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Matrix isolation infrared studies of complexes formed between substituted phenols and trimethylamine

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Abstract

Infrared spectroscopy and matrix isolation technique have been used to study the 1:1 complexes formed between 2,4,5-trichlorophenol (TCP), pentachlorophenol (PCP) or 2-chloro-4,6-dinitrophenol (CNP) and trimethylamine (TMA) isolated in solid argon. The results were analyzed in relation to the type of complex formed. Depending on the proton-donor ability of the phenol three different types of hydrogen bonded complexes have been identified in argon matrices. The weakest phenol in the series, TCP ($pK_a = 6.72$), forms a strong molecular hydrogen bonded complex with TMA as indicated by the broad $\nu(\text{OH}\cdots\text{N})$ absorption with a maximum at 2490 cm^{-1} and a band at 811 cm^{-1} due to the $\nu_s(\text{C}_3\text{N})$ mode of the perturbed amine. The strongest phenol, CNP ($pK_a = 2.01$), interacts with TMA in an argon matrix to form ionic complex with the proton transferred to the base molecule. This is evidenced by the presence of the $\nu(\text{NH}^+\cdots\text{O}^-)$ absorption between $3000\text{--}1800\text{ cm}^{-1}$, by the $\nu_{\text{as}}(\text{C}_3\text{N}^+)$ and $\nu_s(\text{C}_3\text{N}^+)$ absorptions due to the protonated amine and by numerous product bands due to the relatively strongly perturbed modes of the phenol ring. The interaction between TMA and a phenol of intermediate strength, PCP ($pK_a = 4.74$), in solid argon probably leads to the formation of two types of hydrogen bonded complexes: an ionic complex with the proton transferred to the amine molecule and a pseudosymmetric one with the proton more or less equally shared between the phenol and amine molecules. In this case the protonic absorption consists of two broad features situated in the $3000\text{--}1600\text{ cm}^{-1}$ and $950\text{--}400\text{ cm}^{-1}$ regions due to the $\nu(\text{NH}^+\cdots\text{O}^-)$ and $\nu(\text{O}\cdots\text{H}\cdots\text{N})$ modes, respectively. © 1997 Elsevier Science B.V.

Keywords: Phenol; Matrix isolation; Infrared spectra; Hydrogen bond

1. Introduction

A broad protonic absorption of the $\nu(\text{AH})$ stretching vibration observed in the infrared spectra of the $\text{A}\cdots\text{H}\cdots\text{B}$ complexes with a strong hydrogen bond still remains a subject of interest. Various mechanisms have been suggested to explain this anomalous broadening of the $\nu(\text{AH})$ band. Most important seems to be the anharmonic coupling of the $\nu(\text{AH})$ mode with low

frequency bridge vibrations, although other mechanisms may also have an influence on the spectroscopic behaviour of the hydrogen bond [1].

It is still not clear to what extent the environment influences the H-bond properties. From this point of view helpful information may be supplied by infrared low temperature matrix isolation spectroscopy. The $\nu(\text{AH})$ bands of the hydrogen bonded complexes isolated in inert gas matrices are usually narrower than in solutions or in the solid phase. However broad and very broad $\nu(\text{AH})$ absorptions have also been reported [2–10].

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The complexes of hydrogen halides, especially HF and HCl, with a wide range of bases have been most thoroughly studied in low temperature matrices [11–13]. On the basis of a so called correlation diagram [14] a classification of the $AH \cdots B$ hydrogen bonds into three types was introduced. Type I comprises complexes with weak or medium strength bases. In the infrared spectra they give rise to the $\nu(AH)$ band situated between $2700\text{--}2000\text{ cm}^{-1}$; the low frequency shift of this band depends on the base strength. Type II includes complexes with so called “pseudosymmetrical” hydrogen bonds (where the proton is more or less equally shared between the halogen atom and the base) which give rise to the $\nu(A \cdots H \cdots B)$ stretching frequency near 700 cm^{-1} . In the type III complexes the proton is more closely associated with the base molecule; the protonic absorption due to the $\nu(BH^+)$ mode is usually located between $2800\text{--}2000\text{ cm}^{-1}$. Recently, an intermediate type of H-bonds was reported with the $\nu(AH)$ absorption located in the $1750\text{--}1600\text{ cm}^{-1}$ region [13,15,16].

There is very little information on the complexes of other proton donors such as carboxylic acids or phenols in low temperature matrices although they have been extensively studied in solutions and the solid state (see for example Refs. [17–24]). Several papers have been published on complexes of trifluoroacetic acid complexes with different bases in solid argon [3,4,25,26]. The weakly bonded complexes between phenols and carbon monoxide in argon matrices have been studied by Gebicki and Krantz [27]. Recently, phenol complexes with ammonia and methanol have been a subject of ab initio calculations [28–30].

