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SPECTRA AND STRUCTURE OF PYRYLIUM SALTS

I. Infrared Spectra of 5, 6, 7, 8-Tetrahydro-2-benzopyrylium 1, 3-disubstituted Salts

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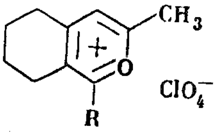
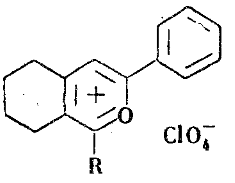
IR spectra of 20 specimens of 5, 6, 7, 8-tetrahydro-2-benzopyrylium 1, 3-disubstituted salts are obtained. The characteristic changes in the valence vibration bands for the pyrylium ring and for aromatic substituents are noted.

A number of papers have been published of recent years, dealing with various methods of synthesis of pyrylium salts and investigations into their chemical properties [1-4]. The infrared spectra of only a comparatively small number of such compounds have been considered. A paper [5] reported alterations in positions of individual bands in the infrared spectra of di-, tri-, tetra- and penta-alkyl (aryl) substituted pyrylium salts, as a function of the nature and positions of the substituents.

The present paper considers the infrared spectra of 1-alkyl-3-methyl-(A), 1-alkyl-3-phenyl-(B), and 1-alkyl-3-(α-thienyl) (C) substituted salts of 5, 6, 7, 8-tetrahydro-2-benzopyrylium, synthesized by acylating cyclohexenylketones with acid anhydrides in the presence of 70% perchloric acid [6-8].



A



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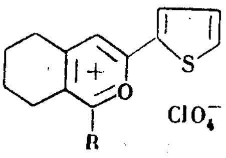

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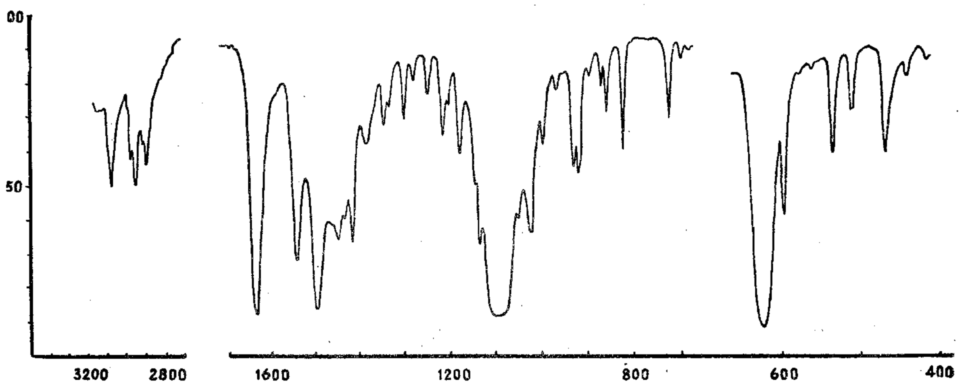


Fig. 1. Spectrum of 1, 3-dimethyl-5, 6, 7, 8-tetrahydro-2-benzopyrylium perchlorate.

Figure 1 shows the infrared spectrum of 1, 3-dimethyl-5, 6, 7, 8-tetrahydro-2-benzopyrylium perchlorate. The absorption bands in the spectra of the rest of the salts are represented in Fig. 2 as lines, whose positions are those of the maxima of the bands and whose lengths give the relative intensities (due to the marked scattering with many of the compounds studied in the 2800-3500 cm^{-1} region, the layer thickness used when examining them with a LiF prism varied considerably).

Characteristic changes in the spectra of the compounds studied are observed in the range 1650-1400 cm^{-1}, where there is a group of bands due to valence vibrations of the pyrylium ring and of aromatic substituents. Two strong bands at 1650-1615 and 1530-1540 cm^{-1} are due to symmetric and antisymmetric valence vibrations of the heterocyclic ring (8a and 8b on Wilson's classification [9]). Usually the first of these is not shifted by other bands, and can serve as one of the criteria for the presence of a pyrylium ring.

