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Heterocyclic Fused Tropylium Ions

V. UV Spectra of Some Dithieno- and Furothienoannelated Tropones and Tropylium Ions

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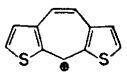
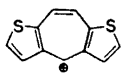
The ultraviolet spectra of a number of furan- and thiophene-annelated tropylium cations and tropones have been measured and compared to theoretical spectra calculated within the Pariser-Parr-Pople approximation. The calculated spectra are in good agreement with the experimental ones. The ultraviolet spectrum of an unknown thiophene-annelated tropylium cation (X) is predicted.

A number of furan- and thiopheneannelated tropylium cations and tropones have recently been prepared by Gronowitz and coworkers. The infrared and proton magnetic resonance spectra of these compounds have been reported.[1] In this paper we wish to report a study of the ultraviolet spectra of the annelated tropylium cations I–IV and the related annelated tropones V–VIII.



I



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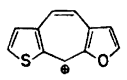

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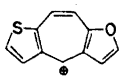

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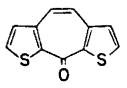
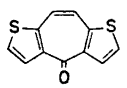
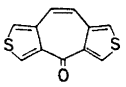


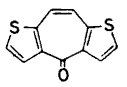
V



VI



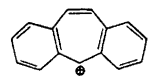
VII



VIII

It is of interest to compare the spectral properties of the cations I–IV with those of the ketones V–VIII, since IR data indicate a pronounced tropylium cation character of the central ring in most of the latter compounds.[1]

The general complexity of the experimental spectra makes it interesting to test the ability of molecular orbital calculations to reproduce them. Calculations may also cast some light on questions concerning the number and positions of transitions making up a band in spectrum. Most successful calculations of ultraviolet spectra of conjugated organic compounds have been made by use of the π-electron approximation of Pariser, Parr and Pople (PPP),[2,3] and this method has been used to calculate the electronic transitions of the molecules considered in this work. Fabian *et al.*,[4,5] by extensive comparisons of ultraviolet spectra of heterocyclic sulphur compounds and the corresponding iso-π-electronic hydrocarbons, have shown the remarkable similarities in the spectra properties of these two classes of compounds. This approach will be used in the present paper to compare the ultraviolet spectra of compounds I – IV with that of 1,2:4,5-dibenzotropylium cation IX.



IX

METHODS OF CALCULATION

As mentioned above, the molecular orbital calculations were made using the PPP π-electron scheme, employing two different sets of parameters A and B. Set A was proposed by Fabian *et al.*[4,5] and is based on a systematic adjustment of the parameters $U_{\mu\mu}$, $\beta_{\mu\nu}$ and $\gamma_{\mu\mu}$ (for notation see Ref. 4) until a good fit between the calculated and experimental ultraviolet spectra of some reference compounds, including cations, was obtained. The parameter values used in the present calculations are given in Table 1. It should be noted that

Table 1. Parameters of set A (eV).

μ	$-U_{\mu\mu}$	$\gamma_{\mu\mu}$	$\mu\nu$	$-\beta_{\mu\nu}$
C	11.42	10.84	CC	2.318
O	27.17	14.58	CO	2.550
S	20.00	10.84	CS	1.623

in set A the resonance integral, $\beta_{\mu\nu}$, is kept constant for a given type of bond, thus neglecting the influence of variations of bond length on this integral. This may be a drastic simplification, but it is at least partly justified by the successful simulation of the ultraviolet spectra of a large number of heterocyclic compounds, by calculations using set A.[4,5] The two-centre repulsion integrals, $\gamma_{\mu\nu}$, were calculated by the Nishimoto-Mataga approximation.[6]

