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INFRARED SPECTRA OF THIOPYRYLIUM AND PYRYLIUM CATIONS

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Abstract—Normal coordinate analysis has been carried out for the in-plane and out-of-plane vibrations of thiopyrylium (1) and pyrylium (2) cations which are isoelectronic with benzene, in order to investigate the structural characteristics (the contribution of the carbonium ion structures and the Kekulé structures to their resonance hybrid). Several sets of parameters for the double bond stretching constants have been chosen considering the delocalization of the positive charge. As a result, much more delocalization of the positive charge in 1 than in 2 has been found.

Thiopyrylium (1) and pyrylium (2) cations are structurally iso-π-electronic with benzene and expected to be aromatic. In fact, behavior of their π-electrons has been shown to be similar to that of benzene.[1] However, there is a structural change including the decreased molecular symmetry by the displacement of the CH group with the hetero-atom. Furthermore, although the considerable positive charge should localize on the hetero-atom (S or O) in the cation because of its 6π aromatic stabilization, an appreciable amount of charge is expected to delocalize over the C atoms. In such an electronic structure the double bond character of the C—C and C-heteroatom bonds in the cations would be different from those benzene or of the Kekulé structure of 1 and 2. Besides the C—C and C-heteroatom bonds, the C—H bonds might also be affected by the electronic states in 1 and 2. In view of these arguments it was of considerable interest to investigate the ground state structural difference in both the cations and benzene by examining their IR spectra. Several sets of the force constants were chosen to calculate the normal vibrations by GF matrix method. The nature of the calculated frequencies were considered in terms of the potential energy distributions (PED). It was found that the C-heteroatom bonds are close to single bonds and the C—H bonds are not like those in aromatic compounds but are tertiary C—H bonds. Also it was concluded that there is much more extensive bond delocalization in 1 than in 2.

EXPERIMENTAL

Preparation of 1 *and* 2. These were prepared as salts by the method by Degani *et al.*[2] and purified by reprecipitation from acetonitrile–ether.

Measurement of IR spectra. IR spectra of 1 and 2 in KBr pellets were recorded on a JASCO 402G spectrophotometer, and the results shown in Fig 1.

The anions, BF_4^- and ClO_4^-, have strong and broad absorption bands at about 1100 cm^{-1} which obscure the 1000–1100 cm^{-1} absorption of 1. To avoid this difficulty, the spectrum of thiopyrylium iodide was measured. This spectrum showed the characteristic band between 1550–1450 cm^{-1} different from that of thiopyrylium fluoroborate. This is due to the difference of the electronic structure in the ground state. That is, the thiopyrylium cation interacts with the iodide anion electronically because of the relatively low ionization potential of the iodide anion compared with that of the fluoroborate anion. This charge–transfer interaction should bring about the change in the electronic potential function, by which the vibronic wave functions of the fluoroborate and the iodide differ from each other.

Method of calculation. Normal coordinate analysis was carried out according to the GF Matrix method.[3] As regards normal vibration and symmetry, it can be assumed that 1 and 2 have planar C_{2v} symmetry as discussed previously.[1] Both cations are constructed from 11 atoms, so the number of normal vibrations are nineteen in-plane vibrations ($10A_1 + 9B_1$) and eight out-of-plane vibrations ($3A_2 + 5B_2$), of which only A_2 species are symmetrically forbidden in IR absorption.

Bond distances and bond angles are assumed as follows; C—C = 1·397 Å, C—S = 1·71 Å, C—O = 1·31 Å, C—H = 1·08 Å, inner angle of ∠C—C—C = 120° and C—H bond is supposed to be on the line which bisects the outer angle of ∠C—C—C or ∠C—C—X. Numbering of the atoms and coordinate axis in 1 and 2 are shown in Fig 2.