The present paper reports the infrared spectra of strong H-bonded complexes formed between substituted phenols: 2,4,5-trichlorophenol TCP, ($pK_a = 6.72$), pentachlorophenol PCP, ($pK_a = 4.74$) or 2-chloro-4,6-dinitrophenol CNP, ($pK_a = 2.01$) and trimethylamine TMA in argon matrices. Infrared spectra of the corresponding complexes of TCP, PCP and CNP with triethylamine (TEA) in different solvents are also presented for comparison. The substituted phenols selected for our studies form with TMA three possible types of H-bonded complexes: molecular (I), pseudosymmetrical (II) and ionic (III).

2. Experimental

2,4,5-Trichlorophenol (TCP), pentachlorophenol (PCP) and 2-chloro-4,6-dinitrophenol (CNP) were obtained from Fluka AG. They were purified and dried by standard methods. Trimethylamine (TMA) (Matheson) was used without further purification. Triethylamine (TEA) (Koch-Light) was distilled and dried over 4A sieves.

Two different deposition systems were constructed for matrix preparation. TCP was evaporated from a small glass tube containing a solid sample of TCP held at a temperature $285\text{--}288\text{ K}$. The phenol container was placed outside the vacuum vessel of the cryostat. TCP vapour was mixed with argon or with TMA/Ar mixture at about 5 cm distance from the cold window. In order to obtain matrices containing PCP or CNP small amounts of these phenols were introduced into a very small glass tube equipped with a heater. The tube was placed inside the vacuum vessel of the cryostat. The PCP and CNP phenol samples were kept at ca. 330 and 320 K , respectively. Argon or TMA/Ar mixture was deposited simultaneously through the separate jet. An accurate concentration of phenols in matrices was not known but it could be varied by changing the temperature of the solid samples. Most spectra were taken at such conditions which allowed us to avoid phenol polymer formation. A large excess of the base was used to increase the concentration of complexes formed in matrices: TMA/Ar was between $1/50$ and $1/300$.

Gas mixtures were condensed onto a CsI window maintained at a temperature 20 K by means of a helium cryocooler CTI Cryodyne Model 21. Infrared spectra between $4000\text{--}300\text{ cm}^{-1}$ were recorded on a Perkin–Elmer 180 spectrophotometer.

For solution measurements a cell with optical length 0.13 mm and KBr windows was used. Typical concentration of the phenols and TEA was equal to 0.2 mol dm^{-3} . All solvents (tetrachloromethane, dichloromethane, 1,2-dichloroethane, acetone and acetonitrile) were freshly distilled before use.

3. Results

3.1. Parent molecules in argon matrices

Blank experiments were conducted for all reagent

molecules deposited separately. The infrared spectrum obtained for TMA in argon agreed well with that previously reported [31]. To our knowledge none of the studied phenols was examined, so far, by matrix isolation spectroscopy.

At the conditions of the experiment mainly phenol monomers were present in matrices as indicated by the $\nu(\text{OH})$ regions of the spectra. For TCP a prominent rather narrow doublet at 3561 and 3550 cm^{-1} was observed. The 3561, 3550 cm^{-1} bands occur in the region expected for monomer OH stretching vibration of phenol involved in a weak intramolecular hydrogen bond (syn-form of TCP) [27]. The doublet structure of the $\nu(\text{OH})$ absorption is probably due to environment effects which are phenomena one often comes across in matrix studies. In addition to the monomer absorption a weak band appeared at 3443 cm^{-1} . It grew in intensity relative to the $\nu(\text{OH})$ bands of the TCP monomer when the deposition temperature of the solid sample increased and it is consequently assigned to the $(\text{TCP})_2$ dimer. A similar position of the $\nu(\text{OH})$ band was observed in the spectra of PCP isolated in argon matrix where a relatively narrow and intense band at 3534 cm^{-1} was found. The $\nu(\text{OH})$ region of CNP in solid argon was different from those for TCP and PCP. One band was observed at 3120 cm^{-1} ($\Delta\nu_{1/2} = 80 \text{ cm}^{-1}$) with a weak shoulder at 3230 cm^{-1} . The position of this absorption is consistent with the

frequency expected for the OH stretching vibration of a hydroxyl group bonded by a strong intramolecular hydrogen bond to a nitrosubstituent [32,33]. No significant absorption was observed at either higher or lower wavenumbers in this region indicating that the intramolecular hydrogen bonded phenol was the only form of CNP present in the studied matrices.

