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AN HMO CORRELATION OF THE FIRST BANDS IN THE ELECTRONIC SPECTRA OF CONJUGATED HYDROCARBON IONS

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Abstract—Ninety-eight alternant and non-alternant hydrocarbon ions of structural types shown in Chart I (with delocalized charge) have been treated by the HMO method. Calculated $E(N \rightarrow V_1)$ energies were correlated with energies of the first bands in the electronic spectra of the ions (Table 1). Regression line constants for ions of the individual structural types, their numbers and the correlation coefficients are given in Table 2. It has been found that points for ions containing an exocyclic carbon atom or a carbon chain in addition to one or more rings are located between the regression line for tropylium-like ions on the lower side and the assumed locations of points for odd polyenic ions which for uncharged hydrocarbon molecules, where points for α,ω-diphenylpolyenes form an S-shaped curve between the regression line for polyenes and that for benzenoid hydrocarbons. In the case of ions, however, additive constants of the regression lines are lower. Interpolation formula (1) and (2) are proposed for a semiquantitative estimate of the position of the first band in the spectra of as yet unsynthesized hydrocarbon ions with delocalized charge.

WITHIN the framework of a systematic examination of the applicability of the Hückel MO–LCAO method (HMO in the following) we have examined hydrocarbon ions with delocalized charge. First four tropylium-like ions and the fluorenyl cation[1] were studied and later a larger series of tropylium-like ions.[2] Additional work treated di- and triarylmethyl cations and some other ions,[3,4] anions of the cyclopentadienide series,[5] α,ω-diphenyl derivatives of odd polyenes (cations,[6,7] anions[6]), ω-fulvenylpolyenylcyclopentadienide anions,[8a] ω,ω-diphenylpolyenylcyclopentadienide anions,[8b] arylphenylmethyl cations[9] and cations of the cyclopentadienyl series.[10] Cations formed by protonation of benzenoid hydrocarbons and containing a methylene group besides

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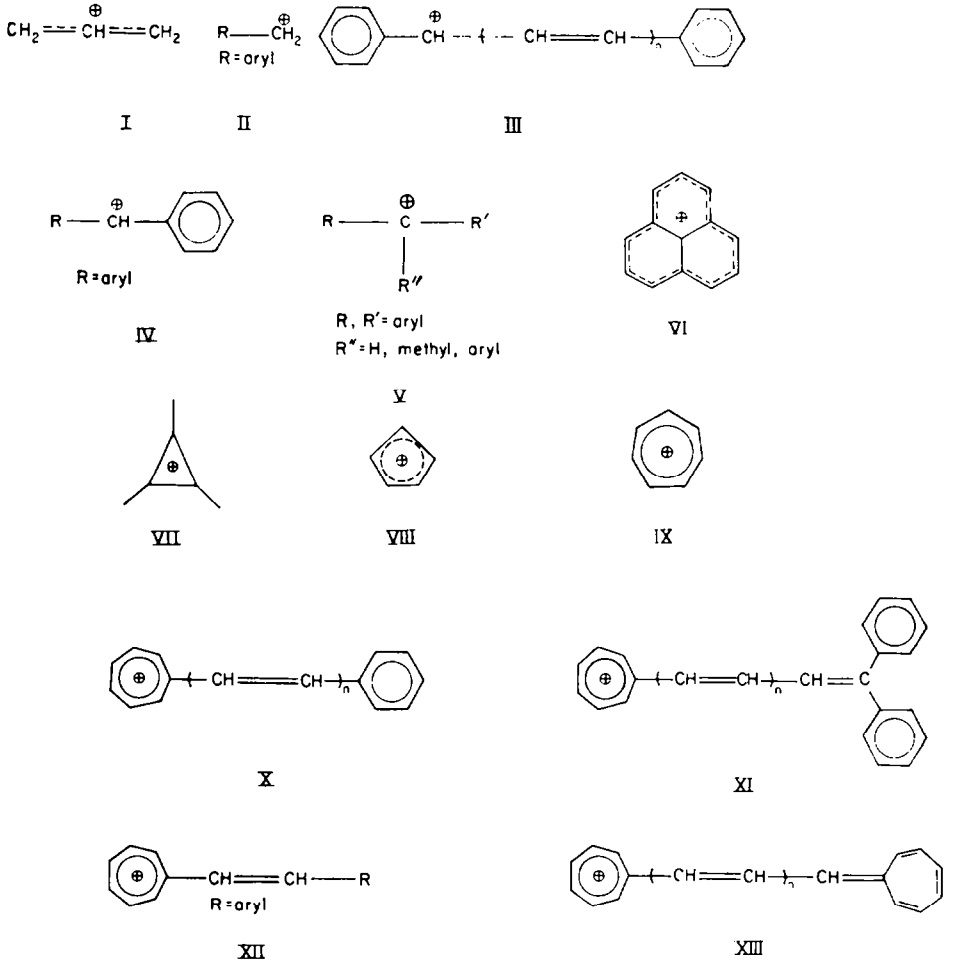
the conjugated skeleton were also studied.[11] Calculations by more sophisticated methods have been reported.[12–16]

