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MOLECULAR ORBITAL CALCULATIONS OF THE FIRST TRANSITION ENERGY OF SUBSTITUTED TROPYLIUM SALTS

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Abstract—The longest wave absorption band in the electronic spectra of 96 tropylium cations of varying complexity has been calculated by the simple MO-LCAO method, using parameters obtained earlier.[1] A good correlation between observed frequencies and calculated energy differences was obtained for all compounds except the tropylium cyanine dyes. The correlation within small groups of structurally similar cations is outstandingly good.

The simple HMO method has recently been applied[1] to a series of substituted pyrylium salts and a good correlation was found between the calculated differences in energy between the highest occupied and lowest unoccupied molecular orbitals (Δm) and the observed frequency ($\tilde{\nu}$) of the longest wave absorption band in the electronic spectra of 65 pyrylium cations. In these calculations Coulomb and bond integrals were chosen so as to minimise deviations from the regression line. The results demonstrated the usefulness of the simple HMO method and gave a semi-quantitative interpretation of the electronic and steric effects of substituents on the first absorption band of complex pyrylium salts. We were thus encouraged to carry out a similar series of calculations for substituted tropylium salts. A summary of results and conclusions for 96 such salts is presented in this paper.

The electronic spectra of many tropylium ions, particularly alkyltropylium (azulenium) ions are available from the work of Heilbronner,[2–7] Hafner,[8,9] Reid[10,11] and, more recently, Jutz.[12–15] HMO calculations on restricted groups of such cations have been done and good correlations established between first transition energies

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[1] G. V. Boyd and N. Singer, *Tetrahedron* **21**, 1263 (1965).
[2] L. H. Chopard-dit-Jean and E. Heilbronner, *Helv. Chim. Acta* **35**, 2170 (1952).
[3] W. H. Schaeppi, R. W. Schmid, E. Heilbronner and A. Eschenmoser, *Helv. Chim. Acta* **38**, 1874 (1955).
[4] W. Simon, G. Naville, H. Sulser and E. Heilbronner, *Helv. Chim. Acta* **39**, 1107 (1956).
[5] H. H. Rennhard, G. DiModica, W. Simon and E. Heilbronner, *Helv. Chim. Acta* **40**, 957 (1957).
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[8] K. Hafner, H. Pelster and J. Schneider, *Liebigs Ann.* **650**, 62 (1961).
[9] K. Hafner, H. W. Riedel and M. Danielisz, *Angew. Chem.* **75**, 344 (1963).
[10] E. C. Kirby and D. H. Reid, *J. Chem. Soc.* 1724 (1961).
[11] E. C. Kirby and D. H. Reid, *J. Chem. Soc.* 3579 (1961).
[12] C. Jutz and F. Voithenleitner, *Chem. Ber.* **97**, 29 (1964).
[13] C. Jutz and F. Voithenleitner, *Chem. Ber.* **97**, 1337 (1964).
[14] C. Jutz, *Chem. Ber.* **97**, 1349 (1964).
[15] C. Jutz and F. Voithenleitner, *Chem. Ber.* **97**, 1590 (1964).

and calculated energy differences, and between acidities and calculated localisation, energies.[7]

The tropylium salts considered in this work are classified in four main groups as set out in Table 1. This division follows that for the pyrylium salts except that no amino- or halogen-substituted salts are included as too few such compounds are reported in the literature. Further, Group I (unsubstituted cations) and Group II (alkyl-substituted cations) have been subdivided because, as will be shown below, rather good correlations exist in the sub-groups.

Table 1. Classification of tropylium salts

Group I		Tropylium salts lacking alkyl and methoxy substituents (28 salts)
	A	Monocyclic tropylium salts with phenyl or phenyl(poly)vinyl substituents (9 salts)
	B	Monocyclic tropylium salts with polycyclic aryl or arylvinyl substituents (8 salts)
	C	Polycyclic tropylium salts (6 salts)
	D	Salts containing two or three seven-membered rings (cyanines) (4 salts)
Group II		Tropylium salts with alkyl substituents (44 salts)
	A	Alkyltropylium salts containing one seven-membered ring (33 salts)
	B	Alkyltropylium cyanines (11 salts)
Group III		Tropylium salts with methoxy substituents (21 salts)
Group IV		Tropylium salts with alkyl and methoxy substituents (3 salts)

In order to save space the cations are named in terms of a few structural types which are shown in Fig. 1. Tables 2–5 list the compounds together with the observed wave length of the first absorption band, the corresponding frequency and the calculated energy difference, Δm.

