THE PICOLINE N-OXIDE SPECTRUM IN THE NO GROUP VALENCY VIBRATION RANGE

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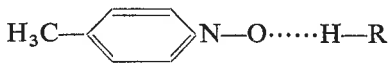
An analysis of the infra-red spectrum of picoline N-oxide in various solvents in the NO group valency vibration range was carried out. The presence of four strong absorption bands and one band of very low intensity is confirmed. The Fermi resonance phenomenon for valency vibrations ν NO and sum frequencies ν_5 was observed and described.

Picoline N-oxide is a strong base capable of forming complexes in which there occur molecular interactions of various type and size. By a suitable choice of proton donor and the physical conditions of the experiment, the occurrence of complexes with a hydrogen bond ranging from weak up to and including proton transfer is produced [1, 2]. Another interesting fact is that the N → 0 bond in picoline N-oxide has features of a double bond; however, sometimes it appears in the resonance modification as a single bond [3, 4]. This latter structure is more often found in associates.

The aim of this work is to analyse the infra-red spectrum of γ-picoline N-oxide in the NO group valency vibration range. The picoline N-oxide to be used in the experiments was first purified by resublimation, and the spectrally clean solvents were dried with 4-Å molecular sieves. Readings were taken on a Perkin Elmer model 521 grating spectrophotometer with a resolution of approximately 1 cm^{-1} or on a Leitz spectrophotometer. These instruments were calibrated by rotation or rotation-vibration spectra of various reference gases.

As results from our readings and the data taken from other papers [1, 3], the frequency for the ν NO valency vibration is about 1250 cm^{-1}. This frequency depends on the character of the solvent; in polar proton donor solvents the shift of the frequency ν NO is significant. This can be explained by the formation of a hydrogen bond:



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The results of the shift of frequency ν NO observed in solutions of different solvent activity are presented in Table I. For the system picoline N-oxide-acid in non-polar solvents such as carbon tetrachloride or carbon disulphide, a strong hydrogen-bond influence

TABLE I

The shift of frequency ν NO observed in solutions

Solvents	ν NO [cm^{-1}]	$\Delta\nu = \nu - \nu_{ass}$ [cm^{-1}]	$\frac{\Delta\nu}{\nu}$ [%]
—	1276	—	—
n-hexane	1265	11	0.9
carbon tetrachloride	1260	16	1.2
carbon disulphide	1258	18	1.4
dichloromethane	1250	26	2.0
nitromethane	1247	29	2.2
acetonitrile	1246	30	2.3
chloroform	1244	32	2.5
methanol	1240	36	2.8
aniline	1232	44	3.4
nitromethane + methanol	1215	61	4.8
nitromethane + buthanol	1213	63	4.9
nitromethane + trichloroacetic acid	1213	63	4.9
nitromethane + trifluoroacetic acid	1211	65	5.1
nitromethane + *p*-chlorophenol	1211	65	5.1
nitromethane + acetic acid	1210	66	5.2
nitromethane + phenol OD	1209	67	5.3
nitromethane + *p*-cresol	1208	68	5.3
nitromethane + phenol	1207	69	5.4

is observed. The shift of the frequency of the NO group valency vibrations in other solvents such as nitromethane, for example, is then of the order of 50 cm^{-1}. The hydrogen bond is partially responsible for such a large value of shift.

An analysis of the infra-red spectra of solutions of picoline N-oxide in certain selected solvents was also carried out. The measurements were made in the range of 1150 cm^{-1} to 1300 cm^{-1}. The concentration of picoline N-oxide was less than 0.01 M/l. In the spectral region under examination results confirmed the presence of four strong absorption bands and one of very low intensity. The measured frequencies of these bands are set out in Table II; in addition, in Fig. 1 sample spectra of picoline N-oxide solution in carbon tetrachloride, nitromethane and methanol are shown.

The band with an approximate frequency of 1250 cm^{-1} undoubtedly comes from the NO group valency vibrations [1]:

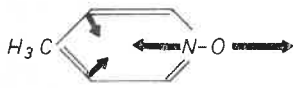

TABLE II

The absorption bands of picoline N-oxide

Solvents	stretching vibrations of NO	in-plane deformation vibrations of aromatic ring			summation bands
	ν_1	ν_2	ν_3	ν_4	ν_5
aniline	1232	1220	1210	1180	1250
methanol	1240	1215	1209	1175	1250
chloroform	1244	1228	1210	1171	1250
nitromethane	1247	1228	1213	1170	1252
acetonitrile	1246	1228	1213	1170	1254
carbon disulphide	1258	1233	1212	1167	1250
carbon tetrachloride	1260	1235	1210	1164	1250
n-hexane	1265				
nujol	1244	1222	1208	1184	

By analogy with the pyridine N-oxide spectrum, investigated by Kida and coworkers [3], we ascribe the frequencies ν_2, ν_3, ν_4 to the in-plane deformation vibrations of the CH groups in the aromatic ring. Such an interpretation conforms with the opinion of

