Theoret. chim. Acta (Berl.) 10, 352—356 (1968)

The π-Inductive Effect of the Ammonio (NH_3^+) Group

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Received January 15, 1968

The influence of the $-NH_3^+$ group on the π electronic structures of 1-azulenyl and 1-naphthyl ammonium cations has been investigated. Using the potential of Bishop and Craig a reasonable account of the electronic spectra and charge distributions in the two molecules has been obtained within the framework of the Pariser-Parr-Pople SCF MO method.

Der Einfluß der $-NH_3^+$-Gruppe auf die π-Elektronenstruktur des 1-Azulenyl- und des 1-Naphthyl-ammoniumkations wurde untersucht. Mit dem von Bishop und Craig angegebenen Potential wurden im Rahmen der PPP-Methode befriedigende Ergebnisse für Elektronenspektren und Ladungsverteilungen der beiden Moleküle erhalten.

Etude de l'influence du groupe NH_3^+ sur les structures électroniques π des cations 1-azulenyl et 1-naphtyl ammonium. En utilisant le potentiel de Bishop et Craig on rend compte raisonnablement du spectre électronique et des distributions de charge dans ces deux molécules dans le cadre de la méthode SCF de Pariser-Parr-Pople.

1. Introduction

In a previous paper [7] we have taken the concept of a substituent π-inductive effect, originally developed [11] in terms of the localized orbital model, and successfully introduced it into a conventional Pariser-Parr [13] -Pople [15] treatment of some monosubstituted benzenes.

For a monosubstituted alternant hydrocarbon, the introduction of a π-inductive effect [7], whilst not altering the calculated electronic spectra significantly, has a large effect on the calculated charge distributions. It is to be expected however that for a monosubstituted non alternant hydrocarbon such as azulene, an inductive substituent should have an appreciable effect on both the electronic spectra and charge distributions. A substituent of considerable interest is the ammonio group ($-NH_3^+$), the effect of which is almost entirely inductive.

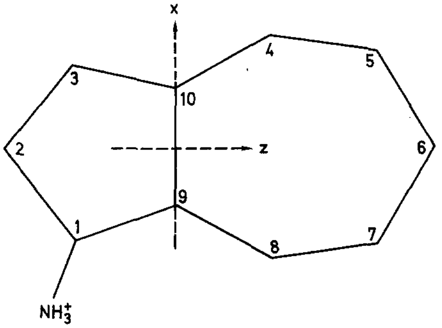

Fig. 1. Co-ordinate axes and numbering system employed for the 1-azulenyl ammonium cation

In an important paper [4] Bishop and Craig developed a perturbation treatment for the effect of the ammonio group on the intensity and frequency shift of the benzene 2600 Å band. More recently Williams [19] has extended and modified Bishop and Craig's treatment to investigate the effect of the ammonio group on the 2600 Å band of benzene, the visible band of azulene and the charge transfer bands of nitrobenzene and aniline.

In this paper we present the results of PPP SCF MO calculations on the electronic spectra and electron distribution of the 1-azulenyl ammonium cation. The attachment of the $-NH_3^+$ group to the non alternant hydrocarbon azulene results in an appreciable shift in the visible and U.V. absorption bands [18]. For comparison similar calculations are presented for 1-naphthyl ammonium cation, the electronic spectrum of which is essentially the same as that of the parent hydrocarbon naphthalene. The numbering system and coordinate axes are shown in Fig. 1.

2. Method of Calculation

The calculations have been carried out by the conventional Pariser-Parr-Pople SCF method. The elements of the F matrix are given by;

$$F_{\mu\mu} = U_{\mu\mu} + \tfrac{1}{2} P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - Z_\sigma)\,\gamma_{\mu\sigma} \tag{1}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{\mu\nu} \tag{2}$$

where we have used the notation of Pople [15].

The influence of the ammonio group is represented by a short range exchange repulsion term and a long range coulombic term. As a starting point the potential suggested by Bishop and Craig [4] Eq. (3) has been employed.

$$V(\text{in a.u.}) = \frac{1}{\varepsilon}\left(-\frac{\alpha}{R} + \frac{3}{R^2}\right). \tag{3}$$

In Eq. (3) R is the distance in atomic units, α is an effective nuclear charge. The dielectric constant ε is included since the σ-electron framework, constitutes a polarizable medium in which the π-electrons are embedded. A value of ε appropriate to this model may be estimated for example from the macroscopic dielectric constant of a substance containing C–C and C–H σ-electrons alone, such as cyclohexane ($\varepsilon = 2.0$). Apart from the constant ε, the potential (3) depends upon the effective nuclear charge parameter α. The value $\alpha = 1.84$ gives a good fit to the calculated ionization potential, using Slater orbitals, of Na^+ which is isoelectronic with NH_3^+, and this value has been employed in these calculations.