The whole range infrared spectra (4000–300 cm^{-1}) of TCP, PCP and CNP isolated in argon matrices are shown in Fig. 1(a), Fig. 2(a) and Fig. 3(a), respectively. The assignments are gathered in Table 1, Table 2 and Table 3.

3.2. Complexes of phenols with trimethylamine in argon matrices

3.2.1. 2,4,5-Trichlorophenol with trimethylamine (TCP–TMA)

Fig. 1(b) shows the infrared spectrum obtained for TCP codeposited with TMA/Ar mixture (1/100). Bands which appeared due to the complex formation are marked with arrows. A new relatively broad band with a maximum at 2490 cm^{-1} extending between 2900–2000 cm^{-1} was observed. A high wavenumber limit of this absorption was overlapped by the $\nu(\text{CH}_3)$ bands of TMA and was difficult to estimate. For very thick matrices an additional extremely weak component at ca. 1850 cm^{-1} could be seen independently

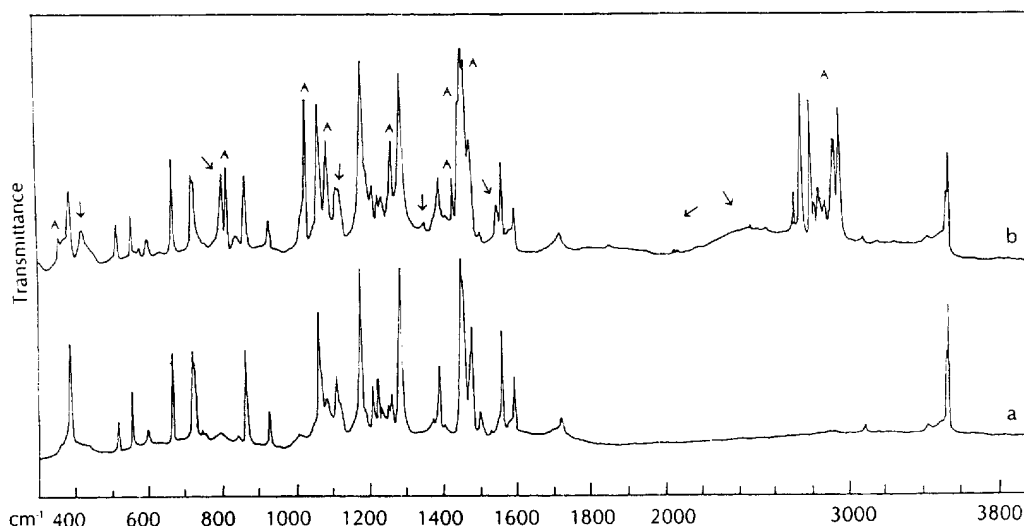


Fig. 1. Infrared spectra of (a) TCP in argon matrix, (b) TCP codeposited with TMA/Ar = 1/100. Arrows indicate TCP–TMA complex bands; A, TMA absorptions.

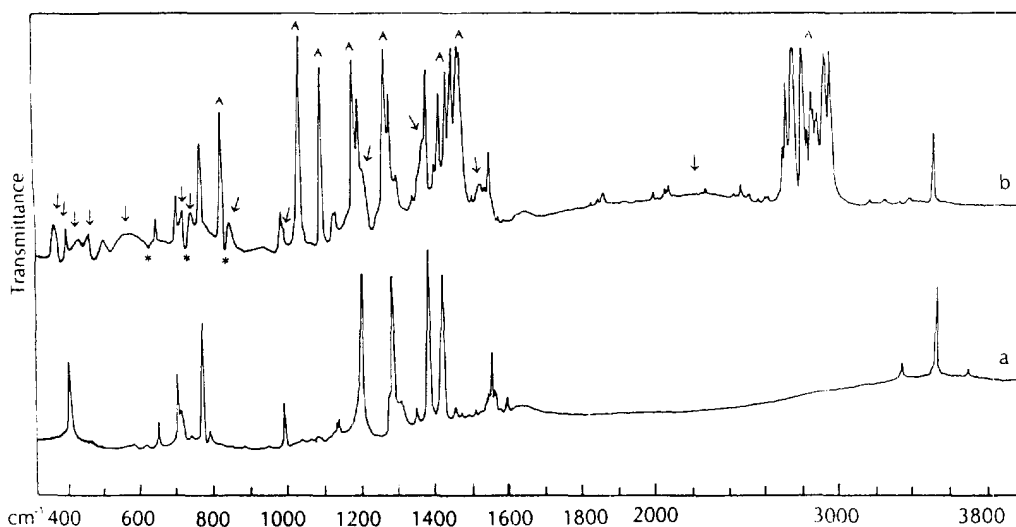


Fig. 2. Infrared spectra of (a) PCP in argon matrix. (b) PCP codeposited with TMA/Ar = 1/50. Arrows indicate PCP-TMA complex bands; *, transmission windows; A, TMA absorptions.

on the matrix concentration. No other product absorptions appeared in this region either when the temperature of the matrix was raised or when the concentration of the TMA/Ar mixture was changed. Thus the broad absorption with a maximum at

2490 cm⁻¹ and a weak component at 1850 cm⁻¹ are assigned to the 1:1 complex of TCP with TMA.