For the in-plane modes, five C—H stretchings ($s_1 - s_5$), six C—C (or C-heteroatom) stretchings ($t_1 - t_6$), six bending of C—C—C and C—C—X ($\alpha_1 - \alpha_6$) and five C—H bending ($\beta_1 - \beta_5$) were chosen as internal coordinates and the numbering is shown in Fig 3. The α's are the changes in the C—C—C and C—C—X angles. Symmetrical properties of these vibrational modes are:

$$s\ 3A_1 + 2B_1;\ t\ 3A_1 + 3B_1;\ \alpha\ 4A_1 + 2B_1;\ \beta\ 2A_1 + 3B_1.$$

Of these 12 A_1 and 10 B_1 species redundancies of $2A_1$ and B_1 are contained. For the out-of-plane modes five C—H bending (δ_1–δ_5) and six ring torsion (τ_1–τ_6) were selected as the internal coordinates which are shown in Fig 3. Symmetrical prop-

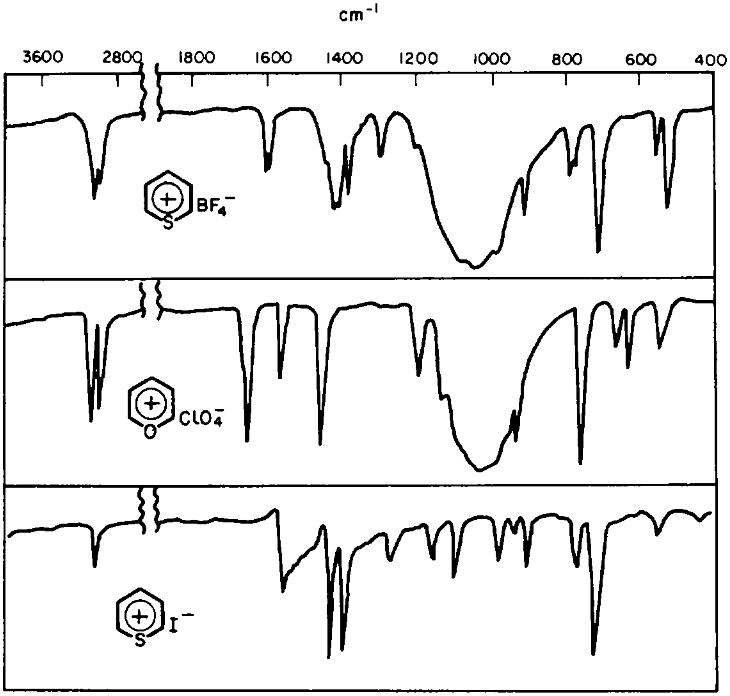

Fig 1. IR spectra of thiopyrylium and pyrylium cations.

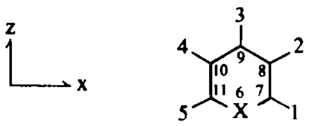

Fig 2. Coordinate and numbering of cation 1 and 2.

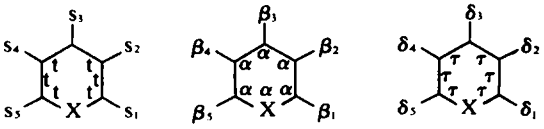

Fig 3. Internal coordinates s, t, α, β, δ and τ.

erties are: δ $2A_2+3B_2$; τ $3A_2+3B_2$. There are $2A_2+B_2$ redundancies in these internal coordinates. Symmetrical coordinates are made up from the internal coordinates defined above, s, t, α, β, δ, and τ, which are shown below ($k = 1/\sqrt{2}$).

A_1	B_1	A_2	B_2
1 $k(s_1+s_5)$	1 $k(s_1-s_5)$	1 $k(\delta_1-\delta_5)$	1 $k(\delta_1+\delta_5)$
2 $k(s_2+s_4)$	2 $k(s_2-s_4)$	2 $k(\delta_2-\delta_4)$	2 $k(\delta_2+\delta_4)$
3 s_3			3 δ_3
4 $k(t_1+t_6)$	3 $k(t_1-t_6)$	3 $k(\tau_1+\tau_6)$	4 $k(\tau_1-\tau_6)$
5 $k(t_2+t_5)$	4 $k(t_2-t_5)$	4 $k(\tau_2+\tau_5)$	5 $k(\tau_2-\tau_5)$
6 $k(t_3+t_4)$	5 $k(t_3-t_4)$	5 $k(\tau_3+\tau_4)$	6 $k(\tau_3-\tau_4)$
7 $k(\alpha_1+\alpha_5)$	6 $k(\alpha_1-\alpha_5)$		
8 $k(\alpha_2+\alpha_4)$	7 $k(\alpha_2-\alpha_4)$		
9 α_3			
10 α_6			
11 $k(\beta_1-\beta_5)$	8 $k(\beta_1+\beta_5)$		
12 $k(\beta_2-\beta_4)$	9 $k(\beta_2+\beta_4)$		
	10 β_3		

Kinetic energy matrix (T) can be definitely determined from the above symmetrical coordinates.

