IR SPECTRA OF SELENOPHENOPYRYLIUM SALTS

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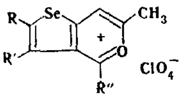
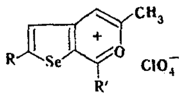
On the basis of the IR spectra of 16 alkyl-substituted selenopheno[2,3-c]- and selenopheno[3,2-c]pyrylium salts and a model calculation of the frequencies and the forms of their normal vibrations, an assignment of the frequencies of the skeletal vibrations of the heterocycles is put forward.

One of the main methods of identifying a pyrylium cation is infrared spectroscopy [1-3].

We have studied the infrared spectra of selenopheno[3,2-c]- and selenopheno[2,3-c]pyrylium salts synthesized by the acylation of acetonyl derivatives of selenophene with carboxylic acid anhydrides in the presence of perchloric acid [4, 5]. To interpret the spectra, a calculation has been made of the frequencies and forms of the normal vibrations of the unsubstituted cations.



I a-h



II a-h

I a $R=CH_3$, $R'=H$, $R''=CH_3$; b $R=CH_3$, $R'=H$, $R''=C_2H_5$; c $R=CH_3$, $R'=H$, $R''=n\text{-}C_3H_7$; d $R=C_2H_5$, $R'=H$, $R''=CH_3$; e $R=C_2H_5$, $R'=H$, $R''=C_2H_5$; f $R=CH_3$, $R'=CH_3$, $R''=CH_3$; g $R=CH_3$, $R'=CH_3$, $R''=C_2H_5$; h $R=CH_3$, $R'=CH_3$, $R''=n\text{-}C_3H_7$;
II a $R=CH_3$, $R'=CH_3$; b $R=CH_3$, $R'=C_2H_5$; c $R=CH_3$, $R'=n\text{-}C_3H_7$; d $R=C_2H_5$, $R'=CH_3$; e $R=C_2H_5$, $R'=C_2H_5$; f $R=H$, $R'=CH_3$; g $R=H$, $R'=C_2H_5$; h $R=H$, $R'=n\text{-}C_3H_7$.

Typical IR spectra of the compounds studied are shown in Fig. 1. The most interesting region of these spectra is between 1650 and 1390 cm^{-1}, where, as calculations show (Fig. 2†) the vibrations of the bonds of the selenophene and pyrylium heterocycles are concentrated. Thus, the band at about 1640-1610 cm^{-1} relates to the vibration in which, mainly, symmetrical stretchings of the C=C bonds of the pyrylium nucleus (ν_1) take place. Another vibration with the participation of these bonds appears in the 1580-1530 cm^{-1} region and is due to the unsymmetrical stretching vibrations of the C=C bonds (ν_2). These two vibrations are similar in form to the 8a and 8c vibrations, respectively, of the pyrylium cation [1].

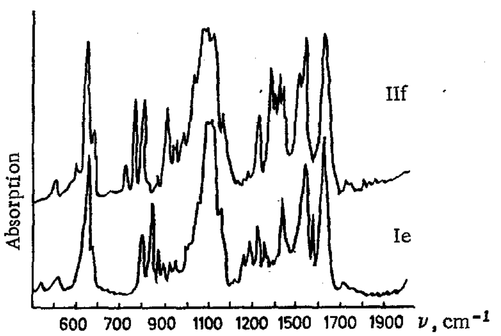


Fig. 1. IR spectra of 2,4-diethyl-6-methylselenopheno[3,2-c]pyrylium perchlorate (Ie) and of 5,7-dimethylselenopheno[2,3-c]pyrylium perchlorate (IIf).

It is interesting that in the selenopheno[3,2-c]pyrylium cation there is a considerable increase in the frequency of the antisymmetrical vibration ν_2 and a decrease in the frequency of the symmetrical vibration ν_1 as compared with the selenopheno[2,3-c]pyrylium cation (Table 1 and Fig. 1). It

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*Deceased.

