity band, assigned to a $^1A_1 \rightarrow {}^1A_1$ transition, should be located at 302 mμ (4·11 eV), corresponding to a moderate bathochromic displacement relative to the position of the second band of indolizine, measured at 294 mμ.[11] The third strong-intensity band, probably composed of two different transitions $^1A_1 \rightarrow {}^1B_1$ and $^1A_1 \rightarrow {}^1A_1$, is expected to appear in the region 219–205 mμ (5·67–6·05 eV), hypsochromically shifted with regard to the corresponding band of indolizine, recorded at 237 mμ.[11]

The predicted origins of these bands appear to be very similar to those previously determined for the related bands of indolizine.[2] Thus, the first band is predominantly due to the excitation of one electron from the top occupied to the lowest unoccupied molecular orbital, i.e. the electron jump 5 → 6, with a minor contribution from excitation 4 → 7. The second band is attributed essentially to excitation 5 → 7, with a small contribution from excitation 4 → 6. The two transitions calculated at 5·67 and 6·05 eV should contribute to the third band. These transitions both originate from a combination of several simple excitations, most important being excitations 4 → 7 and 4 → 6.

A final observation of interest is that on the basis of the present calculations a moderate hypsochromic shift is expected to be shown by the first band on going from the parent I to the derivative compound III. This prediction is in full agreement with both the experimental and theoretical results displayed by the closely related compounds II and IV.

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