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Abstract

Full Text

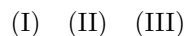
Chemistry

L. A. Kazitsyna, V. V. Mishchenko

IR Spectra of Nitrogen-Containing Derivatives of *o*-Hydroxycarbonyl Compounds of the Aromatic Series

(Presented by Academician A. N. Nesmeyanov on 23 XI 1962)

In the study of the electronic spectra of alkylimines of *o*-hydroxycarbonyl compounds of the type



it was shown that in the region of 400 m μ , in polar solvents, a band is observed whose position changes only slightly with a change in the structure of the compounds, while its intensity depends substantially both on the polarity of the solvent and on the structure of the compound (Table 1) ^(1,2). In the spectra of the compounds themselves without solvent, a band in the 400 m μ region is also observed (Fig. 1).

All the compounds studied are characterized by the presence of a strong intramolecular hydrogen bond. The hypothesis that it is precisely the hydrogen bond in these compounds that is responsible for the appearance of the specific absorption in the 400 m μ region was rejected as a result of a detailed study of the electronic spectra ⁽³⁾.

Table 1

Substance	Methyl alcohol, λ , μ	Methyl alcohol, $\lg \varepsilon$	Chloroform, λ , μ	Chloroform, $\lg \varepsilon$	Isooctane, μ	Isooctane, $\lg \varepsilon$	Without solvent, λ , μ	Without solvent, D
[[structural formula: salicylidene butylimine]]	395	3.08	406	2.27	—	—	405	0.76
[[structural formula: methyl-substituted salicylidene butylimine]]	385	3.67	392	3.23	bend			
[[structural formula: naphthyl salicylidene butylimine derivative]]	406	4.01	413	4.00	413	3.13	* 400-415	0.98

* Paste in vaseline oil.

As the next possible explanation of this phenomenon, the hypothesis was put forward that a benzenoid-quinoid equilibrium is present ⁽²⁾

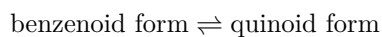


Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

If the assumption of a quinoid structure is correct, then bands of the stretching vibrations of $C=O$ and $N-H$, correspo-

corresponding to a quinoid structure. According to experimental data obtained from the study of electronic spectra, these bands should appear in the spectra of the compounds in polar solvents and in the compounds themselves without solvent; on the contrary, in nonpolar solvents they should not be observed.

We carried out a systematic investigation of the IR spectra of nitrogen-containing derivatives of hydroxycarbonyl compounds in the region of vibrations of multiple

Fig. 1. UV spectrum of salicylalbutylimine without solvent

Fig. 2. a -IR spectrum of salicylaethylamine

in CCl_4 solution and without solvent ($C = 1; 0.2; 0.1$ mol/l).

b -The same in CCl_4 solution ($C = 0.1; 0.01$ mol/l)

bonds ($1500-1700\text{ cm}^{-1}$) on an IKS-12 spectrophotometer and in the region of stretching vibrations of the $N-H$ and $O-H$ groups ($2000-3600\text{ cm}^{-1}$) on an IKS-14 spectrophotometer. IR spectra in the region of multiple bonds were recorded for alkyl- and arylimines of salicylaldehyde, o -hydroxyacetophenone, o -hydroxybenzophenone (IV), and β -hydroxynaphthaldehyde (I. $R = H, C_2H_5, C_4H_9-H, C_4H_9-is\alpha-, -(CH_2)_2-, -(CH_2)_6-, C_6H_5, C_6H_4-CH_3-p, C_6H_4NO_2-p$; II. $R = CH_3, C_2H_5, -(CH_2)_2-, C_6H_5-$; III. $R = C_2H_5-, C_6H_5-, C_6H_4CH_3-p, C_6H_4NO_2-p$; IV. $R = C_2H_5$). In the spectra no absorption is observed that could be assigned to absorption of the carbonyl group of the quinoid form. Nor is any substantial difference observed in the spectra of the compounds themselves compared with their spectra in polar and nonpolar solvents. In the spectra of the compounds investigated, bands that characterize the multiple $C=N$ bond and the phenyl ring are clearly manifested. The absorption band corresponding to $C=N$ stretching vibrations lies within $1620-1640\text{ cm}^{-1}$, has medium intensity, and changes little with the structure of the compound (Table 2). The most substantial shift in the position of the $C=N$ band is observed on going from alkyimines to arylimines and to derivatives of o -hydroxyacetophenone and o -hydroxybenzophenone. IR spectra in the LiF prism region for alkyl- and arylimines of salicylaldehyde (I. $R = H, CH_3, C_2H_5, C_4H_9, iso-C_4H_9, -(CH_2)_2-, -(CH_2)_6-, C_6H_5, p-CH_3C_6H_4, p-NO_2C_6H_4$) in carbon tetrachloride solutions carbon tetrachloride and chloroform in various concentrations (from 1 to 10^{-2}

mole/liter) and for liquid compounds without solvent show the presence of a strong intramolecular hydrogen bond; moreover, the character of the absorption in this region is the same for all the R groups studied and does not change depending on whether the spectrum of the compound is recorded in solvents at different concentrations or without solvent. In Fig. 2a, as an example, the spectra of salicylaethylimine in a CCl_4 solution of various concentrations and without solvent are given. It should be noted that in this region the IR spectra of alkyl- and arylimines differ only in the C – H stretching vibrations (Fig. 2b), whereas the absorption corresponding to the hydrogen bond remains exactly the same. The intensity of the band at 400 μm in the electronic spectra for arylimines decreases by approximately one order of magnitude in comparison with the alkyl derivatives, and for the aryl derivatives the band is shifted into the long-wavelength region ⁽⁴⁾.