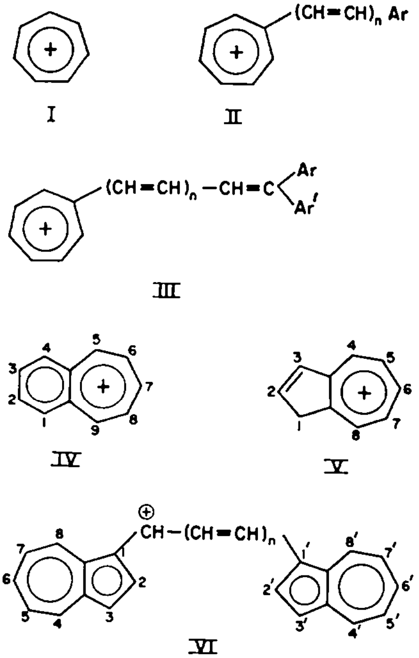

Fig. 1. Types of tropylium cations.

Table 2. Calculated $\pi \rightarrow \pi^*$ transition energies (Δm) for tropylium ions of group I

	No.	Formula (see Fig. 1.)	Ref.	λ_{max} (mμ)	$\bar{\nu}$ (cm^{-1})	Δm (β)
	1	I	16	275	36,400	1·6920
sub-group A	2	II, n = 0, Ar = Ph	12	369	27,100	1·2004
	3	II, n = 1, Ar = Ph	14	440	22,700	0·8887
	4	II, n = 2, Ar = Ph	15	493	20,300	0·6963
	5	II, n = 3, Ar = Ph	15	539	18,600	0·5707
	6	II, n = 4, Ar = Ph	15	582	17,200	0·4831
	7	III, n = 0, Ar = Ar′ = Ph	15	461	21,700	0·7766
	8	III, n = 1, Ar = Ar′ = Ph	15	515	19,400	0·6145
	9	III, n = 2, Ar = Ar′ = Ph	15	560	17,900	0·5106
	10	III, n = 3, Ar = Ar′ = Ph	15	597	16,800	0·4377
sub-group B	11	II, n = 0, Ar = 2-naphthyl	12	430	23,300	0·9464
	12	II, n = 1, Ar = 1-naphthyl	14	495	20,200	0·7400
	13	II, n = 1, Ar = 2-naphthyl	14	477	21,000	0·8018
	14	II, n = 1, Ar = 9-phenanthryl	14	500	20,000	0·7336
	15	II, n = 1, Ar = 9-anthryl	14	586	17,100	0·5514
	16	II, n = 1, Ar = 3-pyrenyl	14	581	17,200	0·6117
	17	II, n = 0, Ar = 4-biphenylyl	12	415	24,100	1·0042
	18	II, n = 0, Ar = 3-biphenylyl	12	363	27,600	1·0560
sub-group C	19	IV	7	426	23,500	1·0281
	20	3,4-benzo-IV	7	458	21,800	0·9803
	21	2,3-benzo-IV	7	608	16,500	0·6717
	22	5,6-benzo-IV	7	457	21,900	0·9285
	23	6,7-benzo-IV	7	540	18,500	0·8237
	24	6,7,8,9-dibenzo-IV	7	560	17,900	0·8049
sub-group D	25	II, n = 1, Ar = tropylidenemethyl	9	604	16,600	0·6022
	26	II, n = 1, Ar = 1-azulenyl	9	632	15,800	0·7118
	27	VI, n = 0	8	617	16,200	0·7376
	28	VI, n = 0, H = 1-azulenyl	8	634	15,800	0·7620