The calculation was carried out including the redundant coordinates. For the in-plane modes Urey-Bradley force field which takes the repulsion among nonbonding atoms into consideration was adopted.[4]

$$2V = \sum_{i} K_i(\Delta r_i)^2 + \sum_{i,j} H_{ij} r_i r_j (\Delta\phi_{ij})^2 + \sum_{i,j} \{2F'_{ij} q_{ij}(\Delta q_{ij}) + F_{ij}(\Delta q_{ij})^2\}. \tag{1}$$

In Eq 1, only ij of Δq_{ij} denotes the non-adjacent atoms which is separated by one atom such as 1–8 and 1–6 in Fig 2, furthermore, in the third term Δq_{ij} is not neglesible because the second order term on Δr_i and $\Delta\phi_{ij}$ are necessary when Δq_{ij} is expanded by them. K_i's are the force constants for the stretching and the H_{ij}'s are that of the bending modes and the F'_{ij}'s and the F_{ij}'s are the non-bonding interaction constants.

For the out-of-plane vibrations following internal potential field, which is used for the benzene system, was assumed,[5]

$$2V = A\sum_i (r_0\delta_i)^2 + B\sum_i (R_0\tau_i)^2 + a_0\sum_i r_0^2\delta_i\delta_{i+1} + b_0\sum_i R_0^2\tau_i\tau_{i+1} + c_0\sum_i r_0R_0(-\delta_i\tau_i + \delta_i\tau_{i-1}) \quad (2)$$

where the r_0 means the C—H bond distance and R_0 stands for the C—C (or C-heteroatom) bond distance.

As a first step of this study, assumption was made that the force constants of these cations were the same as that of benzene. The reason for this is that in spite of the difference in the symmetry, both cations are isoelectronic with benzene and the behavior of the π-electrons in the cation system are well interpreted by this isoelectronic character with benzene.[1] In this assumption the effect of the replacement of hetero-atom instead of C atom is considered as a mass effect. Further, in this calculation same stretching force constants (K) were used for C_7—X_6, C_8—C_7 and C_8—C_9. The force constants used here are summarized in Table 1. The entire procedure was programmed and run on a FACOM 230–60 computer.

Table 1. A set of force constant[6], (md/A)

In-plane		Out-of-plane	
K(C—C, C—X)	5·46	A	0·402
K(C—H)	4·56	B	0·181
H(a)	0·41	a_0	−0·073
H(b)	0·52	b_0	−0·012
F(ring)	0·37	c_0	−0·131
F(X—C—H)	0·54		
F′ = −0·1F			

RESULTS AND DISCUSSION

The calculated results are shown in Fig 4. In these calculations the parametric difference between **1** and **2** are dependent on the bond length of C—X and the mass weights of the heteroatoms. Generally speaking, the thiopyrylium cation yields lower absorption in wave number than the pyrylium cation due to the mass effect. Few mixing of C—H stretching and the other modes of vibrations take place which is evident from the PED of the normal vibration which is shown in Table 2. The discrepancy between the calculated and the observed data show mainly in the region of double bond stretching. The PED shows that the first four absorptions in Fig 4 contain considerable amounts of double bond contribution. As a result, the same force constant for the C—C bond stretching as that of benzene is not suitable for the cations. A smaller force constant than the corresponding value of benzene is necessary to explain the observed spectrum by the calculation. The reason for the discrepancy from benzene can be explained as follows: If the C—C or C-heteroatom double bond in the cation are similar to that of benzene (which means the analogous force constants for the cation and benzene), then the structure of these cations is mainly the Kekulé structure, that is, the onium structure. However, the study of π-electron distribution by quantum mechanical (SCF MO) method shows that the positive charge is delocalized over the ring carbons.[1] This means that the carbonium ion structure as well as the Kekulé structure contribute to the resonance hybrid of these cations. The contribution of carbonium ion structure decreases the double bond character of C—C or C-heteroatom bond to some extent. So the force constant for the double bond stretching in the cation will be smaller than that of benzene.