Relatively small changes of the parent molecules spectra were observed below 1700 cm⁻¹. The product absorptions were found at 1557, 1361, 1130 sh and

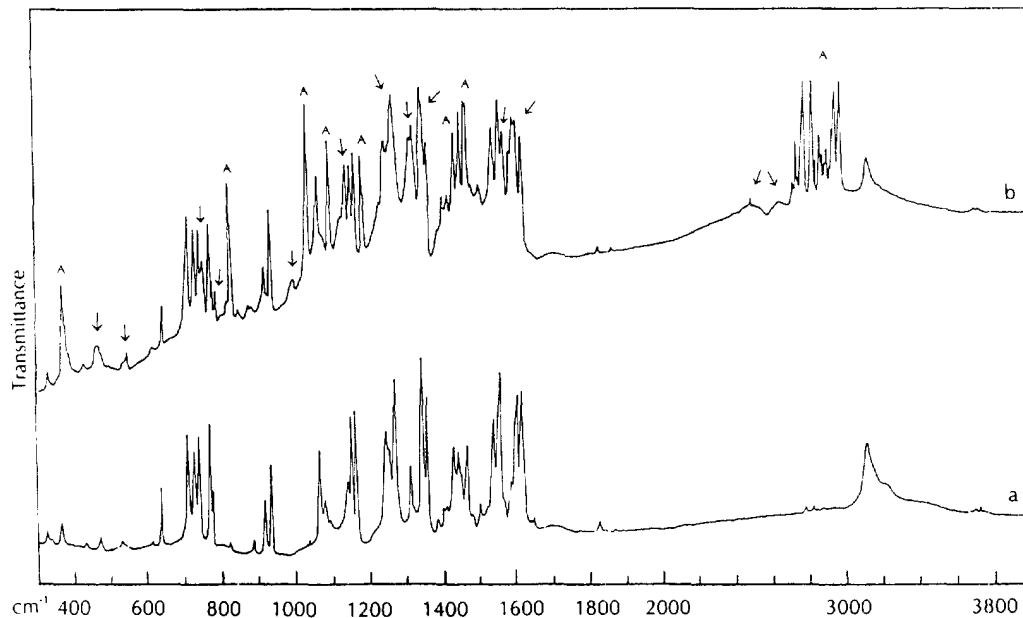


Fig. 3. Infrared spectra of (a) CNP in argon matrix. (b) CNP codeposited with TMA/Ar = 1/300. Arrows indicate CNP-TMA complex bands; A, TMA absorptions.

Table 1

Positions (cm^{-1}) of the infrared bands observed for TCP/Ar and product bands observed for TCP/TMA/Ar matrices

TCP ^a	Assignment	TCP–TMA	TCP	Assignment	TCP–TMA
3561 s	$\nu(\text{OH})$	2490 vw, b	1187 vs	$\nu(\text{C–O}) + \delta(\text{OH})$	1130 w, sh
3550 m		1850 vw, b	1121 w	$\delta(\text{CH})$	
3100 vw	$\nu(\text{CH})$		1095 w	comb.	
1725 vw	comb.		1080 w, sh	comb.	
1604 m	$\nu(\text{C–C})$		1074 s	$\delta(\text{CH})$	
1571 s	$\nu(\text{C–C})$	1557 w	940 w	$\phi(\text{C–C–C})$	
1510 w	$\nu(\text{C–C})$		876 s	$\gamma(\text{CH})$	
1486 s	$\nu(\text{C–C})$			$\nu_s(\text{C}_3\text{N})$ ^b	811 m
1468 vs, sh	$\nu(\text{C–C})$		810 vw	$\phi(\text{C–C–C})$	
1462 vs	$\nu(\text{C–C})$		737 m	$\nu(\text{C–Cl})$	
1402 m	$\nu(\text{C–C})$		731 m	$\nu(\text{C–Cl})$	
1297 vs	$\delta(\text{OH}) + \nu(\text{C–O})$	1361 w	679 m	$\nu(\text{C–Cl})$	
1272 w	comb.		569 w	$\phi(\text{C–C–C})$	
1262 vw	comb.		527 w	$\beta(\text{C–C–C})$	
1244 vw			436 vw	$\phi(\text{C–C–C})$	430 vw
1234 w	$\delta(\text{CH})$		396 s	$\gamma(\text{OH})$	
1219 w	$\delta(\text{CH})$				

^a The assignment of TCP bands is based on that proposed by Pandey and Singh [34].^b The $\nu_s(\text{C}_3\text{N})$ frequency for free amine in argon matrix is equal to 824 cm^{-1} . ν , stretching; δ , in-plane bending; γ , out-of-plane bending; ϕ , planar, and β , nonplanar ring deformation.