METHOD OF CALCULATION

The symbols are those of our previous paper. The first transition energies, Δm, were computed directly from the unpartitioned secular determinants of the molecules on the University of London "Atlas" computer. The simple inductive model for alkyl-substituted cations was again employed. The parameters

$$\alpha_{\text{C-alkyl}} = \alpha_{\text{C}} - 0{\cdot}3\beta_{\text{CC}}$$

$$\alpha_{\text{OMe}} = \alpha_{\text{C}} + 0{\cdot}9\beta_{\text{CC}}$$

$$\beta_{\text{CO}} = 0{\cdot}8\beta_{\text{CC}}$$

which gave the best fit for the pyrylium salts were also used in this study. It was found that the standard deviation from the best correlation line for the 72 molecules in Groups I and II was not very sensitive to a variation of h_{alkyl} from $-0{\cdot}1$ to $-0{\cdot}9$, and that the parameter $-0{\cdot}3$ was in the optimum region. Similar remarks apply to the

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[16] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* 76, 3203 (1954).

TABLE 3. CALCULATED $\pi \rightarrow \pi^*$ TRANSITION ENERGIES (Δm) FOR TROPYLIUM IONS OF GROUP II

	No.	Formula (see Fig. 1.)	Ref.	λ_{max} (mμ)	$\tilde{\nu}$ (cm^{-1})	Δm (β)
sub-group A	29	Me-I	17	288	34,700	1·6089
	30	V	2	352	28,500	1·0894
	31	3-Me-V	2	366	27,300	1·0041
	32	2-Me-V	2	370	27,000	1·0727
	33	6-Me-V	2	353	28,300	1·0895
	34	2,3-Me$_2$-V	2	382	26,200	0·9698
	35	4,8-Me$_2$-V	2	355	28,200	1·1137
	36	4,8-Me$_2$-6-Pr^i-V	2	354	28,300	1·1046
	37	4,8-Me$_2$-2-Pr^i-V	2	374	26,700	1·0939
	38	3,8-Me$_2$-V	2	362	27,600	1·0567
	39	3,8-Me$_2$-5-Pr^i-V	2	358	27,900	1·0886
	40	1-Me$_2$C: -V	8	432	23,200	1·0473
	41	1-Me$_2$C: -3-Pr^i-V	8	450	22,200	0·9516
	42	1-MeCH: -4,6,8-Me$_3$-V	11	440	22,700	1·0054
	43	1-MeCH: -3,8-Me$_2$-5-Pr^i-V	11	425	23,500	0·9660
	44	6-Me-IV	6	432	23,200	0·9936
	45	6,8-Me$_2$-IV	6	435	23,000	0·9656
	46	2,3-benzo-V	4	389	25,700	1·1559
	47	5,6-benzo-V	4	392	25,500	0·9365
	48	II, n = 0, Ar = 3-tolyl	12	376	26,600	1·1827
	49	II, n = 0, Ar = 4-tolyl	12	393	25,500	1·1607
	50	II, n = 1, Ar = 2-tolyl	13	453	22,100	0·8798
	51	II, n = 1, Ar = 3-tolyl	13	448	22,300	0·8853
	52	II, n = 1, Ar = 4-tolyl	13	461	21,700	0·8720
	53	II, n = 1, Ar = 2,4-xylyl	13	473	21,100	0·8656
	54	II, n = 1, Ar = 2,5-xylyl	13	460	21,700	0·8700
	55	II, n = 1, Ar = 3,4-xylyl	13	470	21,300	0·8638
	56	II, n = 1, Ar = mesityl	13	463	21,600	0·8662
	57	II, n = 2, Ar = 4-tolyl	15	513	19,500	0·6881
	58	1-PhCH: -4,6,8-Me$_3$-V	8	435	23,000	0·7781
	59	1-PhCH: -3,8-Me$_2$-5-Pr^i-V	11	456	21,900	0·7337
	60	1-PhCH:CH·CH: -4,6,8-Me$_3$-V	8	485	20,600	0·6562
	61	1-PhCH:CH·CH: -3,8-Me$_2$-5-Pr^i-V	11	513	19,500	0·6106
sub-group B	62	3-Me-VI, n = 0	10	634	15,800	0·6938
	63	3,3′-Me$_2$-VI, n = 0	10	652	15,300	0·6598
	64	4,6,8-Me$_3$-VI, n = 0	10	627	16,000	0·7337
	65	3′,4,6,8-Me$_4$-VI, n = 0	10	644	15,500	0·6275
	66	4,4′,6,6′,8,8′-Me$_6$-VI, n = 0	10	640	15,600	0·7313
	67	3,8-Me$_2$-5-Pr^i-VI, n = 0	10	644	15,500	0·6937
	68	3,3′,8-Me$_3$-5-Pr^i-VI, n = 0	10	663	15,100	0·6619
	69	3,4′,6′,8,8′-Me$_5$-5-Pr^i-VI, n = 0	10	653	15,300	0·6958
	70	3,3′,8,8′-Me$_4$-5,5′-Pr$_2^i$-VI, n = 0	10	680	14,700	0·6684
	71	3,3′,8-Me$_3$-5-Pr^i-VI, n = 2	11	842	11,900	0·4770
	72	3,3′,8,8′-Me$_4$-5,5′-Pr$_2^i$-VI, n = 2	11	860	11,600	0·4751