It is basic to assume that the shifts of vibration bands 8a and 8b in the spectra of substituted pyrylium salts are correlated with the stability of the pyrylium ring. Thus quantum mechanical calculation for the unsubstituted pyrylium cation [10] shows that the maximum values of the positive charge obtains at the 4(γ)-carbon atom, while even a certain negative charge is possible at the 3, 5 (β, β)-positions in the ring. So introduction of a nucleophilic substituent at the γ-position, and more especially at the α, α'-position stabilizes the pyrylium ring, while with β, β'-substituents its stability must decrease. This is clearly exhibited in the chemical nucleophilic properties of pyrylium salts [4], the ease with which nucleophilic addition takes place to pyrylium salts with the γ-position in the ring free, and the high mobilities of the hydrogen atoms of the α- and γ-methyl groups of the pyrylium ring (deuterium exchange reaction [1], condensation with carbonyl compounds [12, 13] and diazonium salts [14]). There are also some difficulties in connection with the synthesis of the quite unstable unsubstituted pyrylium cation, having three open reaction centers [15], while pyrylium salts with substituents at positions 3 and 5 have not so far been prepared.

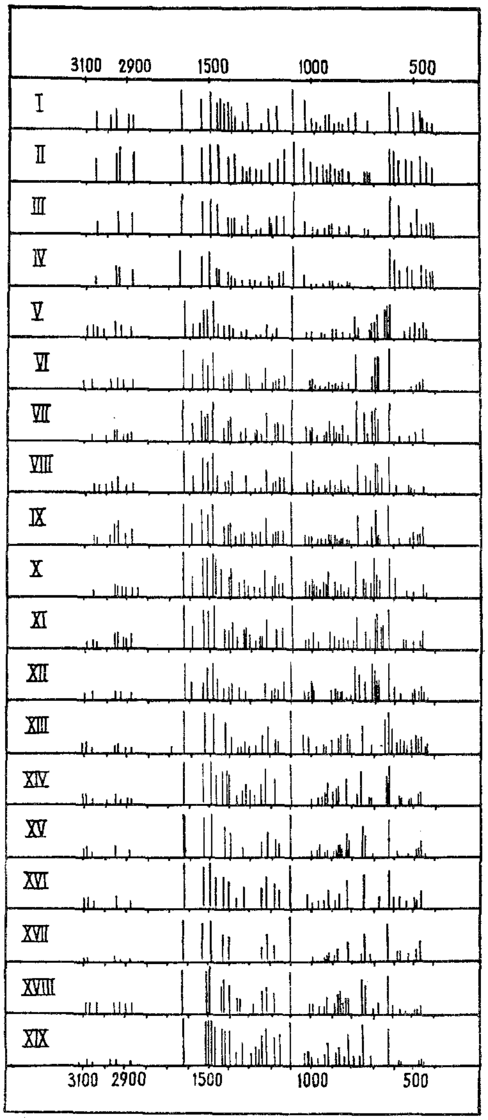
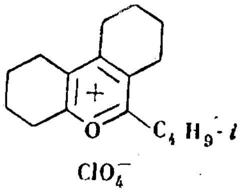


Fig. 2. Spectra of 1, 3-disubstituted 5, 6, 7, 8-tetrahydro-2-benzopyrylium perchlorates: I)1-ethyl-2-methyl-; II) propyl-3-methyl-; III) 1-isopropyl-3-methyl-; IV) 1-isobutyl-3-methyl-; V) 1-methyl-3-phenyl-; VI) 1-ethyl-3-phenyl-; VII) 1-propyl-3-phenyl-; VIII) 1-isopropyl-3-phenyl-; IX) 1-isobutyl-3-phenyl-; X) 1-amyl-3-phenyl-; XI) 1-diethylmethyl-3-phenyl-; XII) 1-benzyl-3-phenyl-; XIII) 1-methyl-3-thienyl-; XIV) 1-ethyl-3-thienyl; XV) 1-propyl-3-theinyl-; XVI) 1-isopropyl-3-thienyl-; XVII) 1-isobutyl-3-thienyl; XVIII) 1-amyl-3-thienyl; XIX) 1-diethylmethyl-3-thienyl-.