430 cm^{-1} in the vicinity of TCP absorptions and at 811 cm^{-1} in the vicinity of the $\nu(\text{C–N})$ band of TMA.

The frequencies of all product absorptions observed in the spectra of TCP/TMA/Ar matrices are collected in Table 1 and compared with the frequencies of TCP isolated in solid argon.

3.2.2. Pentachlorophenol with trimethylamine (PCP–TMA)

The infrared spectrum obtained by codeposition of PCP with TMA/Ar = 1/50 mixture is presented in Fig. 2(b). Two broad diffused bands due to the PCP–TMA complex were observed in the spectrum;

Table 2

Positions (cm^{-1}) of the infrared bands observed for PCP/Ar and product bands observed for PCP/TMA/Ar matrices

PCP ^a	Assignment	PCP–TMA	PCP	Assignment	PCP–TMA
3532 m	$\nu(\text{OH})$		792 vw	comb.	
	$\nu(\text{O}\cdots\text{H}\cdots\text{N})$	2300 vw, b	774 s	$\nu(\text{C–Cl})$	
1562 w	$\nu(\text{C–C})$				850 vw
1553 m	$\nu(\text{C–C})$	1542 w			746 w
1509 vw	$\nu(\text{C–C})$				724 w
1421 s	$\nu(\text{C–C})$		714 w, sh	$\nu(\text{C–C})$	
1385 vs	$\nu(\text{C–C})$	1380 m, sh	705 m	$\nu(\text{C–Cl})$	
1348 w	comb.		650 w	$\beta(\text{C–C–C})$	
1306 w	overtone				580 vw, b
1285 s	$\delta(\text{OH})$				504 vw
1271 w, sh					468 vw
1202 s	$\nu(\text{C–O})$	1213 m, sh			440 vw
1132 w			415 m	$\tau(\text{OH})$	
989 w	$\phi(\text{C–C–C})$?	996 vw, sh			380 w

^a The assignment of TCP bands is partly based on that proposed by Faniran [35] and by Green et al. [36].

Table 3

Positions (cm^{-1}) of the infrared bands observed for CNP/Ar and product bands observed for CNP/TMA/Ar matrices

CNP	Assignment	CNP–TMA	CNP	Assignment	CNP–TMA
3230 w, sh			1258 sh		
3120 m	$\nu(\text{OH})$		1248 m	$\nu(\text{C}-\text{O}) + \delta(\text{OH})$	
	$\nu(\text{NH}^+)$	2640 w, b	1165 s	$\delta(\text{CH})$	
		2520 w, b	1153 s	$\delta(\text{CH})$	
1621 s	$\nu(\text{C}-\text{C})$			$\gamma(\text{NH}^+)$	1142 s
1608 s	$\nu(\text{C}-\text{C})$	1602 s	1140 m		
1605 m, sh			1083 w	$\phi(\text{C}-\text{C}-\text{C})$	
1592 w	$\nu(\text{C}-\text{C})$		1066 m	$\phi(\text{C}-\text{C}-\text{C})$	
1562 vs	$\nu_{\text{as}}(\text{NO}_2)$	1572 s		$\nu_{\text{as}}(\text{C}_3-\text{N}^+)^a$	995 w
1545 s	$\nu_{\text{as}}(\text{NO}_2)$		935 m	$\delta(\text{NO}_2)$	
1507 w			917 m	$\delta(\text{NO}_2)$	
1472 m	$\nu(\text{C}-\text{C})$		887 vw	$\gamma(\text{CH})$	
1450 m	$\nu(\text{C}-\text{C})$			$\nu_s(\text{C}_3-\text{N}^+)^a$	782 w
1435 m	$\nu(\text{C}-\text{C})$		775 m	$\nu(\text{C}-\text{Cl})$	
1420 vw			769 s	$\nu(\text{C}-\text{Cl})$	
1406 vw			741 s	$\nu(\text{C}-\text{Cl})$	751 m
1390 vw			728 m	$\gamma(\text{OH})$	
1362 s	$\nu_s(\text{NO}_2)$		711 s		
1346 vs	$\nu_s(\text{NO}_2)$	1352 vs, sh	639 m	$\beta(\text{C}-\text{C}-\text{C})$	
	$\delta(\text{NH}^+)$	1325 vs	533 vw	$\beta(\text{C}-\text{C}-\text{C})$	542 vw
1316 m			475 vw	$\phi(\text{C}-\text{C}-\text{C})$	460 vw
1273 vs	$\delta(\text{OH}) + \nu(\text{C}-\text{O})$		369 w		
	$\nu(\text{C}-\text{O}^-)$	1270 s, sh	326 vw		