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[17] H. J. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Amer. Chem. Soc.* **79**, 4557 (1957).

TABLE 4. CALCULATED $\pi \rightarrow \pi^*$ TRANSITION ENERGIES (Δm) FOR TROPYLIUM IONS OF GROUP III

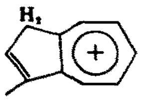
No.	Formula (see Fig. 1.)	Ref.	λ_{max} (mμ)	$\bar{\nu}$ (cm^{-1})	Δm (β)
73	MeO-I	17	315	31,800	1·1603
74	II, n = 0, Ar = 4-methoxyphenyl	12	435	23,000	0·9210
75	II, n = 0, Ar = 3-methoxyphenyl	12	356	28,100	0·9004
76	II, n = 1, Ar = 2-methoxyphenyl	13	481	20,800	0·7625
77	II, n = 1, Ar = 3-methoxyphenyl	13	448	22,300	0·8055
78	II, n = 1, Ar = 4-methoxyphenyl	13	503	19,900	0·7552
79	II, n = 1, Ar = 2,4-dimethoxyphenyl	13	539	18,600	0·7298
80	II, n = 1, Ar = 2,5-dimethoxyphenyl	13	519	19,300	0·6346
81	II, n = 1, Ar = 2,6-dimethoxyphenyl	13	501	20,000	0·7756
82	II, n = 1, Ar = 3,4-dimethoxyphenyl	13	524	19,100	0·6442
83	II, n = 1, Ar = 2,3,4-trimethoxyphenyl	13	513	19,500	0·6273
84	II, n = 1, Ar = 2,4,5-trimethoxyphenyl	13	587	17,000	0·5903
85	II, n = 1, Ar = 2,4,6-trimethoxyphenyl	13	557	18,000	0·7395
86	II, n = 1, Ar = 3,4,5-trimethoxyphenyl	13	495	20,200	0·5910
87	II, n = 1, Ar = 4-methoxy-1-naphthyl	14	568	17,600	0·6461
88	II, n = 1, Ar = 2-methoxy-1-naphthyl	14	552	18,100	0·6728
89	II, n = 2, Ar = 4-methoxyphenyl	15	550	18,200	0·6260
90	III, n = 1, Ar = Ph, Ar′ = 4-methoxyphenyl	15	557	18,000	0·5740
91	III, n = 1, Ar = Ar′ = 4-methoxyphenyl	15	587	17,000	0·5653
92	6-MeO-IV	5	450	22,200	0·8004
93	1,2,3,8-(MeO)$_4$-IV	3	491	20,400	0·5855