Parameter set B is based on a theoretical investigation of the Zero Differential Overlap approximation made by Fischer-Hjalmars.[7] The parameters

in this set were obtained through a least-squares fit to experimental ionization potentials and singlet π-π^* transitions of chosen reference compounds.[8–11] The main feature of the method proposed by Fischer-Hjalmars is the dependence of the diagonal elements, $H_{\mu\mu}^{\text{core}}$, on the neighbouring atoms through formulas (1) [12] and (2)

$$H_{\mu\mu}^{\text{core}} = W_\mu - (n_\mu - 1)\gamma_{\mu\mu} - \sum_\nu n_\nu \gamma_{\mu\nu} \quad (1)$$

$$W_\mu = W_\mu^\circ + \sum_\nu \{\Delta W_\mu^\circ(\nu) + \delta_{\mu\nu}{}^W (R_{\mu\nu} - R_{\mu\nu}^\circ)\} \quad (2)$$

where n_μ is the number of electrons contributed by atom μ and the sum in (2) is a correction due to neighbouring atoms ν and bond distances $R_{\mu\nu}$. The resonance integrals, $\beta_{\mu\nu}$, and the electron repulsion integrals, $\gamma_{\mu\nu}$, for nearest neighbours depend linearly on bond distances according to formulas (3) and (4).

$$\beta_{\mu\nu} = \beta_{\mu\nu}{}^\circ + \delta_{\mu\nu}{}^\beta (R_{\mu\nu} - R_{\mu\nu}^\circ) \quad (3)$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}{}^\circ + \delta_{\mu\nu}{}^\gamma (R_{\mu\nu} - R_{\mu\nu}^\circ) \quad (4)$$

The values for W_μ°, $\Delta W_\mu^\circ(\nu)$, $\gamma_{\mu\mu}$, $\gamma_{\mu\nu}{}^\circ$, $\delta_{\mu\nu}{}^W$, $\delta_{\mu\nu}{}^\gamma$, $\beta_{\mu\nu}{}^\circ$, and $\delta_{\mu\nu}{}^\beta$ were obtained as described above. For non-neighbours $\gamma_{\mu\nu}$ is calculated using the ball approximation.[13] The parameters making up set B are summarized in Table 2.

Table 2. Parameters of set B (eV).

Atom	$-W_\mu{}^\circ$	$\gamma_{\mu\mu}$	Bond μ–x	$-\beta_{\mu\nu}{}^\circ$	$\gamma_{\mu\nu}{}^\circ$	$\delta_{\mu\nu}{}^W$	$\delta_{\mu\nu}{}^\beta$	$-\delta_{\mu\nu}{}^\gamma$	$\Delta W_{\mu(\nu)}{}^\circ$	$\Delta W_{\nu(\mu)}{}^\circ$	R_0(Å)
C	9.84	11.97	C–C	2.42	6.91	9.22	3.05	3.99	0.07	0.07	1.397
Ȯ	19.60	18.89	C–Ȯ	2.46	9.33	0	0	0	−0.71	0	1.22
Ö	11.18	18.89	C–Ö	1.80	6.20	0	0	0	−0.09	1.51	1.35
S	10.62	9.58	C–S	1.37	7.28	9.22	3.05	3.99	−0.70	0	1.714

The excited states were obtained by a limited configuration interaction, including a maximum of 20 configurations in calculations with set A, and all singly excited configurations in calculations using set B.

GEOMETRIES USED IN THE CALCULATIONS

All compounds were assumed to be planar. Preliminary X-ray investigations have shown that compounds I and II are planar in the crystalline state.[14] The geometries used in the calculations on these compounds were based on the X-ray analysis. Bond lengths and bond distances of the other compounds were estimated from the geometries of the tropylium cation,[15] tropone,[16] furan,[17] and thiophene.[18] Table 3 summarizes the values for bond lengths and bond angles used in the calculations. The numbering of the atoms is shown below.

Table 3. Bond distances (a) and bond angles (b) for compounds I – IV and X. The ring structures in compounds V – VIII were assumed to be the same as in the corresponding tropylium cations I, II, and IV. The carbonyl oxygen was placed 1.26 Å from atom 8 on a line bisecting the angle 7–8–9.