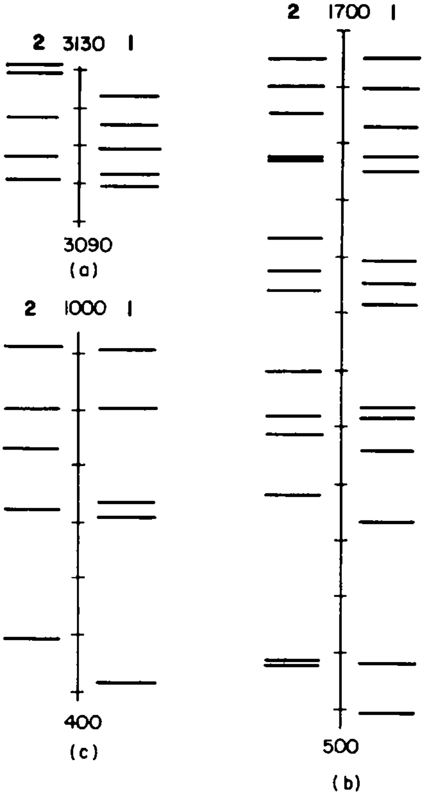

Fig 4. The calculated frequencies for thiopyrylium (**1**) and pyrylium (**2**) cations (cm^{-1}); (a) and (b), in-plane modes, (c) out-of-plane modes.

For the other modes of in-plane vibration, the differences are not as great as for the mode of vibration discussed above. Intensive absorptions of C—H out-of-plane vibrations of the thiopyrylium and the pyrylium cations are observed at 727 and 777 cm^{-1}, respectively. The calculated data corresponding to them are considered to be 707 and 712 cm^{-1}, respectively, from the PED. Therefore, it is probable that the structural difference is small between benzene and **1**, but not between benzene and **2**.

To modify the calculation in in-plane modes, the

Table 2. Potential energy distribution (PED) for 1 and 2

Thiopyrylium cation							Pyrylium cation						
cm^{-1}	3122	3114	3108	3101	3098		cm^{-1}	3130	3128	3116	3106	3100	
A_1	A_1	B_1	A_1	B_1	A_1	B_1	A_1	A_1	B_1	S_1	B_1	A_1	B_1
1	0·16	0·40	0·65	0·60	0·19	1	1	0·77	0·88	0·21	0·12	0·03	1
2	0·50	0·60	—	0·41	0·50	2	2	0·18	0·12	0·30	0·88	0·52	2
3	0·33		0·35		0·32		3	0·05		0·49		0·46	
cm^{-1}	1005	899	732	707	409		cm^{-1}	1006	894	826	712	482	
B_2	B_2	B_2	B_2	B_2	B_2	B_2	B_2	B_2	B_2	B_2	B_2	B_2	B_2
1	0·13	0·83	0·03	0·57	0·09	1	1	0·11	0·69	0·18	0·61	0·02	1
2	0·66	0·03	0·72	0·88	0·18	2	2	0·66	0·03	0·19	0·53	0·26	2
3	0·51	0·39	0·07	0·44	0·20	3	3	0·51	0·41	—	0·42	0·26	3
4	0·02	0·05	0·24	0·35	0·63	4	4	0·01	0·01	0·91	0·09	0·30	4
5	0·06	0·01	0·26	0·34	0·02	5	5	0·05	—	0·38	0·03	0·14	5
6	0·13	—	0·30	0·35	1·13	6	6	0·12	0·01	0·25	0·01	1·51	6