IONS STUDIED

Both alternant and non-alternant ions were included. With the exception of cations of the fluorenyl series and the cycloheptatrienide anion, the non-alternant ions were "natural", i.e. all bonding molecular orbitals were occupied and all antibonding ones vacant. A schematic representation of the structural types involved is presented in Chart I. Among the larger groups, four contain ions composed exclusively of conjugated rings (VI, VIII, IX, XVIII), five contain ions with one exocyclic carbon atom (II, IV, V, XIV, XVI), and the remaining ones contain a polyene chain.

Chart I



I II III IV V VI VII VIII IX X XI XII XIII

[11] G. Dallinga, E. L. Mackor and A. A. Verrijn Stuart, *Mol. Phys.* **1**, 123 (1958).
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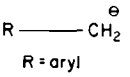
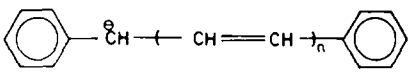
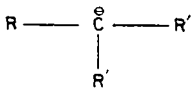


XIV

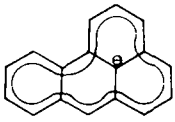


XV



R, R′ = aryl
R″ = H, methyl, aryl

XVI

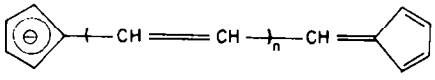


XVII

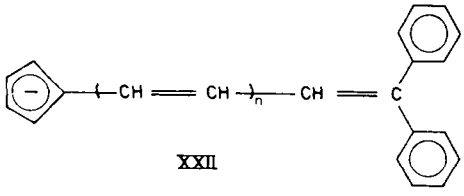
XVIII

XIX

XX



XXI



XXII

RESULTS AND DISCUSSION

Table 1 compiles experimental and theoretical data concerning the first (longest wavelength) intense bands in electronic spectra including information on experimental conditions and references to the experimental work. Calculated $E(N \rightarrow V_1)$ values were taken from references stated in the introduction, from Ref. 17 and some additional ones: III,[18] VI,[19] X–XII,[20] XIII,[21] XV.[18] A large number of the HMO $E(N \rightarrow V_1)$ values presently needed and many additional ones are summarized in Refs. 18 and 22. The

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TABLE 1. SPECTRAL DATA FOR CONJUGATED HYDROCARBON IONS

A. Cations

Type	No.	Cation	Synthesis[a]	Solvent[b]	$\tilde{\nu}$(kcm^{-1})[c]	log ε	Ref. (exp.)	E(N → V_1)(β)
			1. Alternant					
			Odd polyenes					
I	1	Allyl	a	A	~36·6	>3·67	24	1·414
			Arylmethyl cations					
II	2	Benzyl	a	A	~21·2	>3·48	32	1·000
	3	9-Anthrylmethyl	a	A	23·5	4·06	33	—
	4	2-Diphenylylmethyl	b	B	19·6	4·11	26	—
			Odd α,ω-diphenylpolyenes					
III	5	Diphenylmethyl	a	A, C	22·7	4·63	7	1·000
			c	D	23·8	—	34	
	6	1,3-Diphenylallyl	a	A, C	20·1	4·00	7	0·811
			c	D	20·6	—	34	
	7	1,5-Diphenylpentadienyl	a	A, C	17·9	4·13	7	0·662
			c	D	18·0	—	34	
	8	1,7-Diphenylheptatrienyl	a	A, C	16·4	4·20	7	0·554
			c	D	16·1	—	34	
	9	1,9-Diphenylnonatetraenyl	a	A, C	15·2	4·30	7	0·474
			c	D	14·5	—	34	
	10	1,11-Diphenylundecapentaenyl	a	A, C	14·0	4·46	7	0·413
	11	1,13-Diphenyltridecahexaenyl	a	A, C	13·2	4·52	7	0·366
			Arylphenylmethyl cations					
IV	5	Diphenylmethyl[d]	a	A	22·5	4·59	9	1·000
	12	1-Naphthylphenylmethyl	a	A	17·5	4·37	9	0·714
	13	2-Naphthylphenylmethyl	a	A	17·6	4·00	9	0·653
	14	9-Anthrylphenylmethyl	a	A	15·0	4·17	9	0·578
	15	1-Phenanthrylphenylmethyl	a	A	15·6	4·05	9	0·657
	16	3-Phenanthrylphenylmethyl	a	A	17·0	4·51	9	0·660
	17	1-Pyrenylphenylmethyl	a	A	15·6	4·43	9	0·552
	18	6-Chrysenylphenylmethyl	a	A	16·2	4·50	9	0·619
	19	4-Diphenylylphenylmethyl	a	A	18·9	4·66	9	0·772