^a The $\nu_{\text{as}}(\text{C}_3\text{N})$ and $\nu_s(\text{C}_3\text{N})$ frequencies for free amine in argon matrix are equal to 1038 and 824 cm^{-1} , respectively.

the first one was extending from ca. 1600 up to 3000 cm^{-1} and a second one was situated between 950 and 400 cm^{-1} . The first absorption consisted of one very weak band (large excess of TMA was used and weak, narrow subbands superimposed on the broad absorption presented in Fig. 2(b) are due to the amine modes). The shape of the broad absorption in the low wavenumber region is quite complex (see Fig. 4). On the diffuse band appear new peaks at 850, 746, 724, 580, 504, 468 and 440 cm^{-1} and three absorption minima (transmission windows) at 840, 732 and 630 cm^{-1} . Four other product bands were observed in the vicinity of PCP modes at 1542, 1380, 1213 and 996 sh cm^{-1} .

The wavenumbers of all new features observed in the spectra of argon matrices containing PCP and TMA are gathered in Table 2.

3.2.3. 2-Chloro-4,6-dinitrophenol with trimethylamine (CNP–TMA)

Fig. 3(b) shows a representative spectrum of the matrix obtained by codeposition of CNP with TMA/

Ar = 1/300 mixture. In high wavenumber region a broad, weak absorption between ca. 3000 and 1800 cm^{-1} was observed. It consisted of two distinct submaxima situated at 2640 and 2520 cm^{-1} . The high frequency side of the absorption is overlapped by $\nu(\text{CH}_3)$ bands of TMA. The relative intensities of the two maxima were insensitive to matrix annealing and TMA/Ar concentration.

Pronounced changes due to complex formation were observed below 1700 cm^{-1} . The product bands were found at 1602, 1572, 1352, 1270sh, 751, 542 and 460 cm^{-1} in the vicinity of CNP absorptions and at 1325, 1142, 995 and 782 cm^{-1} close to the TMA bands.

All new bands which were not present in the parent molecules spectra are assigned to the 1:1 CNP–TMA complex since their intensities grew with the same ratio when the concentration of the complex in the matrix increased.

For comparison purposes the infrared spectra of complexes of TCP, PCP and CNP with TEA in several different solvents have been investigated. Those

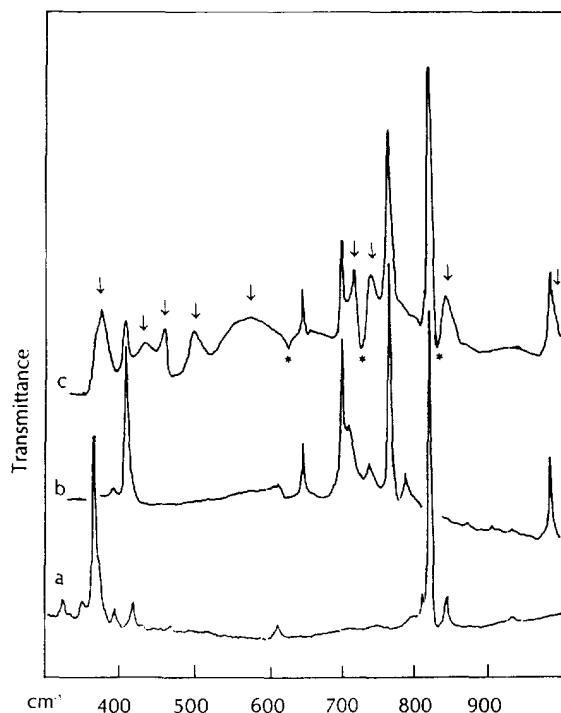


Fig. 4. The 1000–300 cm^{-1} region of the infrared spectra of (a) TMA/Ar = 1/100, (b) PCP in Ar and (c) PCP codeposited with TMA/Ar = 1/50. Complex bands are marked with arrows, transmission windows with asterisks.

obtained in 1,2-dichloroethane solutions are presented in Fig. 5. Selected frequencies observed in the solution spectra are gathered in Table 4.