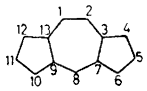
(a) Bond distances (Å)

Compound	1–2	2–3 1–13	3–4 12–13	4–5 11–12	5–6 10–11	6–7 9–10	7–8 8–9	3–7 9–13
I	1.37	1.41	1.44	1.33	1.72	1.735	1.415	1.39
II	1.40	1.42	1.71	1.715	1.365	1.47	1.395	1.46
X	1.41	1.41	1.37	1.714	1.714	1.37	1.409	1.423
			3–4	4–5	5–6	6–7		
III[a]			1.431	1.361	1.362	1.337		
IV[a]			1.362	1.362	1.361	1.420		

(b) Bond angles (°)

Compound	1–2–3 2–1–13	2–3–7 1–13–9	3–7–8 13–9–8	7–8–9	4–3–7 12–13–9	3–7–6 13–9–10	3–4–5 11–12–13	4–5–6 10–11–12	5–6–7 9–10–11
I	129	127	132.5	123	111.5	111.5	112	115	90.5
II	128	131	126	131	110	111.5	93	114.5	110.5
X	128.6	128.6	128.6	128.6	112.4	112.4	111.5	92.2	111.5
					4–3–7	3–7–6	3–4–5	4–5–6	5–6–7
III[a]					106	108.6	106	110.7	108.7
IV[a]					110.7	102	106.6	110.7	110

[a] The geometries of the thiophene and seven-membered rings in these compounds were assumed to be the same as in compounds I and II, respectively.



EXPERIMENTAL

The ultraviolet spectra were recorded on a Unicam SP 800 B UV spectrophotometer. Compounds I – III (as perchlorate) were dissolved in conc. suphuric acid, compound IV (perchlorate) in 0.2 N HCl and compounds V – VIII in abs. ethanol. The calculations were performed on a Univac 1108 computer using programs written by Professor Rolf Manne, University of Bergen, Norway (set A) and Dr. Marianne Sundbom, Institute of Theoretical Physics, University of Stockholm (set B).

Table 4. Experimental ultaviolet spectra of compounds I–VIII.

I		II		III		IV		V		VI		VII		VIII	
λ_{max} (nm)	$\varepsilon \times 10^{-3}$	λ_{max} (nm)	$\varepsilon \times 10^{-3}$	λ_{max} (nm)	$\varepsilon \times 10^{-3}$	λ_{max} (nm)	$\varepsilon \times 10^{-3}$	λ_{max} (nm)	$\varepsilon \times 10^{-3}$	λ_{max} (nm)	$\varepsilon \times 10^{-3}$	λ_{max} (nm)	$\varepsilon \times 10^{-3}$	λ_{max} (nm)	$\varepsilon \times 10^{-3}$
471	4.68	470(sh)	1.11	414(sh)	4.13	404(sh)	3.66	370	6.50	373	12.5	380	0.448	376	10.9
460.5	5.0	440(sh)	2.88	368	17.3	378	8.0	362	6.50	352	16.0	311	2.83	355	15.3
447	4.65	411	7.70	306	42.5	296	52.0	350	6.88	337	15.4	295(sh)	3.58	337	12.0
395	15.7	374	6.0	275	16.5	263(sh)	12.8	330	7.26	254	30.9	269.5	14.2	322(sh)	8.62
375	7.25	312	80.9	220	12.8	210	10.5	289	25.8	205	8.19	264	13.0	285(sh)	5.75
330.5	46.2	230(sh)	15.5					250	25.2			250	10.0	273	7.77
301.5	37.5	223	17.7					204	7.28			205	2.31	250(sh)	18.3
265.5	8.42	205	17.7											243	20.9
235	14.6														
208	17.4														

RESULT AND DISCUSSION

Preliminary calculations showed that only calculations using set A could account for the experimental spectra of compounds I – IV. Calculations using set B gave transition energies which were far too high. The failure of set B to reproduce the spectra of these cations is not unexpected since the parameters making up this set are primarily adjusted to give a good fit between calculated and experimental spectra of *neutral* compounds in the vapour phase, and should thus not be suited for calculations on ions in a solvent such as conc. sulphuric acid. The spectra of the *neutral* compounds V – VIII are, as will be seen later, well accounted for, using parameter set B.