			Di- and triarylmethyl cations					
V	20	Triphenylmethyl[e]	a	A	23·8	4·70	38	1·000
	21	4-Diphenylyldiphenylmethyl[f]	a	E	19·7	~4·55	46	0·751
	22	Bis-(4-diphenylyl)phenylmethyl[g]	a	E	18·4	4·85	46	0·705
	23	Tris-(4-diphenylyl)methyl[h]	a	E	18·4	5·05	46	0·705
	24	Tris-(3-diphenylyl)methyl	a	A	20·0	4·00	47	—
	25	Bis-(4-diphenylyl)methyl	a	A	18·0	4·85	47	—
	26	Diphenylmethylmethyl	a	A	23·4	~4·47	48	1·000
	27	Bis-(4-diphenylyl)methylmethyl	a	A	19·4	4·81	47	—
			Perinaphthylium cations					
VI	28	Perinaphthylium	c	I	18·5	2·56	49	1·000
	29	Tribenzo[a, e, i]perinaphthylium	c	J	16·8	4·36	50	0·674
	30	Naphtho[2,1,8-cde]perinaphthylium	c	A	15·7	3·73	51	0·662
			2. Non-alternant					
			Cyclopropenyl cations					
VII	31	Diphenylcyclopropenyl	a	L	32·6	4·49	53	—
	32	Triphenylcyclopropenyl	a	M	~30·8	3·6	54	—
			Cyclopentadienyl cations					
VIII	33	Fluorenyl[i]	a	A	15·9	—	10,55	0·524
	34	Benzo[a]fluorenyl	a	A	14·0	—	10,55	0·420
	35	Benzo[b]fluorenyl	a	A	15·6	—	10,55	0·519
	36	Benzo[c]fluorenyl	a	A	12·8	—	10,55	0·306
	37	Benzo[def]fluorenyl	a	A	13·4	—	10,55	0·640
			Tropylium cations					
IX	38	Tropylium	c	A	36·5	3·65	2	1·692
	39	Benzotropylium	c	I	23·5	3·25	2	1·028
	40	Dibenzo[a, c]tropylium	c	A	21·9	4·10	2	0·929
	41	Dibenzo[a, d]tropylium	c	A	18·5	3·50	2	0·824
	42	Naphtho[1,2]tropylium	c	I	21·9	3·50	2	0·980
	43	Naphtho[2,3]tropylium	c	N	16·5	3·05	2	0·672
	44	Tribenzotropylium	c	A	17·9	3·30	2	0·805

TABLE 1. (*Cont.*)