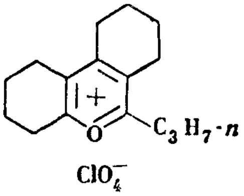
These facts are in good accord with the frequency shifts of the above mentioned vibrations of the pyrylium ring. Thus in the spectrum of the unsubstituted ring band, 8a lies in the 1620 cm^{-1} region, for 4-methylpyrylium at about

1625 cm^{-1}, for 2, 6-dimethyl- and 2, 4, 6-trimethylpyrylium at 1640 and 1650 cm^{-1} respectively [5]. Introduction of an alkyl group at the 3, 5 positions gives rise to an appreciable shift of the 8a band towards the low frequency region, in the spectra of 2, 3, 4, 6-tetramethylpyrylium and 2, 3, 5, 6-tetramethyl-4-ethylpyrylium to 1642 and 1620 cm^{-1} [5] (in the last case steric repulsion between substituents may also have an effect).

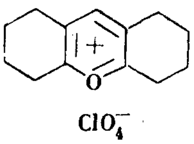
In the spectra of disubstituted salts of 5, 6, 7, 8-tetrahydro-benzopyrylium (Fig. 1; Fig. 2, I-IV) the 8a band is shifted towards the low frequency region (1639-1632 cm^{-1}). Apparently the effect of the cyclohexene ring on these vibrations is conditioned not only by forces of a kinematic nature, but also somewhat by its stress. This is confirmed by the further lowering of 8a vibration frequencies in those compounds which we have synthesized [16, 17] which are pyrylium salts with two cyclohexene rings condensed to the pyrylium heterocyclic ring:



ν_{8a} 1619 cm^{-1}



ν_{8a} 1619 cm^{-1}



ν_{8a} 1615 cm^{-1}

The 8b band of antisymmetric valence vibrations of the pyrylium ring in the dialkyl-substituted salts investigated (1532-1539 cm^{-1}) is also shifted towards the low frequency side in comparison with its position in the spectra of alkyl-substituted pyrylium salts (1540-1545 cm^{-1}) [5].

The difference in frequency between 8a and 8b vibrations ($\Delta\nu$ 8a-8b), which correlates with electronegativity of the hetero-atom, is represented by frequencies which are close together (95-103 cm^{-1}), in the spectra of dialkyl substituted 5, 6, 7, 8-tetrahydro-2-benzopyrylium salts and alkyl substituted pyrylium salts [5].

In the 1490-1500 cm^{-1} region of the spectra of the dialkyl substituted salts investigated there is a marked symmetric valence vibrations band (according to [9] 19a) of the pyrylium ring, which can also be useful for identifying pyrylium compounds. The 19b antisymmetric vibrations band lies in the 1410-1420 cm^{-1} region, and is usually of low intensity.

In all the spectra considered, the position of the pyrylium ring valence vibrations bands is altered but little by lengthening of the alkyl group. The effect of such substituents was observed only when the volume of the alkyl groups at the α, α'-positions was sufficient to give rise to appreciable steric repulsion.

In the spectra of 1-alkyl-3-phenyl substituted 5, 6, 7, 8-tetrahydro-2-benzopyrylium perchlorates (Fig. 2, V-XII), the 8a vibrations band of the pyrylium ring is shifted 8-10 cm^{-1} towards the low frequency region in comparison with its position in the spectra of disubstituted compounds. The 8b antisymmetric vibrations band of the pyrylium ring is situated in the 1535 cm^{-1} region ($\Delta\nu$ 8a-8b is about 90 cm^{-1}).