The $U_{\mu\mu}$ have been calculated from the appropriate ionization potentials using Eq. (4)

$$U_{\mu\mu} = I + V. \tag{4}$$

Two electron one centre integrals have been determined as given by Pariser [14] and the two electron, two centre integrals $\gamma_{\mu\nu}$ estimated by the procedure of Mataga and Nishimoto [9].

The geometries of the 1-azulenyl and 1-naphthyl ammonium cations were taken to be those of the hydrocarbons [17], with a $C{-}NH_3^+$ bond length of 1.35 Å [5], the substituent being located on a line bisecting the internal angle at the substituted carbon atoms. The integral values are collected in Table 1.

Table 1. *Integrals used in the calculations*

I C(tr tr tr π)→C$^+$(tr tr tr) – 11.16 eV		
	Excited states	Ground states
H_{CC}	– 2.236 eV	– 1.75 eV
H_{CC} (9–10 bond azulene)	– 1.856 eV	– 1.292 eV
γ_{CC}	10.98 eV	

The calculations were made using an Algol 60 program written for the University of Newcastle's KDF 9 computer and kindly supplied by Drs. D. R. Armstrong and P. G. Perkins [3]. Configuration interaction between all the singly excited states has been included.

The U. V. spectral data for the 1-naphthyl ammonium cation was measured in 4n perchloric acid on a Unicam SP 800 spectrometer. The data for naphthalene is that of ref. [1, 10] and for azulene and 1-azulenyl cation that of ref. [2, 18].

3. Results and Discussion

In this section we give details of the results of calculation of intensity and energy changes on NH_3^+ substitution for naphthalene and azulene.

The U.V. spectrum of 1-naphthyl ammonium cation (Fig. 2) is not appreciably different from that of naphthalene. Both compounds show three distinct absorption bands. Table 2 shows the calculated and observed singlet-singlet transitions of lowest energy for naphthalene and also the frequency shifts and changes in oscillator strength on introduction of the NH_3^+ group in the 1 position. The agreement is quite good. The introduction of the ammonio group lowers the symmetry from D_{2h} to C_s and all the transitions become symmetry allowed. The absorption in the region of 220 mμ ($^1B_{3u}$ state of naphthalene) is predicted to be due to a superposition of a medium intensity band, a strong band, and a weak band, corresponding to the ^1A_g, $^1B_{3u}$ and $^1B_{1g}$ states of naphthalene respectively. This assignment is supported by the experimental evidence, since the absorption maxima occur at the same wavelength (220.7 mμ), but whereas the absorption band of naphthalene has $\varepsilon_{max} \sim 123700$ and peak width at half height of ~ 2500 cm^{-1}, the correspond-

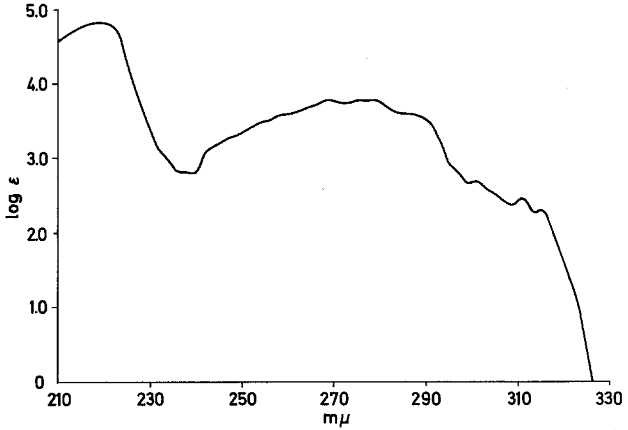

Fig. 2. The electronic spectrum of 1-naphthyl ammonium cation in 4*n* perchloric acid

Table 2. *Calculated and observed excited states, frequency shifts and changes in oscillator strengths for naphthalene on introduction of the* NH_3^+ *group in the 1 position*