1. Annelated tropylium cations (I – IV). Figs. 1 a-d show the experimental spectra of compounds I – IV superimposed on the calculated transitions (set A). (Calculated transitions with intensities corresponding to $\log f < -1.6$ are indicated with dots.) The experimental absorption maxima (λ_{max}) and intensities (ε) are tabulated in Table 4.

As can be seen in Figs. 1 a-d, the calculated transitions account very well for the experimental spectra. The positions and relative intensities of the two

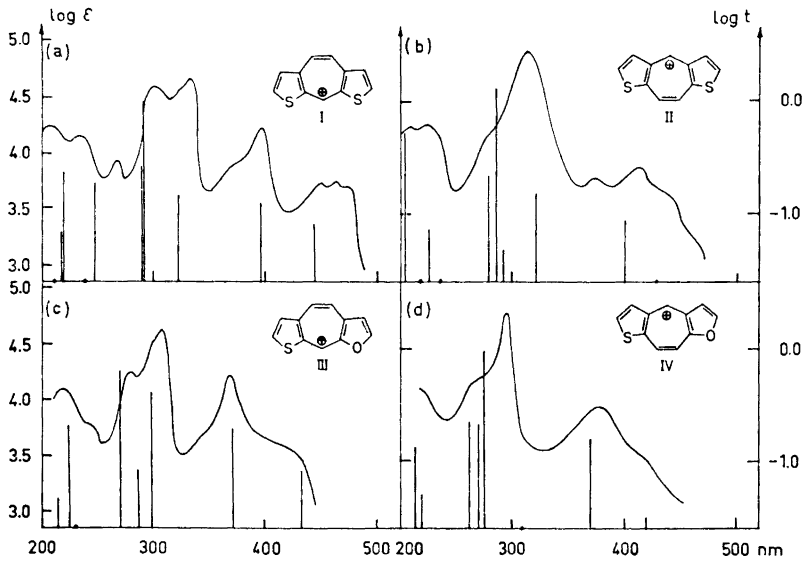


Fig. 1. Experimental and calculated UV spectra of

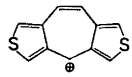
(a) dithieno[2,1-b:4,5-b']tropylium perchlorate,
(b) dithieno[2,1-b:5,4-b']tropylium perchlorate,
(c) furo[3,2-a]thieno[2',3'-d]tropylium perchlorate, and
(d) furo[2,3-a]thieno[2',3'-d]tropylium perchlorate.

bands at longest wavelength are especially well reproduced. The spectrum of compound I shows two well-resolved bands centred at 395 and 460 nm, respectively. The calculation indicates that these bands are due to two transi-

tions with partly resolved vibrational fine structure. This pattern is repeated in the spectra of compounds II – IV with variations in the separation between the two transitions. The small calculated separation between these transitions in the spectrum of compound II, as well as the low frequency of the first transition, accounts very well for the failure to observe two separate bands in this spectrum. Changing one of the sulphur atoms in compounds I and II to an oxygen atom, to give compounds III and IV, has no drastic influence on the ultraviolet spectra. Figs. 1 c and 1 d show that except for a loss of fine structure, the exchange results in small hypsochromic shifts of most of the transitions. This is a common observation in comparisons between the ultraviolet spectra of sulphur heterocycles and those of the corresponding oxygen heterocycles. Benzothiophene, for instance, absorbs at longer wavelengths than benzofuran.[4] This shift has been attributed to the smaller overlap between the p_z orbitals of sulphur and the neighbouring carbon atoms than between the corresponding orbitals of oxygen and carbon. Another factor of importance is the difference in the valence electron ionization potentials of sulphur and oxygen.[4] Both factors show up in the parameter set A, that is $U_O > U_S$, $|\beta_{CO}| > |\beta_{CS}|$ (Table 1).