4. Discussion

The results obtained for TCP–TMA, PCP–TMA and CNP–TMA complexes isolated in argon matrices will be now discussed. The following problems will be considered:

1. which type of hydrogen bond is formed in the studied complexes in argon matrices—to what extent this structure is changed in comparison with the solution results;
2. how strong are the perturbations of the internal vibrations in both interacting molecules.

It is known that acid–base complexes in solutions and in the solid state in addition to the characteristic protonic absorption in the 3000–1500 cm^{-1} region,

exhibit a continuum protonic absorption below 1700 cm^{-1} for a specific ΔpK_a range (see for instance [17,18,37]). This so called inversion range is present when the degree of proton transfer oscillates around 50%.

For the TCP–TEA complex in CH_2Cl_2 solution an equilibrium constant of the proton transfer reaction was estimated between 1 and 1.2 on the basis of NMR [38] and infrared [20] investigations. It means that both molecular and ionic forms of the complex are present in solutions. Our infrared solution results obtained for TCP–TEA system confirmed this conclusions showing, in addition to the absorption observed between 3000 and 1600 cm^{-1} , a broad weak absorption extending from 1600 cm^{-1} down to ca. 400 cm^{-1} (see Fig. 5(A)). On the other hand the argon matrix spectra of TCP–TMA complex did not show a presence of the continuous absorption below 2000 cm^{-1} . The broad band observed at ca. 2490 cm^{-1} and its weak component at ca. 1850 cm^{-1} in solid argon are attributed to the $\nu(\text{OH}\cdots\text{N})$ stretching vibration in the molecular hydrogen bonded complex TCP–TMA. It is worth noting that the infrared spectra of the corresponding Mannich base (2,4,5-trichloro-6-[(diethylamino)methyl] phenol) in the solid state [39], in different solvents [40] and in argon matrix [41] neither manifested any indications of the proton transfer reaction.

The assignment of the observed absorption to the molecular form of the TCP–TMA complex is confirmed by relatively small changes in the spectra of the interacting molecules below 1700 cm^{-1} . The most apparent product absorption in this region is a medium intensity band at 811 cm^{-1} which is assigned to the symmetric stretching vibration $\nu_s(\text{C}_3\text{N})$ of the bonded TMA. The position of this band is very much the same as found for this vibration in a molecular complex formed between acetic acid and TMA in solid argon (809 cm^{-1}) [3]. The corresponding unperturbed $\nu_s(\text{C}_3\text{N})$ mode of the amine is situated at 825 cm^{-1} . In the spectra of TCP in argon two intense bands due to the coupled $\nu(\text{C}-\text{O})$ stretching and $\delta(\text{OH})$ in-plane deformation modes appear at 1297 and 1187 cm^{-1} . Two weak bands at 1361 and 1130 cm^{-1} in the TCP/TMA/Ar spectra are attributed to the corresponding vibrations in the molecular TCP–TMA complex. The small shifts of the $\nu(\text{C}-\text{O}) + \delta(\text{OH})$ bands on complexation are probably due to the strongly mixed

