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INFRARED SPECTROMETRIC STUDY OF THE INTERACTION BETWEEN 2-DIMETHYLAMINO-3,3-DIMETHYL-1 AZIRINE AND SOME PHENOL DERIVATIVES

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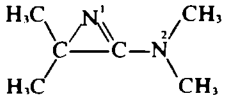
Abstract—The H-bonded compleses between 2-dimethylamino-3,3-dimethyl-1-azirine (TMAAZ) and some phenol derivatives have been studied by IR spectrometry in carbon tetrachloride. The equilibrium constants at 300, 315 and 328 K and the $-\Delta H°$, $-\Delta\nu_{OH}$ and $\Delta\nu_{C-N}$ values have been determined. The comparison with previously studied OH...N complexes shows that TMAAZ forms stronger complexes than would be expected from the pK_a value. These facts are discussed in terms of steric, hybridization, solvation and charge transfer effects. From a pK_a of 8, the IR spectrum shows the appearance of ion pairs N^+–H... O. A predominance of protonated species can be calculated for a pK_a of 6. This can explain why 1,2-ring cleavage whose first step is probably the formation of an azirinium cation, occurs for acids characterized by pK_a values lower than 5 but not for enolizable ketones having pK_a values higher than 9.

INTRODUCTION

Hydrogen-bonded complexes between phenol derivatives and nitrogen bases such as aliphatic amines, pyridines or anilines have been extensively studied by spectroscopic methods; there is however no information on the complexing properties of 3-membered cyclic amidines. In this work, an attempt has been made to report some thermodynamic and spectroscopic properties of the H-bonded complexes formed between phenol derivatives and 2-dimethyl-amino-3,3-dimethyl-1-azirine (TMAAZ).

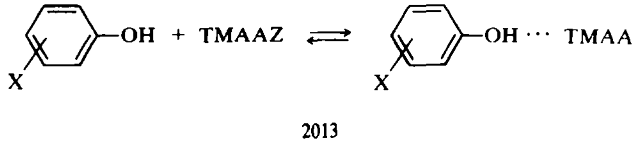


In this molecule, the value of 58.5 kJ mol^{-1} for the barrier to rotation about the C^2–N^2 bond[1] suggests an important delocalization in the $N^1 = C^2$–N^2 chain; this value is about 4 kcal mol^{-1} higher than in the amidines characterized by the same degree of substitution. For these amidines, an IR[2] and dipolemetric study[3] suggest that the formation of an H-bond with hydroxylic derivatives takes place on the imino-N atom; *ab initio* calculations[4] show that in the azirines, the preferential protonation site is the σ pair of the endocyclic N atom.

The minimal basis set (STO-3G) Gaussian *ab initio* method was used in quantum chemical calculations.[4]

EXPERIMENTAL

TMAAZ was synthetized by a method already described.[5] The other materials were obtained commercially. Phenol (Merck p.a.), the halogenated derivatives (Fluka purissimum p.a.) and 3,5-diCF₃ phenol (Pierce Chem. Co.) were recrystallised from petroleum ether. CCl_4 (Baker for spectroscopy) was dried on molecular sieves 4 Å. Spectral measurements were carried out on a P.E. 325 spectrophotometer. The temp. in the cell was measured by means of a thermistor immersed in the cell. The equilibrium constant of the following reaction was calculated by measuring the absorbance of the $1\nu_{OH}$ band at ~3600 cm^{-1},[6] with concentrations ranging from 5 to 25 × 10^{-3} mol dm^{-3} for the phenol derivatives and from 10 to 80 × 10^{-3} mol dm^{-3} for TMAAZ. In this limited range, the value of K remains constant and only complexes of 1:1 stoichiometry contribute to the spectra.



The spectra were recorded in CCl_4 at 300, 315 and 328 K immediately after the preparation of the solns to avoid further reactions. After 5 hr, no variation of the absorbance of the ν_{OH} and ν_{C-N} was observed. It can thus be concluded that at these temps and low concentrations, TMAAZ does not react with phenol. However, on refluxing TMAAZ in the presence of phenol, a dihydropyrazine derivative was obtained.[7] A reaction with CS_2 has been described,[8] but no reaction could be detected with CCl_4.

Table 1. Association constant, K(dm^3 mol^{-1})* at 300(±0.5), 315(±0.5) and 328(±0.5)K

PHENOL DERIVATIVE	K^{300K}	K^{315K}	K^{328K}
3,4-diCH$_3$ phenol	106	59	40
4-CH$_3$ phenol	146	64	45.5
phenol	190	103	71.5
4-Cl phenol	428	246	151
3-Cl phenol	532	367	255
4-I phenol	584	303	226
3-Br phenol	697	346	244
3,4-diCl phenol	1300	615	394
3,5-diCl phenol	2263	1043	642

* standard deviation = $(\frac{\Sigma\Delta K^2}{n})^{1/2}$ = 5%

RESULTS AND DISCUSSION

Figure 1 shows the IR spectrum (3600–3000 cm^{-1}) obtained for TMAAZ-Phenol; by adding TMAAZ, a lowering of the absorbance of the free ν_{OH} band and a new band lying at about 3150 cm^{-1} ascribable to the $\nu_{OH\cdots N}$ vibration were observed.