The experimental spectra show only small differences due to the annelation pattern. The calculations indicate a small bathochromic shift of the first transition in I and III compared to the corresponding transition in II and IV, and also a greater separation between the first two transitions of the former compounds. The calculated closely lying transitions in the region of 280 – 300 nm in the spectrum of compound II, and at 260 – 280 nm in that of compound IV account well for the lower resolution of the corresponding experimental bands in these spectra compared to the equivalent bands in the spectra of compounds I and III.

The ultraviolet spectra of compounds I – IV show a general similarity to spectrum of 1,2:4,5-dibenzotropylium cation (IX), which is shown in Fig. 2 a (solvent: conc. sulphuric acid).[19] Each of the first two bands in this spectrum consists of one transition, according to calculations made by Heilbronner.[20] The position of the second band, centred at about 388 nm, is close to that of the corresponding band in the spectra of I – IV, and this is also true for the band with absorption maximum at 306 nm. The first transition, however, occurs at significantly longer wavelengths in the spectrum of IX than in the spectra of compounds I – IV. In this context it is interesting to study the calculated transitions (set A) of the unknown compound X, the synthesis of which is in progress in our laboratories.



X

The predicted spectrum is given in Fig. 2 b. The annelation pattern in compound X gives, according to the calculations, some significant changes in the ultraviolet spectrum compared to the spectra of compounds I – IV. The first transition of X, for instance, is predicted to occur at 639 nm, which should

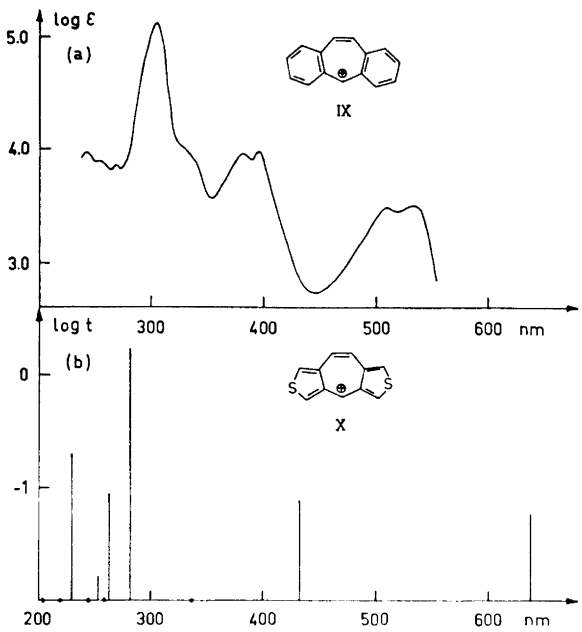


Fig. 2. (a). Experimental UV spectrum of 1,2:4,5-dibenzotropylium perchlorate. (b). Calculated UV spectrum of dithieno[2,1-c:4,5-c']tropylium perchlorate.

be compared to the first transitions in the spectra of I – IV, all of which come below 450 nm. The annelation pattern of compound X is thus predicted to have a similar effect on the ultraviolet spectrum as the exchange of the heterocyclic rings in I – IV for benzene rings. The prediction that compound X absorbs at longer wavelengths than compounds I – IV is not wholly unexpected. Resonance theory indicates restricted conjugation in compound X since more resonance structures with high probability can be written for compounds I – IV than for compound X. This should lead to a higher ground state energy of X than of any of the compounds I – IV, and consequently to lower transition energies of X than of I – IV, assuming that the energies of the excited states are not affected to the same extent.

2. Annelated tropones (V – VIII). The tropone molecule has been shown to be planar, [16] while dibenzotropone is nonplanar, at least in the crystalline state.[21] A thiophene ring is for geometrical reasons more suited than a benzene ring to be annelated to the tropone ring system without destroying the planarity of this ring, and it makes possible a coplanar arrangement of the rings. The experimental and calculated spectra of compounds V – VIII are given in Figs. 3 a – d; the experimental values are given in Table 4. The calculations were made using parameter set B. (No calculations with set A were made since this set does not include parameters for the carbonyl oxygen.) As can be seen in Fig. 3, the ultraviolet spectra of compounds V, VI, and VIII can satisfactorily be reproduced assuming planar systems.

