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Abstract

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INVESTIGATION OF THE STRUCTURE OF HYDROXAMIC ACIDS AND SOME OF THEIR DERIVATIVES BY INFRARED SPECTROGRAPHY

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The properties of benzhydroxamic acids have been studied rather well; however, the question of their chemical structure remains insufficiently clarified. Until recently, in the chemical literature a dual structure has been ascribed to them. For example, two structures are ascribed to monobenzhydroxamic acid:

$$C_6H_5 - C(=O) - N(H) - OH \qquad (I)$$

hydroxamic acid

$$C_6H_5 - C(OH) = N - OH \qquad (II)$$

hydroximic acid

and to dibenzhydroxamic acid, respectively, the structures:

$$C_6H_5 - C(=O) - N(H) - O - C(=O) - C_6H_5 \qquad (III)$$

$$C_6H_5 - C(OH) = N - O - C(=O) - C_6H_5 \qquad (IV)$$

Still greater uncertainty exists concerning the structure of the acyl derivative of dibenzhydroxamic acid—tribenzhydroxylamine, which exists in the form of two crystalline α- and β-modifications with different melting points and different solubility.

Table 1

Fig. 1

Figure 1: Fig. 1

Experiment No.	T_p (C_6H_5)	$T_{p+\beta}$	$T_{p+\beta+\alpha}$	$\Delta\beta$	$\Delta(\beta+\alpha)$	Depression, °C
1	4.885	4.479	4.444	0.406	0.441	0.035
2	4.1515	4.104	4.076	0.411	0.439	0.028
3	4.500	4.091	4.055	0.409	0.445	0.036

Some authors (1−3) believe that these modifications of tribenzhydroxylamine are physical polymorphs; others assign them to tautomeric substances existing in hydroxamic and hydroximic forms, although none of the authors indicates which of the modifications of tribenzhydroxylamine can be assigned one or the other structure.

To decide whether the α- and β-forms of tribenzhydroxylamine are physical polymorphs or chemical isomers, we carried out studies of the possibility and conditions of their interconversion, as well as an investigation by the Sidgwick method and measurement of dipole moments.

No interconversions were observed upon heating and subsequent cooling of the α- and β-forms. Under the influence of nitrogen-containing solvents (pyridine, nitrobenzene, aniline, quinoline), a transition of the less sta-

of the labile β-form into the more stable α-form of tribenzhydroxylamine. The reverse transition of the α-form into the β-form was not observed under any conditions.

This study makes it possible to draw the preliminary conclusion that the α- and β-forms of tribenzhydroxylamine are not polymorphic substances. The results of determinations of cryoscopic lowering of melting points by the Sidgwick method (^4) are given in Table 1.

The depression caused by the addition of the α-form to a saturated solution of the β-form averaged 0.033°. A considerable increase in the depression indicates that the α- and β-forms of tribenzhydroxylamine are isomeric substances.

Measurement of the dipole moments of the α- and β-forms of tribenzhydroxylamine, carried out by the method of dilute solutions (^5), and calculation according to Guggenheim (^6) showed a significant difference in the values of the dipole moments of the forms studied. Thus, the dipole moment of the α-form proved to be 3.78 D, and that of the β-form 4.84 D. Such a difference in the values of the dipole moments confirms the preceding conclusions that the α- and β-forms of tribenzhydroxylamine are isomeric substances.

Fig. 1

Fig. 2

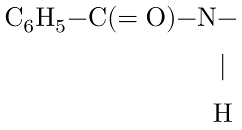
Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2

In order to elucidate the structure of hydroxamic acids and the α- and β-forms of tribenzhydroxylamine in the crystalline state, a study was made of the absorption spectra of these substances in the infrared region of the spectrum from 2.5 to 13 μ, using an IKS-11 infrared spectrophotometer. In the spectrum of monobenzhydroxamic acid (Fig. 1), the intense band at 1661 cm^-1 is typical of monosubstituted amides (^7) and indicates the presence in the molecule of the grouping