The association constants determined at three temps

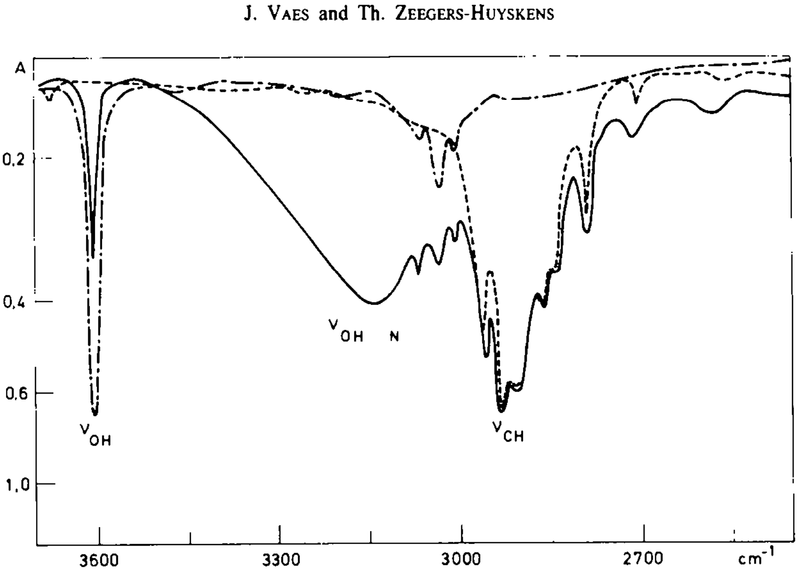


Fig. 1. IR spectrum (3600–2600 cm^{-1}); –·–·– Phenol (C = 10 × 10^{-3} mol dm^{-3}); ----- TMAAZ (C = 15 × 10^{-3} mol dm^{-3}); ——— Phenol + TMAAZ (same concentrations S = CCl_4; d = 0.002 m.

Table 2. Association enthalpy, $-\Delta H\cdot$ (kJ mol^{-1}) and frequency shift $\Delta\nu_{OH}$ and $\Delta\nu_{C=N}$ (in cm^{-1})

PHENOL DERIVATIVE	$-\Delta H°$	$\Delta\nu_{OH}$ *	$\Delta\nu_{C=N}$ **
3,4-diCH_3 phenol	29.7	433	6
4 CH_3 phenol	30.1	437	7
phenol	31.3	451	7
4-Cl phenol	32.6	489	7
3-Cl phenol	32.2	490	8
4-I phenol	31.8	491	8
3-Br phenol	33.4	495	8
3,4-diCl phenol	34.7	521	8
3,5-diCl phenol	35.5	541	8
3,5-diCH_3 phenol	-	543	9

* accuracy = 5 cm^{-1} for the broad absorption bands ($\nu_{OH...N}$) and 1 cm^{-1} for the narrow absorption bands ($\nu_{C=N}$).

** registred in extended scale.

Table 3. Association parameters for OH . . . N bonds

	ANILINE	PYRIDINE	TMAAZ	TRIETHYLAMINE
pK_a	4.57	5.17	6.9	10.65
$K(dm^3.mol^{-1})$	4.6 [6]	46.3 [6]	190	48.5 [11]
$\Delta\nu_{OH}(cm^{-1})$	350 [6]	470 [6]	451	∼ 550 [11]
$-\Delta H°$ (kJ mol^{-1})	21.7 [16]	27.2 [14]	31.3	33.4-37.6 [15]
$-\Delta S°$ (J $mol^{-1}K^{-1}$)	58.5 [16]	62.7 [14]	54 - 58	79 - 88 [15]

(300, 315 and 328 K), the association enthalpies $-\Delta H°$ calculated from the values of K at 300 and 328°K are given in Table 1, which also lists the values of $\Delta\nu_{OH}$, the lowering of the 1 ν_{OH} vibration band and $\Delta\nu_{C=N}$, the enhancement of the wave number of the 1 $\nu_{C=N}$ vibration.