Type	No.	Cation	Synthesis[a]	Solvent[b]	$\tilde{\nu}$(kcm^{-1})[c]	log ε	Ref. (exp.)	E(N → V_1)(β)
			ω-Phenylpolyenyltropylium cations					
X	45	Phenyltropylium	c	O	26·0	—	56	1·200
				K	27·1	4·18	56	
	46	Styryltropylium	c	O	21·5	—	56	0·889
				K	22·7	4·53	56	
	47	4-Phenyl-1,3-butadienyltropylium	c	O	18·7	—	56	0·696
				K	20·3	4·69	56	
	48	6-Phenyl-1,3,5-hexatrienyltropylium	c	O	16·9	—	56	0·571
				K	18·6	4·76	56	
	49	8-Phenyl-1,3,5,7-octatetraenyltropylium	c	O	15·5	—	56	0·483
				K	17·2	4·84	56	
			ω,ω-Diphenylpolyenyltropylium cations					
XI	50	2,2-Diphenylvinyltropylium	c	O	20·6	—	56	0·777
				K	21·7	4·32	56	
	51	4,4-Diphenyl-1,3-butadienyltropylium	c	O	18·1	—	56	0·614
				K	19·4	4·64	56	
	52	6,6-Diphenyl-1,3,5-hexatrienyltropylium	c	O	16·2	—	56	0·511
				K	17·9	4·71	56	
	53	8,8-Diphenyl-1,3,5,7-octatetraenyltropylium	c	O	14·9	—	56	—
				K	16·8	4·81	56	
			β-Arylvinyltropylium cations					
XII	46	2-Phenylvinyltropylium (Styryltropylium)	c	D	21·5	—	57	0·889
				K	22·7	4·53	57	
	54	2-(1-Naphthyl)vinyltropylium	c	D	18·5	—	57	0·740
				K	20·2	4·38	57	
	55	2-(2-Naphthyl)vinyltropylium	c	D	19·3	—	57	0·802
				K	21·0	4·55	57	
	56	2-(9-Anthryl)vinyltropylium	c	D	14·9	—	57	0·551
				K	17·1	4·08	57	
	57	2-(9-Phenanthryl)vinyltropylium	c	D	18·0	—	57	0·734
				K	20·0	4·40	57	

	58	2-(1-Pyrenyl)vinyltropylium	c	D	15·0	—	57	0·612
				K	17·2	4·53	57	
			ω-Heptafulvenylpolyenyltropylium cations					
XIII	59	Di-(Heptafulven-8-yl)methyl	c	K	16·6	4·1	58	0·602
			B. Anions					
			1. Alternant					
			Arylmethyl anions					
XIV	60	Benzyl (Na)	a	P	28·2	4·08	59	1·000
		(Li)	a	P	30·3	—	60,61	
	61	1-Naphthylmethyl (K)	a	Q	17·9	2·9	62	0·714
			Odd α,ω-diphenylpolyenes					
XV	62	Diphenylmethyl (Na)	a	R	19·9	—	63	1·000
	63	1,3-Diphenylallyl (Na)	a	R	18·7	—	63	0·811
	64	1,5-Diphenylpentadienyl (Na)	a	R	17·6	—	63	0·662
	65	1,7-Diphenylheptatrienyl (Na)	a	R	16·7	—	63	0·554
	66	1,9-Diphenylnonatetraenyl (Na)	a	R	15·8	—	63	0·474
			Di- and triarylmethyl anions					
XVI	62	Diphenylmethyl (K)	a	Q	22·7	4·6	62	1·000
		(K)	a	R	23·0	4·34	64	
	67	Diphenylmethyl-(n-pentyl)(Li)	a	S	23·5	3·72	48	1·000
	68	Diphenylmethyl (K)	a	Q	20·8	4·3	62	1·000
	69	Triphenylmethyl (K)	a	Q	20·2	4·4	62	1·000
		(Na)[b]	a	R	20·8	3·76	45	
		(Li)	a	T	20·5	—	5	
	70	Bis-(4-diphenylyl)methyl (K)	a	R	18·4	5·19	47	—
	71	Tris-(4-diphenylyl)methyl (K)	a	R	17·3	4·86	47	0·705
		(Li)	a	T	16·5	—	5	
	72	Tris-(3-diphenylyl)methyl (K)	a	R	20·6	4·66	47	—
	73	Bis-(4-diphenylyl)methylmethyl (K)	a	R	17·0	5·16	47	—
			Benzanthrenide anions					
XVII	74	Benzanthrenide (Li)	a	T	15·6	3·83	5	0·718

TABLE 1. (*Cont.*)