Pyrylium cation

cm^{-1}	1646	1596	1550	1472	1470	1327	1266	1232	1091	1009	974	862	572	563	
A_1	B_1	A_1	B_1	B_1	A_1	B_1	B_1	A_1	B_1	A_1	A_1	A_1	B_1	A_1	B_1
4	—	0·03	0·50	0·13	0·15	0·22	0·04	—	0·06	0·21	0·10	0·50	0·05	—	3
5	0·21	0·53	0·25	0·07	0·05	0·03	—	0·10	0·41	0·03	0·17	0·05	—	0·08	4
6	0·75	0·22	0·04	0·02	0·06	—	0·02	0·04	0·14	0·32	0·29	0·03	0·05	0·01	5
7	0·02	0·02	0·01	0·01	—	0·02	—	—	0·02	0·11	0·13	0·08	0·45	0·19	6
8	0·02	0·01	0·05	—	0·01	—	—	—	0·03	0·13	0·12	0·11	0·45	0·14	7
9		0·04			—			0·01		—	0·09	0·14		0·24	
10		0·02			0·01			—		—	0·08	0·08		0·33	
11	—	0·04	0·20	0·02	0·55	0·66	0·03	0·32	0·11	0·09	—	0·01	—	—	8
12	0·06	0·26	—	0·44	0·27	0·01	0·47	0·43	0·04	0·05	—	0·01	—	—	9
	0·06		0·10	0·35		0·01	0·38		0·11				—		10

Thiopyrylium cation

cm^{-1}	1649	1599	1525	1474	1447	1285	1248	1208	1025	1009	953	823	567	482	
A_1	B_1	A_1	B_1	A_1	B_1	B_1	A_1	B_1	A_1	B_1	A_1	A_1	B_1	A_1	B_1
4	0·01	0·04	0·15	0·14	0·10	0·03	0·02	0·25	0·19	0·36	0·09	0·50	0·11	0·03	3
5	0·22	0·54	0·37	0·05	—	0·01	0·10	0·06	0·03	0·32	0·16	0·05	—	0·09	4
6	0·74	0·21	0·06	0·07	—	0·01	0·02	0·07	0·42	0·10	0·19	0·06	0·04	0·01	5
7	0·02	0·01	—	—	0·01	—	—	0·02	0·08	0·10	0·17	0·03	0·40	0·24	6
8	0·02	0·01	0·05	0·01	—	—	—	0·04	0·07	—	0·18	0·15	0·44	0·08	7
9		0·04		—			—		—		0·10	0·19		0·18	
10		0·01		0·01			—		—		0·08	0·02		0·39	
11	—	0·04	0·26	0·57	0·27	0·29	0·33	0·20	0·07	0·01	—	—	—	—	8
12	0·06	0·25	0·03	0·26	0·45	0·39	0·42	0·04	0·08	0·05	—	0·01	—	—	9
	0·06		0·25		0·21	0·22		0·24		0·04			—		10

force constant for double bond was changed. If the positive charge is localized on the hetero-atom, then the double bonds are assumed to be equivalent to those of benzene, however, in the carbonium ion structure, the double bond character decreases by amount of $\frac{1}{3}$ (because in a Kekulé structure, the number of the double bonds are three whereas in a carbonium ion structure it is two as visualized in Fig 5. So if we assume the linear relationship between the force constant for the double bond and the positive charge distribution on the hetero-atom, the force constant K is given by:

$$K = K^0 - (1 - q^x)(K^0 - \tfrac{2}{3}K^0) \qquad (3)$$

where the second term is the ámount of decrease in the force constant from that of benzene because of the contribution of the carbonium ion structure, K^0 and q^x being the force constant of double bond of benzene and the positive charge on the hetero-atom, respectively. The difference in the positive charge delocalization between 1 and 2 are taken into account explicitly by this assumption. The values of K are 5·19 and 4·94 md/A for 1 and 2, respectively, and the H(b) was changed to 0·42 md/A. Positive charge distribution on the hetero-atom have been obtained by the SCF-MO calculation.[1] The results are shown in Fig 6.

An alternative method for the evaluation of the force constants which makes use of the decrease in the positive charge on the hetero-atom is derived from the dissimilarity of the degree of the double bond characters of the C_7—C_8 and the C_8—C_9 bonds in the carbonium ion structures. If the positive

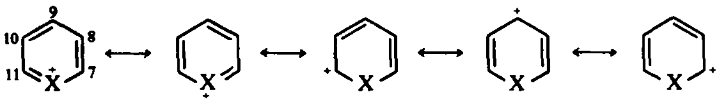

Fig 5. Resonance hybrid of 1 and 2.