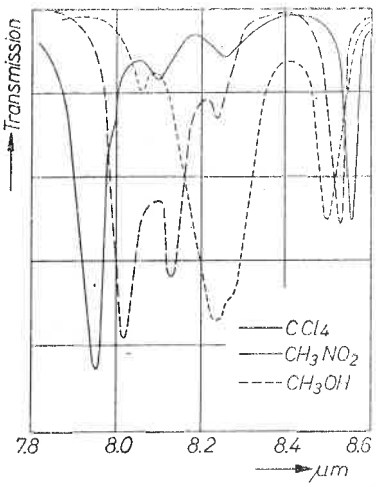

Fig. 1

Bellamy [5]. It appears that the weak ν_5 band found as a result of our analysis of the shape of the absorption contour is the sum of out-of-plane deformation vibrations of the CH group with frequencies of approximately 750 cm^{-1} and a band in the region of 510 cm^{-1}, attributed to the NO group. The latter correspondence confirms the fact that in

picoline no absorption band in the 600 to 400 cm^{-1} range is observed. The position of the ν_5 band depends only slightly on the character of the solvent.

Our attention was focused on the vibrations of the N → O bond which, as we already know, behaves similarly to the C = 0 bond in carbonyle compounds. Bellamy [6] showed there exists a straightforward dependence between ν NO of the system XN = 0

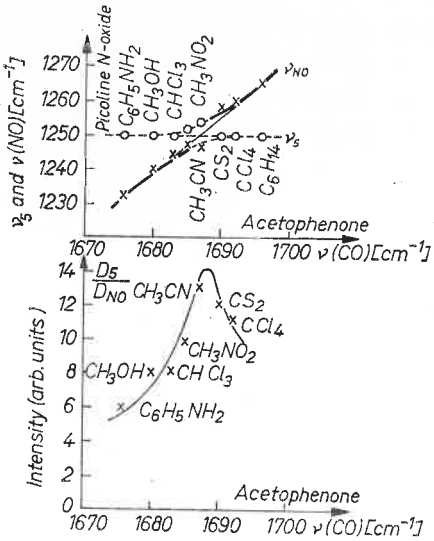

Fig. 2

and the corresponding values ν CO for CH_3COX compounds on the assumption of identical substituents X and solvents.

Making use of the above information, it is possible to compare the ν NO frequency observed for picoline N-oxide with the ν CO frequencies of acetophenone measured in the same solvents. The dependence of ν NO on ν CO is presented in Fig. 2a.

It can be seen that in a majority of the solvents used the frequency of the NO group valence vibrations is proportional to the vibration frequency of the CO group. Deviations from linear dependence between $\nu_1 \equiv \nu$ NO and ν CO can be observed when the NO valency vibration frequency falls near 1250 cm^{-1}. This occurs, for example, in such solvents as acetonitrile, carbon disulphide and nitromethane.

The second of the two examined bands maintains an almost constant frequency equal to 1250 cm^{-1}. This means that the energy $E_5^0 = h\nu_5$ is only very slightly affected by the reactions with the solvent. Deviations from the linear dependence ν_1 and ν_5 on ν CO are observed around the intersection point of the corresponding straight lines. From Fig. 2a it can be seen a marked disruption of the energy levels occurs here.

Also characteristic is the shape of the dependence of the relative optical density of the bands ν_1 and ν_5 presented in Fig. 2b. A maximum is observed in the neighbourhood of the frequency at which the energy levels E_1^0 and E_5^0 should cross.

These two experimental facts can be probably explained by the Fermi resonance [7, 8, 9] between the ν NO valency vibration frequency and the sum frequency ν_5.

In quasi-inert solvents, such as *n*-hexane and carbon tetrachloride, the level E_1^0 is above E_5^0 and the distance between them $\delta = |E_5^0 - E_1^0|$ is approximately equal to 15 cm^{-1}. Such an energy gap is large enough to make the resonance interaction impossible. A similar situation occurs in solvents with strong proton donor properties. The distances between the levels under consideration are also of the order of 15 to 20 cm^{-1} but the energy E_5^0 is greater than E_1^0. The energy difference δ in acetonitrile, is of the order of 0.5 cm^{-1} and similar small energy differences are observed in carbon disulphide and nitromethane. In such cases the energy levels E_1^0 and E_5^0 are so near to each other that strong coupling takes place between them. As a result of the resonance interaction there appears a shift of the energy levels $\Delta = |E_5 - E_1|$, where E_5 and E_1 are energies of the transitions ν_5 and ν_1 after the occurrence of Fermi resonance. From experimental data it can be seen that in acetonitrile Δ equals about 6 cm^{-1}, that is, an order higher than δ. The energy difference in such solvents as nitromethane or carbon disulphide is approximately the same as Δ in acetonitrile.

An outcome of the strong resonance interaction is the removal of the degeneracy of levels E_1^0 and E_5^0, which appears in the infra-red spectrum as two markedly separate absorption bands of relatively high intensity.

The frequencies ν_2, ν_3 and ν_4 do not show anomalous changes in the series of solvents investigated.

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