Type	No.	Anion	Synthesis[a]	Solvent[b]	$\tilde{\nu}$(kcm^{-1})[c]	log ε	Ref. (exp.)	E(N → V_1)(β)
		2. Non-alternant Cyclopentadienide anions						
XVIII	75	Fluorenide (Cs)	a	T	19·8	2·8	5	0·993
		(K)	a	Q	20·8	2·9	62	
		(Li)	a	T	19·6	2·9	5	
	76	Benzo[a]fluorenide (Li)	a	T	20–22·2	—	5	0·940
	77	Benzo[b]fluorenide (Li)	a	T	15·4	3·11	5	0·681
	78	Benzo[c]fluorenide (Cs)	a	T	19·7	3·29	5	0·886
		(Li)	a	T	19·3	3·31	5	
	79	Benzo[def]fluorenide (Li)	a	T	19·8	3·87	5	0·734
	80	Indeno[1,2,3-jk]fluorenide (Fluoradenide)	a	T	17·8	3·67	5	0·940
XIX	81	Cycloheptatrienide (K)	a	P	~13·3	—	65	0·357
XX	82	Cyclononatetraenide (Li)	a	P	30·8	3·9	66	1·347
		(NMe_4)	a	K	31·0	3·83	67,68	
		ω-Fulvenylpolyenylcyclopentadienide anions[69]						
XXI	83	(Fulven-6-yl)cyclopentadienyl	a	—	20·9	—	70,71	0·975
	84	Di(fulvenyl-6-yl)methyl	a	—	17·7	—	70,71	0·758
	85	1,3-Di(fulven-6-yl)allyl	a	—	15·0	—	70,71	0·619
	86	1-(Benzo[a]fulven-8-yl)indenyl	a	—	17·7	—	70,71	0·744
	87	Di-(benzo[a]fulven-8-yl)methyl	a	—	16·0	—	70,71	0·595
	88	1,3-Di(benzo[a]fulven-8-yl)allyl	a	—	13·9	—	70,71	0·499
	89	9-(Dibenzo[a, c]fulven-10-yl)-fluorenyl	a	—	17·8	—	70,71	0·727
	90	Bis-(dibenzo[a, c]fulven-10-yl)methyl	a	—	15·8	—	70,71	0·583
	91	1,3-Bis(dibenzo[a, c]fulven-10-yl)allyl	a	—	14·2	—	70,71	0·487
	92	11-(Naphtho[2,3-a]benzo[c]fulven-12-yl)benzo[b]fluorenyl	a	—	16·9	—	72	0·668
	93	Bis-(naphtho[2,3-a]benzo[c]fulven-12-yl)methyl	a	—	15·0	—	72	0·557
	94	11-(Naphtho[2,1-a]benzo[c]fulven-12 yl)benzo[c]fluorenyl	a	—	16·8	—	72	0·658

TABLE 1. (*Cont.*)

Type	No.	Anion	Synthesis[a]	Solvent[b]	(kcm^{-1})[c]	log ε	Ref. (exp.)	E(N → V_1)(β)
	95	Bis-(naphtho[2,1-a]benzo[c]fulven-12-yl)methyl	a	—	15·0	—	72	0·549
	96	11-(Naphtho[2,1-a]benzo[c]fulven-12-yl)fluorenyl	a	—	15·4	—	72	0·563
		α,ω-Diphenylpolyenylcyclopentadienide anions						
XXII	97	9-(2,2-Diphenylvinyl)fluorenide	a	U	18·3	—	73	0·721
	98	9-(4,4-Diphenyl-1,3-butadienyl)-fluorenide	a	U	17·4	—	73	0·577

[a] a: By dissociation of OH^- or X^- (X = halogen) or H^+ from the corresponding pseudobase or pseudoacid, resp; b: by protonation of a benzenoid hydrocarbon in HF; c: an isolated salt.

[b] Solvent: A conc. H_2SO_4; B HF + BF_3; C $HClO_4$; D CH_2Cl_2; E H_2SO_4 (20%)—CH_3COOH (80%); F H_2SO_4 (10%)—CH_3COOH (90%); G H_3PO_4 (90%); H liquid SO_2; I H_2SO_4 (60%); J hydrochloric acid (17%); K CH_3CN; L a buffer solution in aqueous ethanol (23%); M H_2SO_4 (10%)—CH_3COOH (4%)—H_2O; N H_2SO_4 (70%); O $CHCl_3$; P tetrahydrofuran; Q liquid NH_3; R ether; S C_6H_6; T cyclohexylamine; U dimethylformamide.

[c] The first intense band.

[d] Additional reported values[7,23,35–41] in A (or E) lie between 22·6 and 23·4 kcm^{-1}. The isolated[42] hexachloroantimonate in D has $\bar{\nu}_{max}$ at 22·2 kcm^{-1}.