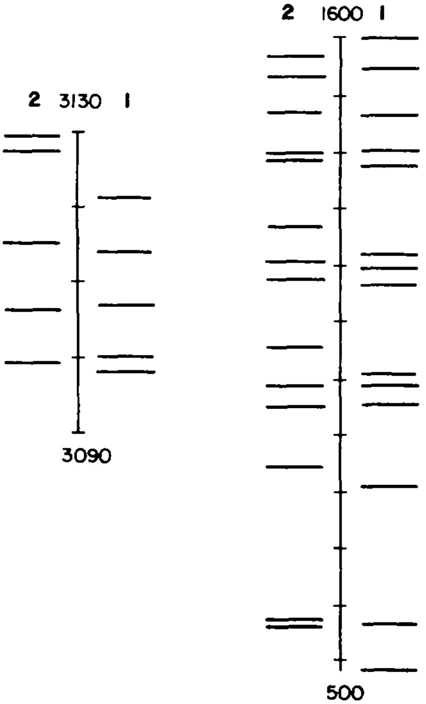

Fig 6. The calculated frequencies (cm^{-1}) (fixed K model).

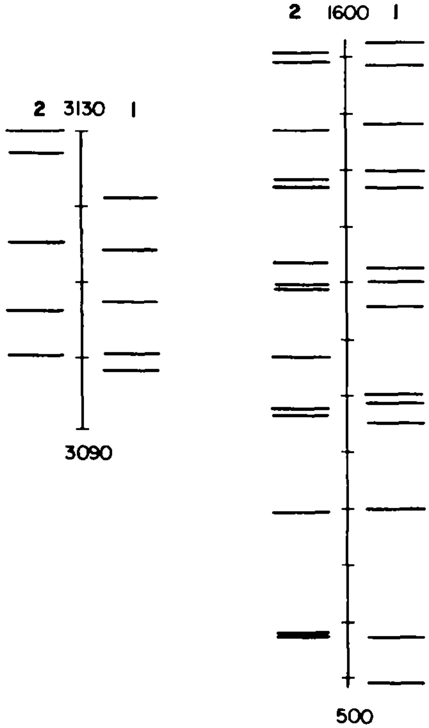

Fig 7. The calculated frequencies (cm^{-1}) (variable K method).

charge in the carbonium ion structure is equally distributed at carbon 7, 9, and 11, then the double bond character of C_7—C_8 bond is considered to be twice as large as the C_8—C_9 bond as is evident from Fig 5, i.e., the double bond character for the former increases by amount of $\frac{1}{3}$ in contrast to the latter bond. There is no double bond character for C-heteroatom bond in the carbonium ion structure. In such approximation, the corrected K's are

$$K(C—C_8) = K^0 + (1 - q^x)(K^0 - \tfrac{2}{3}K^0) \qquad (4)$$

$$K(C—X) = K^0 - (1 - q^x)K^0. \qquad (5)$$

The formula for $K(C_8—C_9)$ is equal to (3). Thus obtained parameters are listed in Table 3 and the results are shown in Fig 7.

Table 3. Force constants obtained by variable K method

	C—X	C_7—C_8	C_8—C_9
Thiopyrylium cation	4·66	5·73	5·19
Pyrylium cation	3·91	5·98	4·94

If we restrict our concern to the region of the double bond stretching, the fixed K method gives a more favourable result than the variable K method for 1, whereas for 2 the variable K method yields better result than the fixed K method. In the fixed K scheme all the double bonds in the cation are considered to be equivalent, and to be analogous to that of benzene, which is a resonance hybrid of Kekulé structure, on the other hand, in the variable K scheme, contribution of the carbonium ion structure is taken into account clearly. A comparison of π electron distribution shows the presence of the more carbonium ion character for pyrylium cation than for thiopyrylium cation, which is consistent with the calculated results.

The nature of the calculated frequencies

The correspondence of the frequencies for both the cations to the numbering of them is shown in Fig 8 where the fixed K method for 1 and the variable K method for 2 was adopted and the PED are shown in Table 4. The characters of the frequencies are summarized in Table 5.