TABLE 5. CALCULATED $\pi \rightarrow \pi^*$ TRANSITION ENERGIES FOR TROPYLIUM IONS OF GROUP IV

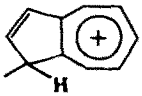
No.	Formula (see Fig. 1.)	Ref.	λ_{max} (mμ)	$\bar{\nu}$ (cm^{-1})	Δm (β)
94	II, n = 1, Ar = 4-methoxy-2-methylphenyl	13	508	19,800	0·7613
95	II, n = 1, Ar = 4-methoxy-3-methylphenyl	13	514	19,500	0·7323
96	II, n = 1, Ar = 2-methoxy-5-methylphenyl	13	498	20,100	0·7326

value 0·9 for h_{OMe}. We made no detailed study of the effect of varying the bond integral parameter, k_{OMe}; but a series of computations showed that the correlation between the cations of Groups I and III could not be significantly improved by altering this parameter from the original value of 0·8.

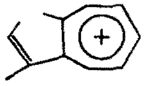
The models of the unsubstituted cations (Group I) are straightforward and require no comment except to emphasis that co-planarity of the molecule is assumed. For the alkyl salts of Group II, which include many protonated azulenes, the more highly conjugated model of two possible tautomers was chosen[8] except where such a form would be precluded by steric considerations. For example, 1-methylazulene in acid solution (31) is formulated as A rather than B because in A the methyl group is attached to the double bond. The model for the 1-methylazulenium ion is thus C.



A

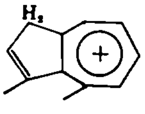


B

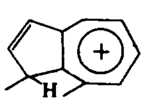


C

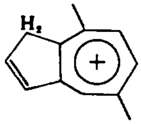
On the other hand, the more highly conjugated of the two cations derived from 1,8-dimethylazulene, D, may not be favoured over the tautomeric form E because in the latter the steric clash between the two methyl groups is relieved by bending one of them out of the molecular plane. Similar considerations apply to the 4,5-benzazulenium ion.[4] Such ambiguous cases, as well as those in which the position of protonation cannot be readily predicted by considering the extent of conjugation, e.g. in the 4,7-dimethylazulenium ion (F or G), are not included in the calculations.



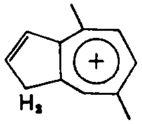
D



E

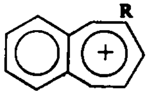


F



G

As before, we make no distinction between the various alkyl groups. This is justified by the constancy of the position of the long wave absorption band of the cations **44** and **45** at 432 and 434 mμ, respectively, as R varies from methyl through ethyl to propyl.[6]



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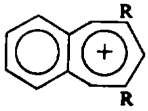

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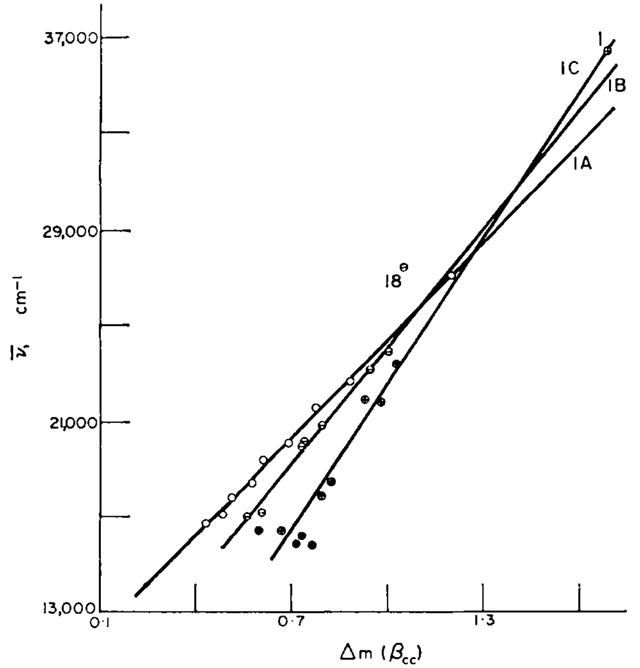

FIG. 2. Regression line of compounds of Group I.