[e] Additional reported values of $\bar{\nu}_{max}$: 23·1 (E),[40] 24·0 (A),[43] 22·7 (G),[44] 22·8 (H).[45]

[f] Additional reported values of $\bar{\nu}_{max}$: 19·8 (F),[43] 22·0 (G)[44].

[g] Additional reported values of $\bar{\nu}_{max}$: 18·6 (F),[43] 18·7 (G)[44].

[h] Additional reported values of $\bar{\nu}_{max}$: 18·6 (F),[43] 18·7 (G),[44] 19·6 (A).[47]

[i] $\bar{\nu}_{max}$ 16·1 (K).[52]

[j] Additional reported values of $\bar{\nu}_{max}$: 15·1–15·3 kcm^{-1} (A).[22,25,26]

[k] $\bar{\nu}_{max}$ 21·1 (R).[64]

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assignment of the first intense bands in absorption curves was straightforward in most cases: the bands are well developed and are only very rarely preceded by weak bands. The assignment is uncertain in anions of the cyclopentadienide type.[5] Problems connected with assignment of the corresponding cations are discussed elsewhere.[10,16] Experimental excitation energies (Table 1) were plotted against the $E(N \rightarrow V_1)$ energies for the individual classes of ions (I–XXI) provided the number of ions in the group was not too small. In each case with the single exception of anions XVIII a close linear relationship was found. Constants of the regression lines are given in Table 2. Figure 1 shows the regression lines (the experimental points were omitted for clarity) and also points for ions which do not belong to one of the large groups.

TABLE 2. REGRESSION LINE CONSTANTS a AND b ($\tilde{\nu}_{exp}(kcm^{-1}) = a\ E(N \rightarrow V_1)(\beta) + b$), CORRELATION COEFFICIENTS r AND NUMBER OF COMPOUNDS n

No.[a]	a	b	r[b]	n
III	14·88	7·98	0·999	7
IV	16·46	6·02	0·975	9
VIII	13·95	8·60	—	4[c]
IX	19·90	2·83	0·996	7
X	14·58	8·53	0·999	5
XI	14·41	8·85	0·996	(3)8[d]
XII	20·47	3·11	0·987	6
XV	7·66	12·37	0·995	5
XVIII	11·48	9·28	0·720[e]	5
XXI	14·21	7·15	0·981	14

[a] See Chart I.

[b] Correlation on a 1% significance level.

[c] The value for benzo[def]fluorenylium cation not included.

[d] Data are available for three compounds of type XI; the values a, b and r refer to combined groups X and XI.

[e] The correlation is not significant; the value for fluoradenide not included.

We expected a similar situation to that found with benzenoid hydrocarbons and polyenes,[23] i.e. the points for ions without exocyclic atoms would lie approximately on one straight line while points for polyenic ions would lie on one another, situated above the former in Fig. 1, and that points for ions of the α,ω-diphenylpolyenyl type would form some kind of an S-shaped curve representing a transition between the two extremes similar to the points for even α,ω-diphenylpolyenes.[23] It has been reported previously[12] that ionic charge brings about a decrease of additive constants of regression lines as compared to otherwise analogous but uncharged molecules and that points for allyl cation and the pentadienyl cation (represented by a protonated polymethylbenzene) lie in the vicinity of the regression line for uncharged benzenoid hydrocarbons while points for carbonium ions containing a benzene ring are located near the regression line for tropylium-like ions. Our results confirm this and show

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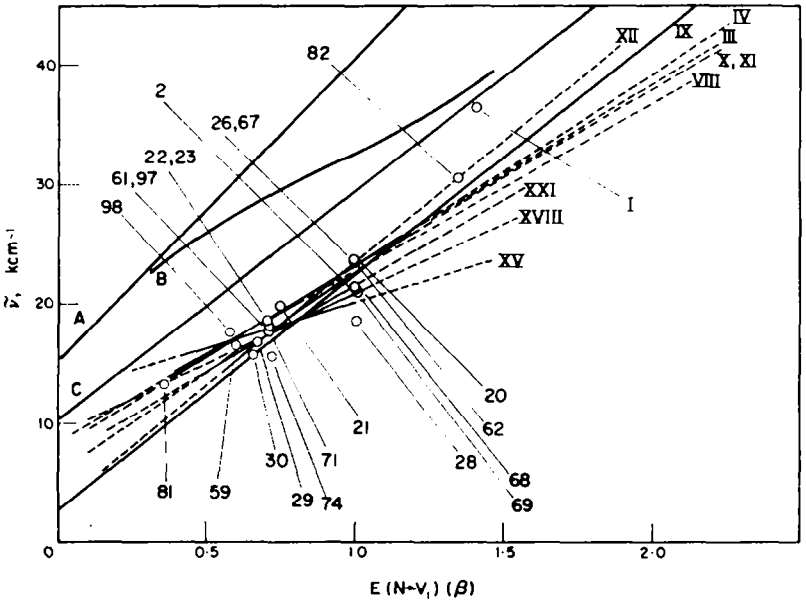