(1) *Influence of the substitution on the association parameters*

The influence of the substitution on the stability of the complexes can be expressed by a Hammett relation; for each temp., the least squares method leads to the following equations (r = correlation coefficient)

$$\log K^{300K} = 2.34 + 1.32\,\Sigma\sigma_H \quad (r = 0.997)$$
$$\log K^{315K} = 2.05 + 1.29\,\Sigma\sigma_H \quad (r = 0.998)$$
$$\log K^{328K} = 1.89 + 1.25\,\Sigma\sigma_H \quad (r = 0.999)$$

showing that ρ diminishes slightly with increasing temp. At room temp. (300 K) the ρ value can be compared with values obtained for other systems, such as the complexes of the same phenol derivatives with aniline ($\rho = 0.67$),[9] with pyridine ($\rho = 0.98$)[10] and with triethylamine (ρ = 1.32).[11] This suggests that ρ cannot be related to the pK_a value of the base; better correlations—although not linear—are obtained using the values of $-\Delta H°$, the association enthalpy.[12]

Substitution on the phenol ring has also a marked influence on $\Delta\nu_{OH}$ values; these are greater for electron-attracting substituents and the Hammett relation can be written

$$\Delta\nu_{OH} = 456 + 109\,\Sigma\sigma_H. \qquad (r = 0.992)$$

In the same family of complexes, the $\Delta\nu_{OH}$ values are linearly related to the association enthalpies.

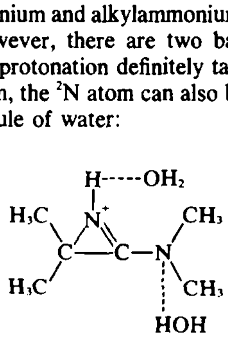
(2) *Comparison with other* OH . . . N *complexes*

The values listed in Table 3 allow comparison of the pK_a values of some nitrogen bases and the K, $-\Delta H°$, $\Delta\nu_{OH}$ and $-\Delta S°$ values relative to the unsubstituted phenol taken as reference acid.

It is clear that the K value relative to the complex phenol-TMAAZ is higher than would be predicted from the pK_a of the base and some factors may affect the pK_a in aqueous solutions and the association parameters differently.

On the one hand, the cyclic amidines are characterised by lower pK_a values than the amidines of the same degree of substitution, in spite of a greater delocalisation in the N^1=C-N^2 group. The weak basicity can be explained by *hybridization* effects in the strained cyclic molecules; in such molecules, the endocyclic atoms of the ring contain more pure 2p orbitals.[17,18] As a result, the s character of the free electron pair on the endocyclic N atom is more pronounced. Hybridization plays an important role in the basicity of nitrogen bases[19,20] and the lower the p character, the lower the basicity.

The basicity is also affected by solvation stabilization of the basic sites; these effects tend to stabilize ions such as anilinium, pyridinium and alkylammonium.[21,22] In the case of TMAAZ however, there are two basic centres and eventhough the protonation definitely takes place on the ^{1}N nitrogen atom, the ^{2}N atom can also be solvated by at least one molecule of water:



In such a structure, the electronic pair of the N^2 atom is partially engaged in the hydrogen bond and the delocalisation in the N^1=C–N^2 is lowered. The value of 58.5 kJ mol^{-1} for the barrier to rotation around the C–N^2 bond has been determined experimentally in $CDCl_3$ and does not appreciably differ from the value calculated theoretically for the isolated molecule[4] but this barrier may be lower for a solvated molecule. In the extreme case, the rotational barrier calculated for the molecule protonated on the N^2 atom was found equal to 0 kJ mol^{-1}.[4]

Basicity measured in water does not provide a completely accurate scale of basic strength. Proton affinity measurements should give a better scale but have not yet been carried out for the azirines.

On the other hand, the thermodynamic parameters of H-bonded complexes are influenced by several factors. First of all, theoretical calculations based on Murrell's second-order perturbation theory of intermolecular forces have shown that H-bonding becomes stronger as the acceptor lone pair orbital possesses less s character.[23] Increase in the s character of the lone pair of ^{1}N should discourage both H-bond formation and protonation. This suggests that hybridization does not play a determining role in the stability of the complexes studied in this work.

Two other factors must be taken into account in order to explain the great complexing ability of TMAAZ.

1. The accessibility of the endocyclic nitrogen atom; the CN^{1}C angle—determined by X-ray crystallography—was found to be 61° (for 2 N,N-Dimethyl-3 phenoxy-3 amido-1 azirine)[24] and the approach angle available for the formation of a H-bond is about 300°; this angle is estimated as 244° for pyridine and is much smaller for triethylamine where the accumulation of three alkyl groups produces an important steric strain; this agrees with the high $-\Delta S°$ values usually found for complexes of tertiary aliphatic amines.