Of the compounds listed above, only for the imine of salicylaldehyde itself are there some differences in the IR spectrum (region 2000–3600 cm^{-1}): a band of the free O – H group is observed, as well as absorption in the region 3300–3260 cm^{-1} , which may be attributed to intermolecular hydrogen bonding; the intensity of these bands changes with a change in concentration. Such features in the spectrum of salicylalimine are explained by the fact that it is a trimer having the following structure:

[cyclic trimeric structure of salicylalimine with intramolecular/intermolecular O – H...N hydrogen bonds]

The spectra of the remaining compounds studied in the region 2000–3600 cm^{-1} are characterized by still greater merging of the absorption band

Vibrations of the C = N and C = C bonds of the phenyl ring in alkyl- and arylimines of *o*-hydroxycarbonyl compounds

Compound	Medium	C = N, cm^{-1}	Ph, cm^{-1}
<i>o</i> - HO–C ₆ H ₄ –CH=NR, <i>R</i> = C ₂ H ₅ , H–C ₄ H ₉ , iso–C ₄ H ₉	a	1620	1578; 1498
<i>o</i> - HO–C ₆ H ₄ –CH=NR, <i>R</i> = C ₂ H ₅ , H–C ₄ H ₉ , iso–C ₄ H ₉	b	1634	1584; 1498

Compound	Medium	C = N, cm^{-1}	Ph, cm^{-1}
<i>o</i> - HO-C ₆ H ₄ -CH=NCH ₂ - / corresponding salicylidene fragment	a	1634; 1624	1580; 1498
<i>o</i> - HO-C ₆ H ₄ -CH=N(CH ₂) ₃ - / corresponding salicylidene fragment	a	1634; 1618	1580; 1508
<i>o</i> - HO-C ₆ H ₄ -CH=NC ₆ H ₄ -X, X = H	a	1622	1598; 1522; 1500
<i>o</i> - HO-C ₆ H ₄ -CH=NC ₆ H ₄ -X, X = <i>p</i> -CH ₃	a	1618	1600; 1576; 1500
<i>o</i> - HO-C ₆ H ₄ -CH=NC ₆ H ₄ -X, X = <i>p</i> -NO ₂	a	1618	1602; 1538; 1508
<i>o</i> - HO-C ₆ H ₄ -C(CH ₃)=NR, R = CH ₃ , C ₂ H ₅ , -(CH ₂) ₂ -	a	1616	1576; 1504
<i>o</i> - HO-C ₆ H ₄ -C(CH ₃)=NR, R = CH ₃ , C ₂ H ₅ , -(CH ₂) ₂ -	e	1616	1596; 1576; 1504
<i>o</i> - HO-C ₆ H ₄ -C(CH ₃)=NC ₂ H ₅	a	1612	1578; 1500
<i>o</i> - HO-C ₆ H ₄ -C(C ₆ H ₅)=NC ₂ H ₅	a	1620	1630
<i>o</i> - HO-C ₆ H ₄ -CH=NR, R = C ₂ H ₅	a	1630	—
<i>o</i> - HO-C ₆ H ₄ -CH=NR, R = C ₆ H ₅	a	1620	—
<i>o</i> - HO-C ₆ H ₄ -CH=NR, R = <i>p</i> - C ₆ H ₄ CH ₃	a	1618	—

Fig. 3. IR spectra of imines of *o*-hydroxycarbonyl compounds in CCl₄ solution.

Figure 3: Fig. 3. IR spectra of imines of *o*-hydroxycarbonyl compounds in CCl₄ solution.

Compound	Medium	C = N, cm ⁻¹	Ph, cm ⁻¹
<i>o</i> - HO-C ₆ H ₄ -CH=NR, <i>R</i> = <i>p</i> - C ₆ H ₄ NO ₂	a	1620	—

Notes. a —paste in Vaseline oil; b —without solvent and in CCl₄ and CHCl₃; e —in CCl₄ and CHCl₃; g —in CCl₄ and CHCl₃; a —in CCl₄ and CHCl₃.

...corresponding to hydrogen bonding, toward longer wavelengths as the conjugation in the system increases. Figure 3 gives the spectra of alkyl- and arylimines of salicylaldehyde, *o*-hydroxyacetophenone, *o*-hydroxybenzophenone, and β -hydroxynaphthaldehyde, which well illustrate what has been said above.

Fig. 3. IR spectra of imines of *o*-hydroxycarbonyl compounds in CCl₄ solution:

- 1 —salicylaldehyde ethylimine;
- 2 —*o*-hydroxyacetophenone phenylimine;
- 3 —*o*-hydroxybenzophenone ethylimine;
- 4 — β -hydroxynaphthaldehyde ethylimine.

Thus, in the region 2000–3600 cm⁻¹ we also did not observe absorption that could characterize a quinoid structure. The totality of the data on the IR absorption spectra of the studied alkyl- and arylimines of *o*-hydroxycarbonyl compounds makes it possible to reject the hypothesis of the existence of a benzenoid-quinoid equilibrium for the systems studied.

It is possible that the features of the electronic spectra of alkyl- and arylimines of *o*-hydroxycarbonyl compounds are explained by the formation of a bipolar inner-ion structure. The validity of this assumption can be tested by measuring the dipole moments of such compounds, which have an absorption band in the region of 400 m μ in a nonpolar solvent in which the dipole moment is measured.

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