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INVESTIGATION OF H-COMPLEX FORMATION OF DERIVATIVES OF NAPHTHALIMIDE WITH PHENOL BY IR SPECTROSCOPY

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The H-complex-forming reaction of naphthalimide derivatives with phenol has been investigated by IR spectroscopy. It was shown that for the majority of compounds studied the carbonyl group is the main center of basicity. In the case of amino-substituted imides of naphthalic acid transfer is possible of the reaction center from the carbonyl group to the nitrogen atom of the substituent introduced into the naphthalene ring. However because of steric hindrance this occurs only for amino- and methylamino-substituted naphthalimide.

Keywords: naphthalic acid imides, H-complex formation, proton donor, reaction center, IR spectroscopy.

The spectral–luminescence and electrochemical characteristics of N-imide derivatives of 4-amino-substituted naphthalic acid were investigated in [1] with the aim of studying their structure. Analysis showed that at significant differences in the electron-donating properties of the 4-amino component the fluorescence of these compounds lies in close spectral regions. The value of the electrochemical characteristics (oxidation–reduction potentials) also proved to be close together [2]. Such a leveling of the properties of substituents is probably explained by the different degree of flattening of the molecules caused by steric hindrance arising between the atoms of the substituents and the α-hydrogen atoms of the naphthalene ring. Consequently information obtained from the investigations can hardly be considered adequate. In addition, the lack discovered by us of a linear correlation between the spectral and electrochemical characteristics in the series of 4-amino-substituted imides of naphthalic acid [3] indicates that differences in the properties of the investigated compounds exist and may be detected with appropriate methods of investigation.

Since the electron density distribution is the result of the mutual influence of all the possible effects in a molecule (which is naturally the overall result and our investigations reflect this), we considered it expedient to study its change in one fragment of the molecule, the carbonyl group, as a function of the nature of the substituent in the naphthalene ring, the effect of which is transmitted mainly by the conjugation mechanism. It is possible to obtain a comparative assessment of the electron density at a C=O group by studying its proton accepting ability. Infrared spectroscopy is a convenient method for this, enabling the determination of the values of frequency shifts of hydroxyl group stretching vibrations of the proton donor ($\Delta\nu_{OH}$), forming the H-complex with the compound being studied [4]. This method seems of interest since it displays a high sensitivity towards a factor of the molecular structure, which is very valuable when studying series of compounds with a varying structural parameter. It is sufficiently reliable since $\Delta\nu_{OH}$ is determined with a low relative error compared with other methods. The change in shift ($\Delta\Delta\nu_{OH}$) is sufficiently large and exceeds the error of measurement.

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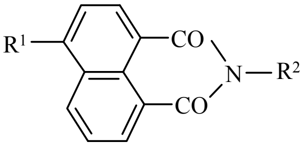
However in view of the inadequate solubility of many of the compounds being studied, it was not possible to carry out measurements in the known system (proton donor–base–carbon tetrachloride). We therefore considered the possibility of investigating such compounds in the proton donor without a solvent, and consequently the choice of proton donor proved to be an important factor in our investigations. It must be a sufficiently weak proton donor, capable of dissolving the compound under investigation. We proceeded from studies on the investigation of carbonyl compounds, according to which the use of the weak proton donor phenol has enabled a solution to problems of the fine structure of organic compounds, the mutual influence of centers of basicity, and other problems having important theoretical significance [4,5]. With the aim of clarifying such a possibility we carried out a comparative study of the compounds of this series, readily soluble in carbon tetrachloride and in a phenol melt. A good linear dependence was obtained between the values of $\Delta\nu_{OH}$ in solution and in the melt: $\Delta\nu_{OH}{}^{s} = \Delta\nu_{OH}{}^{m}\cdot 0.9\text{-}9.36$ (correlation coefficient 0.965). The results obtained agree completely with the literature data.

Proceeding from this, samples of the compounds **1-15** being investigated were prepared by dissolving them in a phenol melt (mp 41°C).