FIG. 1. Plot of wavenumbers of the maxima of the first bands $\tilde{\nu}$ against calculated E(N→V$_1$) energies. For series of ions included in Table 2, only regression lines without the individual experimental points are shown, labelled as in Chart I. Points for other ions are shown individually, labelled as in Table 1. The regression lines are drawn in full only in sections corresponding to available experimental points (with the exception of the straight line IX for tropylium-like ions). Schematic plots for even polyenes (A), even α,ω-diphenylpolyenes (B), and benzenoid hydrocarbons (C) are shown for comparison.

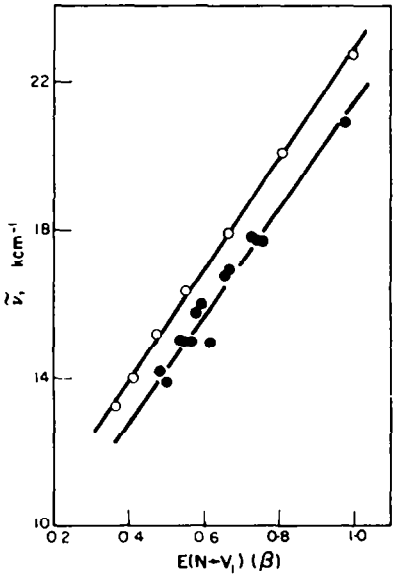


FIG. 2. Plot of wavenumbers of the maxima of the first bands in the spectra of ions III (○) and XXI (●) against calculated E(N → V$_1$) energies.

that the trend is quite general. Although there is no clear-out case of an S-shaped series of points for any of the vinylogous series studied, some of the expected deviations from the straight line may be observed, e.g. in the case of odd α,ω-diphenylpolynic ions (ions III, Fig. 2).

Almost all experimental points lie in a region delimited by the regression line for benzenoid hydrocarbons (points for odd polyenic ions are in this vicinity) and that for tropylium-like ions (Fig. 1). As the $E(N \rightarrow V_1)$ values decrease, the regression lines for systems containing a polyenic chain approach the assumed region for odd polyenic ions, i.e. get close to the regression line for benzenoid hydrocarbons [the $E(N \rightarrow V_1)$ values are between 0·7 and 1·0 β].

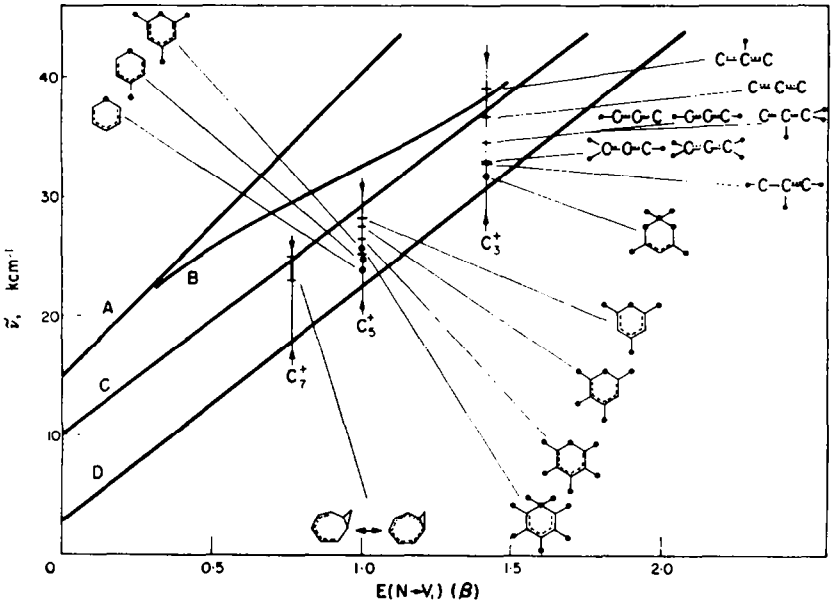
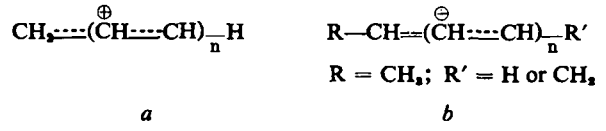