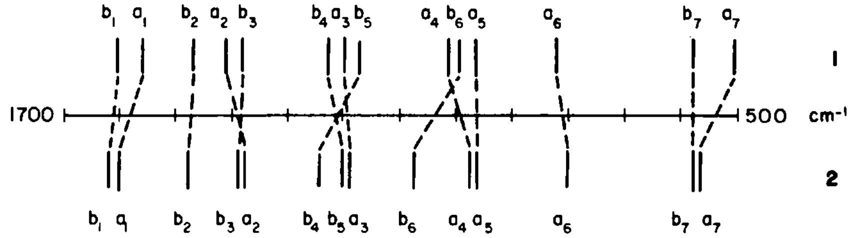

Fig 8. Correspondencies between the frequencies (cm^{-1}) of 1 and 2.

Table 4. The PED's for 1 (fixed K model) and 2 (variable K model)

Thiopyrylium cation							Pyrylium cation						
cm^{-1}	3121	3114	3107	3100	3098		cm^{-1}	3130	3127	3115	3106	3100	
A_1	A_1	B_1	A_1	B_1	A_1	B_1	A_1	A_1	B_1	A_1	B_1	A_1	B_1
1	0·16	0·40	0·65	0·60	0·19	1	1	0·76	0·87	0·21	0·14	0·03	1
2	0·50	0·59	—	0·41	0·50	2	2	0·19	0·13	0·31	0·87	0·51	2
3	0·33		0·35		0·32		3	0·05		0·48		0·47	

cm^{-1}	1607	1550	1465	1402	1373	1221	1194	1166	1003	987	945	811	565	481	
A_1	B_1	A_1	B_1	A_1	B_1	B_1	A_1	B_1	A_1	B_1	A_1	A_1	B_1	A_1	B_1
4	0·01	0·05	0·18	0·15	0·10	0·04	0·01	0·20	0·18	0·35	0·05	0·53	0·12	0·03	3
5	0·24	0·59	0·39	0·05	—	—	0·06	0·04	0·02	0·31	0·16	0·05	—	0·09	4
6	0·75	0·22	0·08	0·09	—	—	0·01	0·05	0·36	0·10	0·23	0·06	0·05	0·01	5
7	0·02	0·01	—	0·01	0·01	—	—	0·02	0·10	0·10	0·15	0·02	0·39	0·23	6
8	0·02	0·02	0·06	0·01	—	—	—	0·03	0·10	—	0·17	0·13	0·44	0·08	7
9		0·05		—			—		—		0·12	0·18		0·18	
10		0·02		0·01			—		—		0·09	0·01		0·39	
11	—	0·04	0·23	0·53	0·22	0·37	0·37	0·18	0·09	0·01	—	—	—	—	8
12	0·04	0·19	0·02	0·28	0·47	0·35	0·44	0·08	0·09	0·06	—	—	—	—	9
	0·04		0·21		0·23	0·18		0·31		0·04			—		10

Pyrylium cation

cm^{-1}	1611	1591	1469	1377	1367	1234	1194	1181	1065	971	958	788	565	564	
A_1	B_1	A_1	B_1	B_1	A_1	B_1	B_1	A_1	B_1	A_1	A_1	A_1	B_1	A_1	B_1
4	0·01	0·02	0·12	0·23	0·10	0·27	0·16	—	0·15	0·07	0·04	0·75	0·08	—	3
5	0·42	0·07	0·28	—	0·04	—	—	0·06	0·27	0·05	0·10	0·03	—	0·07	4
6	0·58	0·18	0·22	—	0·09	—	0·02	0·01	0·15	0·39	0·27	0·02	0·05	0·02	5
7	0·02	0·02	—	0·02	—	0·03	0·01	—	0·03	0·15	0·15	0·02	0·42	0·19	6
8	0·01	0·01	0·07	—	0·01	—	0·01	—	0·02	0·17	0·17	0·02	0·44	0·14	7
9		0·04			—			—		0·01	0·14	0·08		0·24	
10		0·02			0·01			—		0·01	0·09	0·06		0·33	
11	—	0·04	0·14	0·18	0·50	0·54	—	0·39	0·15	0·07	0·01	0·01	—	—	8
12	0·06	0·16	0·02	0·45	0·34	0·03	0·39	0·45	0·07	0·04	0·01	0·01	—	—	9
	0·01		0·30	0·16		0·05	0·39		0·11				—		10

The classifications of the A_1 species are rather easy when compared with those of B_1 species because of the less mixing among the normal modes. Considerable amount of mixing between the double bond stretching and the C—H bending modes take place in the b_2 and b_5 for 1 and in the b_2, b_3, b_4 and b_6 for 2. So the correspondencies of the frequencies which belong to B_1 species are tentative, and the analysis of the spectra is more complicated for 2 than for 1.