State Number	Symmetry	Energy in eV		Oscillator strength		Frequency shifts in cm^{-1} [a]		Changes in oscillator strength	
		Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
1	B_{3u}	4.00	3.933	0.0003	0	0	36	0.0001	0.0046
2	B_{2u}	4.50	4.354	0.180	0.221	−330	−323	−0.050	−0.009
3	A_g		5.513		0		145		0.110
4	B_{3u}	5.62	5.591	1.70	2.00	~ 0	− 97	−0.100	−0.140
5	B_{1g}		5.658		0		− 97		−0.023
6	B_{1g}		5.994		0		−186 [b]		0.0005
7	B_{2u}	5.90	6.156	0.60	0.60		−121 [b]		0

[a] A negative figure indicates a bathochromic shift on substitution.

[b] The measured spectrum in 4*n* perchloric acid excludes this region from the discussion.

Table 3. *Calculated and observed excited states, frequency shifts and changes in oscillator strengths for azulene on introduction of the* NH_3^+ *group in the 1 position*

State Number	Symmetry	Energy in eV		Oscillator strength		Frequency shifts (cm^{-1})		Changes in oscillator strength	
		Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
1	B_1	2.137	2.084	0.009	0.027	500	686	0.010	0.010
2	A_1	3.636	3.441	0.08	0.007	350	1073	−0.002	−0.002
3	B_1	4.180	4.259		0.170	1200	1403		−0.013
4	A_1	4.492	4.701	1.10	1.848	400	306	−0.110	−0.045
5	B_1	5.220	5.560	0.38	0.398	[a]			

[a] The published spectrum of 1-azulenyl ammonium cation is that for a formic acid solution [18] so that there is no information on this band.

ing figures for 1-naphthyl ammonium cation are ~63800 and ~4250 cm^{-1} respectively.

The visible and U.V. spectra of azulene differ considerably from that of the 1-azulenyl ammonium cation [18, 2]. Table 3 shows the calculated and observed singlet-singlet transitions of lowest energy for azulene and also the frequency shifts and changes in oscillator strength on introduction of the NH_3^+ group in the 1 position. The agreement is fortuitously good, particularly for the visible band. This is in marked contrast to the perturbation treatment of Williams [19] using the same potential. The calculated shift for the second absorption band is roughly three times too large. There is some doubt concerning the assignment of the third absorption band [11]. Azulene itself shows a sharp band system starting at ~296 mμ to the long wavelength side of the intense absorption at ~276 mμ. The former is absent in the substituted azulene and assuming this band undergoes a hypsochromic shift and underlies the more intense absorption at shorter wavelengths an estimated shift of ~ 1200 cm^{-1} is in good agreement with experiment.

4. Electron Distribution

Table 4 shows the calculated *change* in electron density on introduction of the NH_3^+ group at the 1 position in naphthalene and azulene. As expected there is an appreciable drain of electron density towards the substituted carbon atoms.

Table 4. *Calculated change in π-electron density on introduction of the NH_3^+ group in the 1 position of naphthalene and azulene. (A positive value indicates that the electron density is increased at that position on substitution)*

Atom number[a]	1	2	3	4	5	6	7	8	9	10
Naphthalene	0.0097	0.0510	−0.0188	−0.0324	−0.0149	−0.0455	−0.0370	0.0458	0.0561	−0.0141
Azulene	0.0198	0.0623	−0.0304	−0.0462	−0.0377	−0.0443	−0.022	0.0288	0.0596	0.0093

[a] Conventional numbering system.

An interesting feature which appears here however, in contrast to the work of Bishop and Craig [5], on the anilinium ion, is that the build up of charge is smaller at the substituted carbon atoms than at the ortho carbon atoms. It has been pointed out that the potential Eq. (3) does not have a strong enough dependence on R at distances around a bond length, when used in a perturbation treatment. Williams [6] suggested a modified potential which would almost certainly have the effect of reducing large build up of charge at the position of substitution predicted by Craig and Bishop. The potential suggested by the latter authors, however is quite satisfactory in the context of a normal Pariser-Parr-Pople treatment as described here.

Conclusions

The electronic spectra of 1-naphthyl and 1-azulenyl ammonium cations have been investigated by the PPP SCF MO method. Using the potential originally suggested by Craig and Bishop in their perturbation treatment of the anilinium cation, a satisfactory account of the electronic spectra and charge distributions has been presented.

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