(2) The net charge density on the ^{1}N atom found by *ab initio* calculations[4] is $-0.25\,e$ in the isolated molecule. This value is probably very similar in apolar solvents of low dielectric constant. This value is higher than the net charge density on the N atom of pyridine $(-0.14\,e)$[25] or aniline $(+0.06\,e)$[26] and the enhancement of the dipolar and polarization effects favorizes the formation on an H-bond. High charge density also facilitates charge transfer from the non-bonding electrons to the σ^*_{OH} antibonding orbital of the OH group

(3) *Frequency shift of the* $\nu_{C=N}$ *vibration*

Figure 2 indicates that the wavenumber of the $\nu_{C=N}$ stretching vibration of TMAAZ, lying at 1771 cm^{-1} in the free molecule, shifts to higher value when complexed with 3-Cl phenol; the shifts are higher for more acidic phenols. This frequency enhancement is rather unusual but has been observed for the $\nu_{C\equiv N}$ vibration of nitriles complexed with Lewis acids such as $SnCl_4$, $AlCl_3$, BF_3.[27-29] In these complexes, the increase in the force constant of the C≡N bond is usually explained by a lowering of the distance between the two atoms and by a more pronounced s character of the bond. This explanation is not consistent with the theoretical data relative to TMAAZ; calculations show that the C=N^1 distance increases from 1.296 to 1.306×10^{-8} cm and the C–N^2 distance decreases from 1.366 to 1.315×10^{-8} cm on protonation.[4] Thus the two distances become very *similar* in the protonated species and, in our case, the enhancement of the $\nu_{C=N}$ band could be better explained in terms of coupling between the ν_{C-N^2} and $\nu_{C=N^1}$ vibrations. The variations in the two distances in the H-bonded complex are of course less than in the ion but are expected to vary in the same sense.

(4) *Proton transfer in the hydrogen bond*

For H-bonded complexes of phenols whose pK_a is higher than 8.20 (CH_3, H, 4-Cl, 3,4-diCl) the IR shows a broad absorption band lying at 3200–3100 cm^{-1} (ν_{OH} N

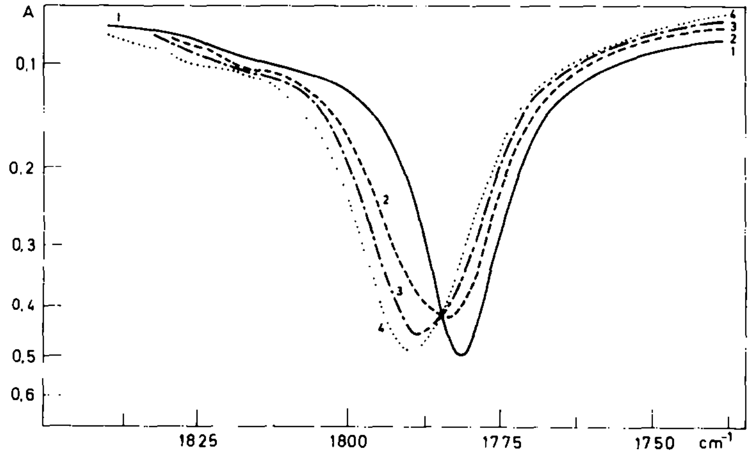


Fig. 2. IR spectrum in the $\nu_{C=N}$ region. $C_{TMAAZ} = 15 \times 10^{-3}$ mol dm^{-3}; $C_{3\text{-Cl phenol}}$: (1) = 0; (2) = 7×10^{-3}; (3) = 9×10^{-3}; (4) = 15×10^{-3} mol dm^{-3}.

vibration) but for 3,5-diCl phenol (pK_a = 8.18) a second band was observed in the range 2800–2500 cm^{-1}; the intensity of this band increases for the more acidic 3,5-diCF$_3$ phenol (pK_a = 7.80). The presence of this band can be ascribed to the formation of proton transferred species[30] ($O^- \ldots H^+N$ bonds). From a pK_a of 8 it thus seems that ionic complexes appear in solution. On the other hand, some recent experiments by Vittorelli *et al.*[31] indicate that the reaction of carboxylic acids (pK_a = 3.75–4.75) or enolizable ketones (p$K \simeq 5$) with TMAAZ yields adducts resulting from a 1,2-opening of the 3-membered ring; in these reactions the first step is probably the formation of an azirinium cation. However, the enolizable ketones (pK_a = 9) do not react. The results of the present work suggest that from a pK_a = 8, formation of protonated species occurs; moreover, previous work suggests that the transition from the case where the fraction of ion pairs is only 0.1 to the case where it reaches 0.9, takes place within a range of 2 pK_a units.[32] For the complexes of the present work, an important proportion of ion pairs should be obtained when the pK_a of the hydroxylic compound is about 6. Below this pK_a, in solvents of low dielectric constants (pentane, xylene), TMAAZ will be protonated and will, in a further step, undergo 1,2-cleavage. The enolizable ketones (pK_a = 9, or higher) are not strong enough acids to protonate TMAAZ and only form hydrogen-bonded complexes with this molecule.

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