- ○ Phenyltropylium salts (Group IA)
- ⊖ Aryl tropylium salts (Group IB)
- ⊕ Annelated tropylium salts (Group IC)
- ● Cyanine tropylium salts (Group ID)

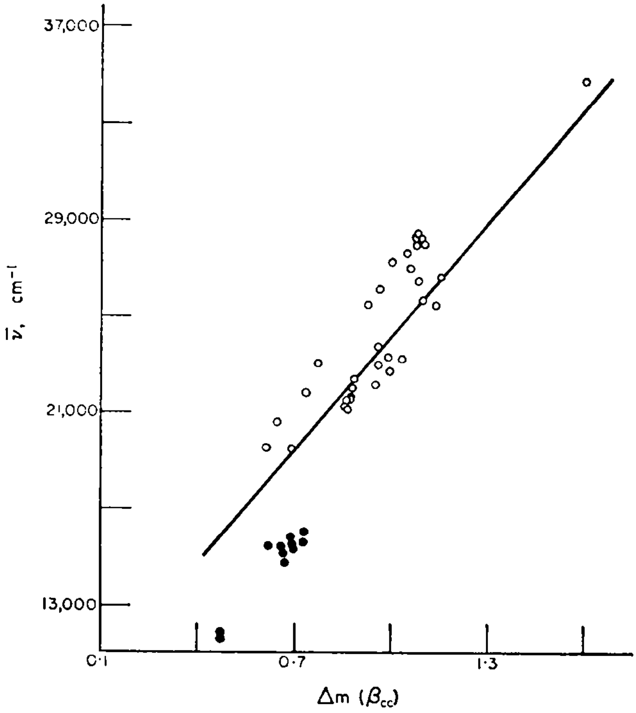

FIG. 3. Regression line for alkyltropylium salts.
● Cyanine tropylium salts.

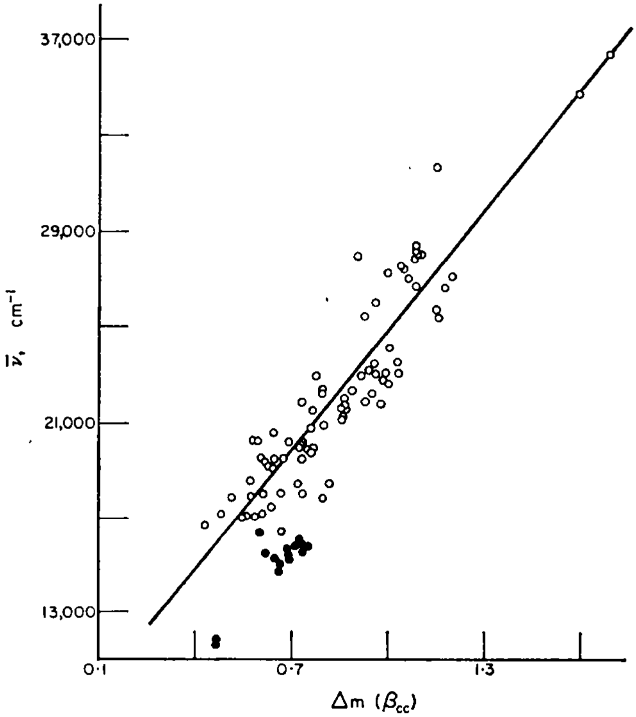

FIG. 4. Final regression line.
● Cyanine tropylium salts.

RESULTS AND DISCUSSION

The calculated energy differences, Δm, are given in Tables 2–5. Equations of regression lines and standard deviations, σ, for the various groups are collected in Table 6.