$$C_6H_5{-}C(=O){-}\underset{\displaystyle H}{\underset{|}{N}}{-}$$

In the high-frequency region there are frequencies at 3280 and 2730 cm^-1, which apparently belong to vibrations of NH and OH bonds. On the basis of the data presented, it may be considered that the structure of monobenzhydroxamic acid in the crystalline state can most probably be expressed by formula (I). In the spectrum of dibenzhydroxamic acid (Fig. 2), in the region 1600-1750 cm^-1 there are two high-intensity bands at 1650 and 1772 cm^-1. The high intensity and position of these bands make it possible to assign them to vibrations of the CO group in the molecule. The band at 1650 cm^{-1} is characteristic of monosubstituted amides and, as in monobenzhydroxamic acid (1661 cm^{-1}), indicates the presence in the molecule of the grouping

$$C_6H_5 - C(=O) - N - H.$$

The band at 1772 cm^{-1} is due, in our opinion, to an ester carbonyl group. The increase in this frequency (CO) is caused by the presence of a bond of the ester group (through oxygen) with a nitrogen atom possessing an unshared electron pair. The band at 3120 cm^{-1} is assigned to vibration of an NH bond involved in strong intermolecular interaction. Thus it must be recognized that dibenzhydroxamic acid in the crystalline state has structure (III).

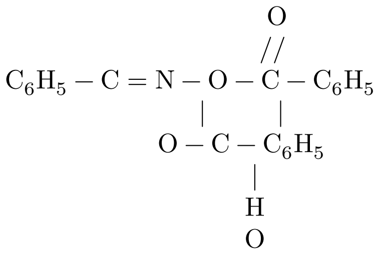
Fig. 3

Fig. 4

Figure 4: Fig. 4

Comparison of the infrared absorption spectra of the α- and β-forms of tribenzhydroxylamine (Figs. 3, 4) shows a great difference between them. This once again indicates that the substances studied are isomeric compounds.

In the spectrum of the β-form (Fig. 3), in the region of double bonds there are three absorption bands: two very intense ones at 1762 cm^{-1} and 1754 cm^{-1}, and a third weak band at 1624 cm^{-1}. On the basis of the considerations given above, 1762 cm^{-1} may be assigned to an ester grouping bound through oxygen to a nitrogen atom, and the band at 1754 cm^{-1} to an ester grouping bound to a carbon atom. The band at 1624 cm^{-1}, owing to its low intensity and low frequency value, is most consistent with the characteristic frequency of C=N (^{8,9}). Proceeding from these data, the β-form of tribenzhydroxylamine may be assigned the hydroxime structure:

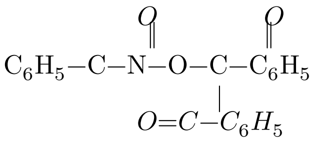


$$\begin{array}{ccccccccccc} & & & & & & & & \mathrm{O} & & \\ & & & & & & & & // & & \\ C_6H_5 & - & \mathrm{C} & = & \mathrm{N} & - & \mathrm{O} & - & \mathrm{C} & - & C_6H_5 \\ & & & & | & & & & | & & \\ & & & & \mathrm{O} & - & \mathrm{C} & - & C_6H_5 & & \\ & & & & & & & & | & & \\ & & & & & & & & \mathrm{H} & & \\ & & & & & & & & \mathrm{O} & & \end{array} \quad (\mathrm{V})$$

Fig. 4

In the spectrum of the α-form (Fig. 4) of tribenzhydroxylamine, in the region of carbonyl frequencies there are two absorption bands. The band at 1776 cm^{-1}, as in the cases considered above, characterizes the ester bond of the carbonyl group in the ester grouping bound through oxygen to a nitrogen atom. The intense band at 1715 cm^{-1} is an amide C=O band. The increase in this frequency is explained by the fact that electronegative groups are bound to the nitrogen atom (^{10}).

No bands were found in the region of double bonds (1620-1640 cm^{-1}). Thus, the molecule of the α-form may be assigned the hydroxamic structure (VI):



$$\begin{array}{ccccccccccc} & & & & O & & & & & & O \\ & & & & \| & & & & & & \| \\ C_6H_5 & - & \mathrm{C} & - & \mathrm{N} & - & \mathrm{O} & - & \mathrm{C} & - & C_6H_5 \\ & & & & & & & & | & & \\ & & & & O & = & C & - & C_6H_5 & & \end{array}$$

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