It is noteworthy that the strong interaction mentioned above between the double bond stretching and the C—H bending modes are recognized. The reason for this interaction of normal modes is interpreted by the contribution of the carbonium ion structure to the resonance hybrid of the cation. In a carbonium ion structure the double bond character disappears at the C—X bond and the C—H bonds also are not those of aromatic, but tertiary C—H bonds. As result, strong interaction between the C—X single bond stretching and the C—H bending modes give rise to, and the wave numbers will be shifted higher by this change of the character of the C—H bond. The larger interaction in 2 than in 1 is expected because the former has the larger contribution of carbonium ion structure than

Table 5. The characters of the frequencies

	A_1	B_1
Thiopyrylium cat.		
$\nu_{C—C}$	a_1, a_4, a_6	b_1, b_2, b_5, b_6
$\delta_{C—H}$	a_2, a_3	b_2, b_3, b_4, b_5
$\delta_{C—C}$	a_5, a_7	b_7
Pyrylium cat.		
$\nu_{C—C}$	a_1, a_4, a_6	b_1, b_2, b_3, b_4, b_6
$\delta_{C—H}$	a_2, a_3	b_2, b_3, b_4, b_5, b_6
$\delta_{C—C}$	a_5, a_7	b_7

the latter. This is consistent with the calculated results which are clear in the Table 4.

The difference of the degrees of the contribution of the carbonium ion structure have influence on the C—H stretching and out-of-plane bending. As the contribution of the carbonium ion structure becomes larger, smaller force constants than those of benzene are necessary for the C—H stretching of both the cations. On the other hand, for the C—H out-of-plane bending, the frequencies of the observed intensive bands are higher than the calculated frequencies corresponding to them. This is probably due to the contribution of the planar tertiary C—H bond which give higher frequency for out-of-plane bending than that of aromatic one. Furthermore, the discrepancy between the observed and the calculated frequencies are greater in **2** than in **1**, suggesting that C—H bond of **1** is considered to be more aromatic one than that of **2**. Balaban *et al.*[7] have tried the assignments of the IR bands of the unsubstituted pyrylium cation on the basis of the parallelism in aromaticity among benzene, pyridine, pyridinium cation. They assigned the band 1620 cm^{-1} and 1474 cm^{-1} as double bond stretchings, however, these bands are not simple absorptions as shown in Fig 1, the former have 1620, 1615 cm^{-1} and the three components, 1476, 1469 and 1461 cm^{-1} belong to the latter. The pyrylium cation as well as thiopyrylium cation is aromatic due to the 6π electron delocalization but they are not as aromatic as benzene, pyridine and pyridinium salts, in which the contribution of carbonium ion structure is zero or negligibly small in the ground state. The positive charge delocalization in the ring would be the main reason for the complexities of the analysis of the IR spectra of **1** and **2**.

CONCLUSION

The main reason for the difference in the IR spectra between benzene and the thiopyrylium and pyrylium cations is ascribed to the contribution of the carbonium ion structure in the latter cations which are not expected in benzene. The force constants of the double bonds in the cations are smaller than those of benzene except for the $C_7—C_8$ and $C_{10}—C_{11}$ in the latter, because the double bond character in the cations decreases when compared to that of benzene due to the contribution of the carbonium ion structures to the resonance hybrid of the cations. The large mixing between double bond stretching vibration and C—H in-plane bending modes in the cations also arise from the contribution of their carbonium ion structures.

The difference between **1** and **2** is attributed firstly to the mass effect of the hetero-atom and not to the force constants of C-heteroatom double bond, and secondly to the difference of the degree of the contribution of the carbonium ion structure. The larger contribution of the carbonium ion structure in **2** than in **1** makes the analysis of the spectra of the former difficult because of the above mentioned larger mixing of the normal vibrations. Finally in the carbonium ion structure, the positive charge in **1** is more delocalized over the five carbons than in **2** because the fixed K model gives better results for the former than for the latter, whereas in the variable scheme the results are *vice versa*.

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