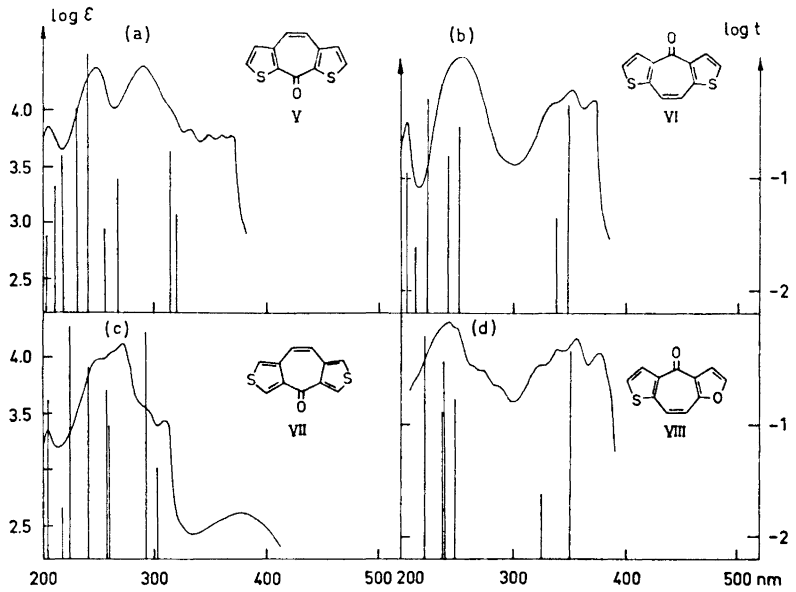


Fig. 3. Experimental and calculated UV spectra of
(a) 9H-cyclohepta[2,1-b:4,5-b′]dithiophene-9-one,
(b) 4H-cyclohepta[1,2-b:5,4-b′]dithiophene-4-one,
(c) 4H-cyclohepta[2,1-c:4,5-c′]dithiophene-4-one, and
(d) 4H-thieno[5,4-b′]cyclohepta[1,2-b]furan-4-one.

The overall similarities between the pattern of the ultraviolet transitions of compounds I – IV (Figs. 1 a – d) and that for compounds V, VI, and VIII, taking into consideration the fact that different solvents were used for the two groups of compounds, suggest a significant tropylium cation character of the central ring in V, VII, and VIII, in accordance with the previously reported IR data.[1] Further support for the proposed tropylium cation character of these compounds comes from the calculated carbon-oxygen bond orders, which are 0.6896, 0.6681, and 0.6824 for compounds V, VI, and VIII, respectively. These values are very low compared to the values for other carbonyl compounds calculated in the same way,[10] indicating an unusually strong polarity of the carbon-oxygen bond in V, VI, and VIII.

The low intensity band at 380 nm ($\varepsilon = 448$) in the spectrum of compound VII can not be reproduced by the calculations. An analogous band in the spectrum of benzophenone, which is displaced towards shorter wavelengths with increasing polarity of the solvent,[22] makes it probable that the low intensity band in the spectrum of VII is due to an $n - \pi^*$ transition. The calculated carbon-oxygen bond order of compound VII is 0.7577, which is significantly higher than the corresponding bond orders in the other ketones. This is in good agreement with the conclusion made from IR data that the tropylium cation character of the central ring is lower in compound VII than

in either of the compounds V and VI,[1] due to the restricted conjugation in the former compound. The ultraviolet spectrum of compound VII is also quite different from the spectra of the other annelated tropones (Fig. 3). Furthermore, the spectrum of VII shows no similarities to the predicted spectrum of the corresponding tropylium cation derivative X.

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