†Figure 2 shows the displacements of the atoms of the selenopheno[2,3-c]pyrylium cation; the form of the vibrations considered does not change fundamentally for the selenopheno[3,2-c]pyrylium cation.

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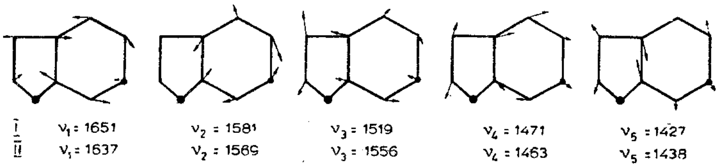

Fig. 2. Diagram of the displacements of the atoms and the calculated frequencies of the main skeletal vibrations of the selenophenopyrylium cations (the lengths of the vectors are proportional to the magnitudes of the displacements).

TABLE 1. Frequencies of the Main Skeletal Vibrations in the IR Spectra of Selenophenopyrylium Salts

Compound	Vibrations of the selenophenopyrylium cation, cm^{-1}				
	ν_1	ν_2	ν_3	ν_4	ν_5
Ia	1616	1576	1530	1436	1410
Ib	1615	1580	1530	1440	1400
Ic	1620	1580	1530	1443	1400
Id	1611	1570	1525	1442	1390
Ie	1611	1568	1521	1440	1410
If	1620	1576	1521	1446	1400
Ig	1614	1580	1514	1446	1415
Ih	1614	1578	1511	1440	1410
IIa	1635	1537	1522	1433	1410
IIb	1633	1534	1525	1423	1412
IIc	1627	1537	1523	1431	1415
IId	1634	1540	1530	1433	1415
IIe	1626	1538	1526	1430	1412
IIf	1622	1530	1510	1432	1420
IIg	1621	1532	1509	1423	1395
IIh	1623	1536	1517	1425	1400

is obviously impossible to explain these changes solely by kinematic influences, since the calculated figures, which take into account the change in kinematic factors, predict (Fig. 2) an increase in the frequency of both migrations. Apparently, the decrease, rather than increase, in the frequency of the symmetrical vibration on passing from (II) to (I) is connected with a change in the conditions of conjugation of the d,π-electrons of the selenophene and pyrylium aromatic systems. This is confirmed by the considerable change in the ratio of the intensities of the vibrations considered in the two series of compounds [6, 7].

What has been said agrees well with the features of the IR spectra of thienopyrylium salts [8]. Thus, the bands of vibrations analogous to those considered above are found at about 1630 and 1540 for thieno-[2,3-c]pyrylium salts and at about 1616 and 1561 cm^{-1} for thieno[3,2-c]pyrylium salts.

The following band of the skeletal vibrations in the spectra of the salts of both series is located at about 1520 cm^{-1} and its appearance is due mainly to the vibrations of the C=C bond of the selenophene ring (ν_3). As is well known [9], for selenophene itself the analogous vibration is recorded at about 1582 cm^{-1}, and the decrease in the $\nu_{C=C}$ frequency in our case is obviously connected with the electron-donating action of the pyrylium cation.

The two bands at ~1440 and ~1410 (ν_4 and ν_5) correspond to the vibrations of the atoms of the selenophene and pyrylium heterocycles and are therefore less specific than the vibrations considered above.

The vibrations of the C–Se bonds are found in the 800-600-cm^{-1} region. The alkyl groups can be identified from the absorption in the 1480-1450- and 1380-cm^{-1} regions. Two intense bands in the spectra of all the compounds considered at about 1100 and 625 cm^{-1} are due to the vibrations of the ClO_4^- anion [3].

The spectra of the salts were obtained on a UR-20 spectrometer with KBr and NaCl prisms at a rate of scanning of 64 cm^{-1}/min. The samples were prepared in the form of tablets with KBr. The calculation of the frequencies and forms of the normal vibrations and of the displacements of the atoms was performed by the usual method [10, 11]. The force fields of thiophene and pyridine [12] were taken as a basis and were subsequently varied.

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