We first consider the twenty-eight unsubstituted salts in Group I. Fig. 2 shows that the correlation between the observed frequency, $\tilde{\nu}$, and Δm is not very impressive. It is, however, possible to subdivide the cations in this group into four sub-groups within which there are stronger structural similarities. These are: A, the phenyltropylium salts (structural types II and III, Ar = Ar′ = Ph, Fig. 1); B, aryltropylium salts (II, Ar $\neq$ Ph); and C, the annelated tropylium salts (IV). The correlations within these groups are excellent and the mean deviation from the best line never exceeds 630 cm^{-1} in an observed frequency range of 20,000 cm^{-1}. The assignment of the tropylium ion itself to one of these groups is difficult but on structural grounds it seems to belong to sub-group C, because there are no bonds in these molecules about which rotation can occur. A correlation for cations of sub-group IC has already been established by Heilbronner *et al.*[7] It is possible to continue the process of subdivision within the sub-groups so that only structurally very closely related compounds are considered to belong together. For example, the salts of sub-group IA may be divided into α-tropylium-ω-phenylpolyenes (**2–6**) and α-tropylium-ω,ω-diphenylpolyenes (**7–10**). If this is done the correlation within these smaller groups becomes really outstanding, σ being 125 cm^{-1} for the first group, and 30 cm^{-1} for the second. Even without this further subdivision, the mean deviation for sub-group 1A is only 180 cm^{-1}. Similarly, if in sub-group IB only cations containing a naphthalene, anthracene or phenanthrene residue are considered (**11–15**) the standard deviation is reduced to 100 cm^{-1}. Only one cation, *m*-biphenylyltropylium (**18**) does not fit the regression line for IB.

The four cyanine-like tropylium ions (**25–28**) are entirely different from the other ions of Group I and do not fit any of the three regression lines for this group.

The alkyltropylium salts of Group II (Fig. 3) exhibit a spread similar to that of the unsubstituted salts. The regression line for these cations is virtually identical with that for Group I, thus the simple inductive model for alkyl substituents is suitable for this type of calculation. Again, it was not found possible to correlate the properties of the eleven cyanine cations (**62–72**) with the other cations of their group.

The results for the twenty-one methoxy compounds of Group III, which are included in the final correlation graph (Fig. 4), are not as good as those previously considered. This group comprises cations in which the substituent is directly attached to the tropylium ring or to a substituent phenyl group, as well as salts with up to four methoxy substituents. The regression line for this group is much steeper than that for the previous groups and the slope could not be improved significantly to fit that of the other compounds by altering the value of the methoxy Coulomb and bond integrals.

Little comment can be made on Group IV (alkyl and methoxy substituents) as the spectra of only three such salts have been reported. The three points fit the final regression line rather well.

The final correlation is shown in Fig. 4. For all ninety-six cations the standard deviation is 1,970 cm^{-1} in the observed frequency range of 22,000 cm^{-1}, i.e. almost 10 %. If the fifteen cyanine salts are excluded the standard deviation for eighty-one

TABLE 6. REGRESSION LINES ($\bar{\nu} = a_1\Delta m + a_0$) AND STANDARD DEVIATIONS (σ)

Group or sub-group	Number of salts	Regression line a_1	a_0	σ (cm^{-1})
I	28	16,000	7,700	1,900
IA + IB + IC + **1**	24	15,400	8,600	1,500
IA	9	13,600	10,800	180
2–6	5	13,600	10,700	125
7–10	4	14,400	10,500	30
IB (excluding **18**)	7	16,300	7,800	340
11–15	5	15,600	8,500	100
IC + **1**	7	20,000	2,500	630
IIA	33	15,900	8,900	1,580
III	21	22,000	4,600	1,750
All	96	19,000	5,500	1,970
All (excluding ID and IIB)	81	16,600	8,200	1,630

cations is 1,630 cm^{-1}, 8 % of the frequency range. The regression line for this case is

$$\bar{\nu} = 16{,}600\ \Delta m + 8{,}200$$

giving $\beta = -47{\cdot}3$ kcal/mol^{-1}, and is in fair agreement with that obtained by Streitwieser[18] for seventeen hydrocarbon anions and cations,

$$\bar{\nu} = 16{,}000\ \Delta m + 7{,}200$$

We conclude that the simple Hückel method is moderately successful when applied to such a great variety of structural types as are encountered here. The results obtained for the cations of Group I show that the method can become extremely reliable within more restricted series of closely related molecules.

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[18] A. Streitwieser Jr., *Molecular Orbital Theory for Organic Chemists* p. 229, J. Wiley, New York (1961).