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Abstract

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INFRARED SPECTRA AND STRUCTURE OF SOME NONBENZENOID AROMATIC COMPOUNDS

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Among aromatic nonbenzenoid compounds are, in particular, such carbonyl-containing compounds as tropone, diphenylcyclopropenone, and sydnones. It is assumed that the oxygen atom in such compounds withdraws the ring electron to a considerable extent, and that 6-π or 2-π electrons remain in the field of the ring nuclei, in accordance with Hückel' s rule $(4n + 2)$ ([1]).

[structural formulas]

As a consequence, the $C = O$ bond in such compounds should be polarized to a noticeable degree. This bond polarization should affect the position and intensity of the bands of the carbonyl group in the IR spectra.

Therefore, investigation of the position and intensity of the carbonyl band can serve to characterize the degree of aromaticity of these compounds, although one should always bear in mind that other factors may also influence the intensity of the $C = O$ band.

Table 1

Intensities of the $C = O$ band of some nonbenzenoid aromatic compounds*

Compound	Intensity, $\text{mole}^{-1} \cdot \text{liter} \cdot \text{cm}^{-2} \cdot 10^4$	Intensity, $\text{mole}^{-1} \cdot \text{liter} \cdot \text{cm}^{-2} \cdot 10^4$	Intensity, $\text{mole}^{-1} \cdot \text{liter} \cdot \text{cm}^{-2} \cdot 10^4$
Compound	CCl_4	dioxane	CH_3CN
Diphenylcyclopropenone	7.4	5.0	4.9
3-Ethylsydnone	7.9	6.3	6.6
Tropone 1635 cm^{-1}	0.95	0.93	0.89
Tropone 1585 cm^{-1}	2.6	2.7	3.2

Fig. 1. IR spectra: 1—diphenylcyclopropenone (crystalline); 2—3-ethylsydnone (liquid); 3—tropone (liquid)

Figure 1: Fig. 1. IR spectra: 1—diphenylcyclopropenone (crystalline); 2—3-ethylsydnone (liquid); 3—tropone (liquid)

* The intensity measurements were carried out by the Bourgin method ([3]); the spectra were recorded on an IKS-14 instrument.

We found the positions and intensities of the carbonyl-group bands in three compounds (tropone, diphenylcyclopropenone, and 3-ethylsydnone) in the liquid and crystalline states and in various solvents (Fig. 1 and Table 1).

The comparatively high values of the frequencies found for $C = O$ in the compounds investigated (tropone 1635 cm^{-1}, 3-ethylsydnone 1751 cm^{-1}, diphenylcyclopropenone 1855 cm^{-1}) and comparison with the frequencies of the $C = O$ group in certain other compounds (benzophenone, γ-lactone, azlactone, etc.) ([2]) do not give grounds—

grounds for concluding that there is strong polarization of the C=O bonds in the compounds studied. However, since the compounds used for comparison are not exact analogues of those studied, the observed position and shift of the C=O frequency should not be regarded as unambiguously characterizing the degree of polarity of the bond. More suitable for this purpose should be the integral intensities of the bands of the C=O group of the compounds studied, since it is known that the intensity of characteristic

Fig. 1. IR spectra: 1 —diphenylcyclopropenone (crystalline); 2 —3-ethylsydnone (liquid); 3 —tropone (liquid)

absorption in the IR region is, in general, the greater, the greater the polarity of the corresponding bond.

The integral intensity of the C=O bands of diphenylcyclopropenone and 3-ethylsydnone is equal to 5-8 units, i.e., 4-5 times higher than in ordinary ketones (~2) (4) and 2 times higher than in amides (5). The increase in the intensity of the carbonyl group in diphenylcyclopropenone and 3-ethylsydnone, as compared with ordinary ketones and amides, indicates a greater polarization of the C=O group in the compounds studied and, to some extent, confirms the concept of the aromaticity of these compounds. In contrast to the data for the two compounds named, the integral intensity of the C=O band for tropone (to which the band at 1635-1638 cm^{-1} is usually assigned) proved to be very small (~1.0).

The result obtained is difficult to explain, since a number of properties of tropone indicate a certain aromaticity of this compound.

In our opinion, the explanation of the observed anomaly is as follows. Alongside the band at 1635 cm^{-1}, in the IR spectrum of tropone there is a very intense band at 1585 cm^{-1}, which is usually assigned to vibrations of the double bonds

of the ring. We assume that in reality this

the band is wholly or partly associated with vibrations of the carbonyl group. It should be said that an analogous splitting of the C=O-group band is also observed in the spectra of sydnones (in solutions), and the intensities indicated by us are the summed intensity of the two bands. If the summed intensities of the bands at 1635 and 1585 cm^{-1} in tropone are calculated, intensities of the order of 4 units are obtained, i.e., considerably greater than for simple ketones, and approaching those found by us for diphenylcyclopropenone and sydnones. We also investigated the hydrobromide salt of diphenylcyclopropenone. In the spectrum of this salt the carbonyl band at 1855 cm^{-1} is absent, and a broad intense band appears at 2976 cm^{-1}, due to the presence of a hydroxyl group in the molecule. These data are consistent with the structure of the salt proposed earlier ([6]).

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Note: Figure translations are in progress. See original paper for figures.