1–15

We successfully obtained samples of composition 1 : 1 sufficiently homogeneous and transparent in the region of the spectrum being investigated. Consequently the spectrograms taken enabled reliable determination of the values of $\Delta\nu_{OH}$ (Table 1). As is evident from the structure the studied compounds have several centers of basicity and consequently the problem of the point of addition of phenol requires proof. A carbonyl group is the chief center of basicity for some (compounds **1-3**), since the imide nitrogen atom, due to the acceptor influence of the two carbonyl groups, is practically devoid of basic properties. The sensitivity of the method to the structure of the studied compounds is easily overlooked in these compounds for which the problem of the reaction center is not in doubt. Changes in the imide portion of the molecule, in which conjugation with a C=O group is practically absent, are clearly consolidated in the shifts of the stretching vibrations of the phenolic hydroxyl group. The same may be said about compounds **6** and **15**, although in them, unlike the previous compounds, addition of proton occurs at the nitrogen of the amino group. It is known that amines are more strongly basic than carbonyl compounds, and in the presence of nitrogen-containing substituents separated from the carbonyl group, interaction at the nitrogen atom of the substituent is also possible. However in the case of conjugation of amino-containing substituents and carbonyl groups in the composition of one compound, transfer of the reaction center to the oxygen atom of the carbonyl group is possible. To clarify such a possibility, additional investigations were carried out allowing for the circumstance that on forming an H-complex at a carbonyl group its absorption band must be displaced in the direction of low frequencies. If complex formation occurs at an atom of the substituent, the value of $\Delta\nu_{C=O}$ must remain practically unchanged or even slightly increased. Analysis of the obtained results (Table 1) shows that for the amino-containing compounds **5** and **8** $\Delta\nu_{C=O}$ in the melt, compared with $\Delta\nu_{C=O}$ in KBr disks, is either unchanged or slightly increased. This is caused by certain acceptor properties, which the amino group acquires on adding a molecule of phenol. The same picture is also observed for 4-methylamino-substituted compound **9**. It is as if the structure of the methylamino group, undergoing partial rehybridization from the sp^2 to the sp^3 state [6], i.e. while acquiring any intermediate structure between these states, remains free to conjugate with the π-electron system of naphthalene and sufficiently available to the proton donor. In the case of compounds **7** and **10**, with two methyl groups, the probability of forming a bond at the nitrogen atom falls sharply, probably due to steric hindrance, and addition

TABLE 1. Data on $\Delta\nu_{OH}$ and IR Spectra of Compounds **1-15**

Compound	R^1	R^2	$\Delta\nu$, cm^{-1}	$\Delta\nu_{C=O}$, cm^{-1}	
				KBr	Melt
1	H	H			1673, 1697
2	H	Ph	174	1692, 1656	1688, 1656
3	H	4-BuC_6H_4	179	1698, 1663	1687, 1653
4	Cl	4-BuC_6H_4	198	1706, 1663	1700, 1651
5	NH_2	Ph	304	1650, 1693	1707, 1674
6	H	4-$H_2NC_6H_4$	221	1678, 1696	1700, 1676
7	NMe_2	Ph	264	1648, 1695	1690, 1644
8	NH_2	4-BuC_6H_4	308	1683, 1656	1684, 1658
9	MeNH	4-BuC_6H_4	235	1656, 1683	1684, 1658
10	NMe_2	4-BuC_6H_4	228	1655, 1695	1688, 1654
11	Piperidyl	4-BuC_6H_4	224	1656, 1702	1698, 1655
12	Morpholyl	4-BuC_6H_4	201	1658, 1697	1689, 1656
13	Morpholyl	MeNH	234	1657, 1695	1700, 1675
14	Morpholyl	NHCOMe	225	1685, 1705, 1745	1720, 1692, 1667
15	H	NH_2	239	1660, 1705	1708, 1660

occurs at the carbonyl group, which is displayed as a reduction of its frequency. It should be mentioned that imides containing cycloaliphatic amines as substituents (compounds **11**, **12**) behave analogously and the influence exerted by them on the stability of the hydrogen bond corresponds to their electronic character. For example, a very small shift of frequency of the hydroxyl group stretching vibrations of phenol, i.e. a very low basicity for the carbonyl group, is observed for the morpholine substituted imide **12** and this substituent exerts a very weak influence on the absorption spectrum [1]. For the compounds in which additional centers of basicity are introduced into the imide portion of the molecule (compounds **13** and **14**), proceeding from the grounds given above it may be stated that in compound **13** protonation occurs at the nitrogen atom of the amino group in the imide portion of the molecule, and in compound **14** at the oxygen atom of the acetyl group. Such a conclusion is in good agreement with the position of the absorption band of the carbonyl group.

The fact discovered by us, that transfer of the reaction center from the nitrogen atom of the substituent in compounds **5**, **8**, and **9** to a carbonyl group in all the remaining amino-substituted imides, confirms indirectly the conclusions made previously that only compounds **5**, **8**, and **9** have a planar structure, while all the remaining substituted imides experience significant steric difficulties. The deviation from the correlation line describing the linear dependence between the transition energy (λ_{max}^{abs}) and the difference in oxidation–reduction potentials, characteristic of just **8** and **9**, indicate that the transfer of reaction center observed by us in the H-complex-forming reaction is also characteristic of oxidation–reduction reactions. In agreement with literature data, together with steric effects, the change in reaction mechanism is the main reason for the disturbance of the linear correlation [7].

EXPERIMENTAL

The IR spectra were obtained on a Specord IR 75 spectrometer in a phenol melt in the range 3000-3700 cm^{-1}.

Compounds **1-15** were synthesized according to known procedures [2,8].

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