Unlike the spectra of aryl and alkylaryl substituted pyrylium salts [5], the spectra of 1-alkyl-3-phenyl-5, 6, 7, 8-tetrahydro-2-benzopyrylium perchlorates are found to contain a phenyl group antisymmetric valence vibrations band of medium intensity in the 1580 cm^{-1} region. Its appearance (intensity increase) is connected with conjugation of the phenyl group with other structural elements in the molecule. Increase in intensity of this band was also observed with the spectra of monosubstituted benzene derivatives with strong electron-accepting substituents [18]. Both of the above effects probably affect the aromatic ring in molecules of 1-alkyl-3-phenyl-5, 6, 7, 8-tetrahydro-2-benzopyrylium salts.

The phenyl ring symmetric valence vibrations band 8a at ~1600 cm^{-1} in the spectra of the alkylphenyl substituted compounds overlaps the strong 8a band of the pyrylium ring, and it is found as a small shift only in some of them (Fig. 2 does not show this band).

The strong phenyl group valence vibrations band 19a [9] at 1505-1512 cm^{-1} is not overlapped by the nearby pyrylium ring band 8b, and it, along with the absorption in the 1580 cm^{-1} region can be used to identify these compounds. A band at about 1430 cm^{-1} may be ascribed to phenyl ring 19b vibrations, the reason for this being shift of the 19a absorption in the spectra of monosubstituted benzene derivatives containing electron-donating and electron-accepting substituents [18].

A pyrylium ring antisymmetric vibrations band 19b of medium or low intensity is present in the region 1400-1420 cm^{-1}.

The spectra of 1-alkyl-3-(α-thienyl) substituted 5, 6, 7, 8- tetrahydro-2-benzopyrylium perchlorates (Fig. 2, XIII, XIX) show further shift of the pyrylium ring valence vibrations band 8a towards the low frequency side (1616-1620 cm^{-1}). In contrast to the spectra of 1-alkyl-3-phenyl substituted salts V-XII considered above, the spectra

XIII-XIX exhibit, in the region 1600-1500 cm^{-1}, only one pyrylium ring antisymmetric vibrations band 8b, at 1517-1525 cm^{-1}. Evidently the thiophene ring antisymmetric vibrations band is displaced into the same region, and overlaps the pyrylium ring band 8b. Consideration of frequency changes for these vibrations in 2-substituted thiophenes [20] leads to the same assumption. For example, in the spectrum of 2-methylthiophene, the antisymmetric vibrations band of the C=C and C–S bonds in the ring lie in the 1537 cm^{-1} region, and is of low intensity. With 2-phenylthiophene the band is shifted to 1537 cm^{-1}, and it is more intense. The spectra of 2-monosubstituted thiophenes with powerful electron-accepting substituents show a further shift of the band towards the low frequency region, [2-chlorothiophene, 1518 cm^{-1}; 2-methoxythiophene, 1514 cm^{-1}], with simultaneous increase in intensity.

The strong band in the region 1418-1428 cm^{-1} in spectra XIII-XIX is due to symmetric valence vibrations of the thiophene ring (in the spectra of 2-methyl-, 2-phenyl-, and 2-methoxythiophene this band occurs respectively at 1444, 1433, and 1415 cm^{-1} [20]). However, use of this band to identify 3-(α-thienyl) substituted salts is made rather difficult as 1-alkyl-3-phenyl substituted salts also absorb in that region (phenyl ring vibrations band 19b).

Two medium intensity vibration bands for C=C and C–S of the thiophene ring are found in the ~1340 and 1230 cm^{-1} regions of the spectra of 1-alkyl-3(α-thienyl) substituted salts (XIII-XIX). These are useful for identifying these substances.

Two intense bands, at ~620 cm^{-1} and 1100 cm^{-1} (wide), occurring in the spectra of all the compounds which we have studied, are due to vibrations of the ClO_4 anion.

An IKS-14 infrared spectrophotometer was used to obtain the spectra of the salts investigated over the range 400-3500 cm^{-1}, samples being made into a paste with vaseline or mixed fluorinated hydrocarbons.

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