FIG. 3. Plot of wavenumbers of maxima of the first bands in the spectra of methyl and methylene substituted derivatives of the allyl and pentadienyl cations against calculated $E(N \rightarrow V_1)$ energies. The experimental values are plotted against values calculated for allyl (C_3^+), pentadienyl (C_5^+) and heptatrienyl (C_7^+). Experimental data: C_3^+ according to Ref. 24 (—) and Ref. 25 (●); C_5^+ according to Refs. 11, 24 (—) and Ref. 26 (●); C_7^+ according to Ref. 28. Schematical plots for even polyenes (A), even α,ω-diphenylpolyenes (B), benzenoid hydrocarbons (C) and tropylium-like ions (D) are shown for comparison.

Since simple odd polyenyl cations have not yet been prepared with the possible exception of the allyl cation,[24] an examination has to be limited to their methylene and methyl substituted derivatives. Experimental work on methyl substituted allyl[24,25] and pentadienyl[11,26,27] cations has been published recently. Another recently synthesized ion[28] has a π-electronic structure similar to that of the heptatrienyl cation although it is not planar as a whole (cf. Fig. 3). Excitation energies of the maxima of the first bands of these ions are plotted against the calculated $N \rightarrow V_1$ energies of the allyl,[29] pentadienyl, and heptatrienyl cations neglecting the presence of the substituents (Fig. 3). Although the result is not unequivocal, it seems at present probable that points for odd polyenyl cations will be situated above points for other ions with delocalized charge

in the $\tilde{\nu}$(exp)–E(N→V_1) plot (Fig. 3). A synthesis of ions of type *a* or at least *b* still remains a highly topical task.



a *b*

The following comment may be made on the difference which exists between polyenic and cyclic compounds, both hydrocarbons and hydrocarbon ions, when treated by the HMO method. In uncharged hydrocarbons, it seems to be due both to the neglect of electron repulsion terms whose contribution to the total excitation energy is not the same in the two classes of compounds[23] and to the neglect of bond strength alternation which is much more serious in even polyenes than in the cyclic compounds[31] while only the former effect is important in ions.

One final remark seems appropriate: although the ninety-eight ions studied do not represent a structurally homogeneous set they may, surprisingly enough, be statistically treated as a whole. This might be useful for semiquantitative predictions of the energy of the first band in the spectra of as yet unknown ions. A treatment including eighty two ions yielded the empirical formula (1) and a treatment including only ions of the α,ω-diarylpolyenyl type (including also ions containing a polyenic chain with odd-numbered rings at each or one end) resulted in formula (2):

$$\tilde{\nu}(\text{kcm}^{-1}) = 16{\cdot}60\ \text{E(N}\rightarrow V_1)(\beta) + 6{\cdot}17;\ r = 0{\cdot}940;\ n = 82 \quad (1)$$

$$\tilde{\nu}(\text{kcm}^{-1}) = 14{\cdot}18\ \text{E(N}\rightarrow V_1)(\beta) + 7{\cdot}91;\ r = 0{\cdot}944;\ n = 41 \quad (2)$$

Equations (1) and (2) may be used as interpolation formulas for E(N→V_1) varying between approximately 0·5 and 1·2 β. The error in the predicted wavenumber is unlikely to exceed $\pm 1{\cdot}5$ kcm^{-1} and $\pm 1{\cdot}0$ kcm^{-1} in the case of Eq. (1) and (2), respectively.

In the case of new ions which unequivocally belong into one of the foregoing classes, a much better prediction is usually possible using regression coefficients of Table 2.

Note added in proof: In a recently published paper by I. Hanazaki and S. Nagakura, *Tetrahedron* **21**, 2441 (1965), the benzyl and α-methylbenzyl cations were found to be unstable even at low temperature and their absorption spectra could not be observed. It is, therefore, very doubtful whether the band of the "benzyl cation" was observed by Grace and Symons[32] in strong acid at room temperature although it may be attributable to some unstable species.

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