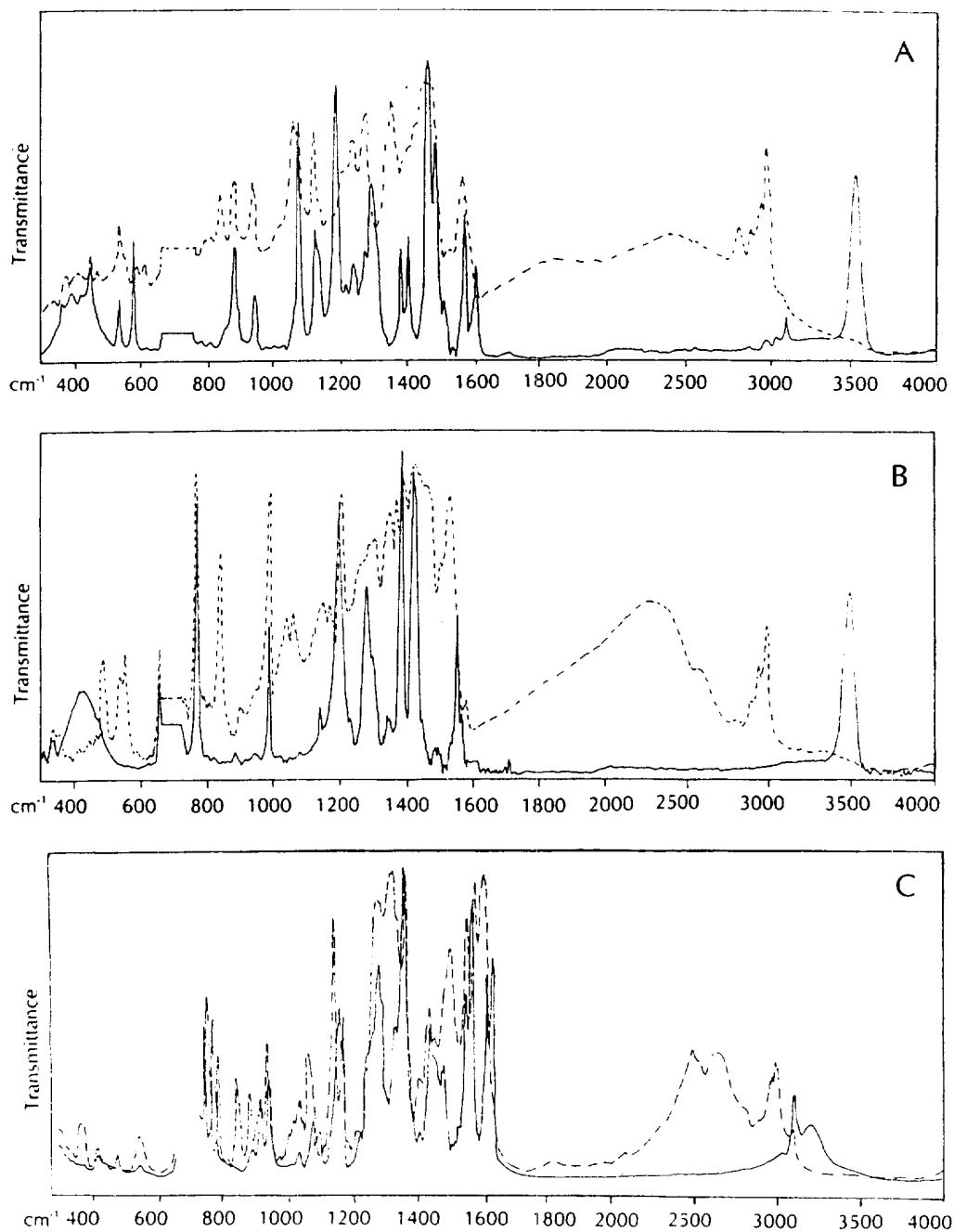


Fig. 5. Infrared spectra of 1,2-dichloroethane solutions. (A) —, TCP; ---, TCP-TEA (1:1). (B) —, PCP; ---, PCP-TEA (1:1). (C) —, CNP; ---, CNP-TEA (1:1). Concentration, 0.2 mol dcm^{-3} ; path length, 0.13 mm.

Table 4

Selected frequencies (cm^{-1}) observed in the infrared spectra of TCP–TEA, PCP–TEA and CNP–TEA complexes in different solvents

TCP–TEA				
$\nu(\text{OH})$	$\delta(\text{OH})$	$\nu(\text{C–O})$	Solvent	ξ
2480, 1800	1270	1235	CCl_4	2.3
2425, 1800	1270	1240	CH_2Cl_2	9.1
2400, 1800	1275	1240	1,2- $\text{C}_2\text{H}_4\text{Cl}_2$	10.4
PCP–TEA				
$\nu(\text{NH}^+)$	$\delta(\text{NH}^+)$	$\nu(\text{CO}^-)$	Solvent	ξ
2100	1365	1205	CCl_4	2.3
2260	1350	1206	CH_2Cl_2	9.1
2290	1350	1206	1,2- $\text{C}_2\text{H}_4\text{Cl}_2$	10.4
2390	1353	1203	CH_3CN	37.5
CNP–TEA				
$\nu(\text{NH}^+)$	$\delta(\text{NH}^+)$	$\gamma(\text{NH}^+)$	Solvent	ξ
2640, 2480	1315	1140	1,2- $\text{C}_2\text{H}_4\text{Cl}_2$	10.4
2680, 2485	1308	1135	$(\text{CH}_3)_2\text{CO}$	20.7
2680, 2485	1312	1139	CH_3CN	37.5

character of these modes. No bands characteristic for the protonated amine [3] were found in the studied spectra confirming that only molecular hydrogen bonded complex TCP–TMA of the $\text{O–H}\cdots\text{N}$ type was present in the studied matrices.

The NMR and IR literature data on the complexes of nitro-substituted phenols with triethylamine in solutions [21,42,43] indicate formation of ion pairs regardless of the solvent used. The infrared spectra obtained for the strongest of the phenols studied showed that 1:1 CNP–TMA complex in argon matrix has also an ionic form with the proton transferred to the amine molecule. This conclusion is evidenced by the following arguments.

The protonic absorption $\nu(\text{NH}^+\cdots\text{O}^-)$ was observed as a broad band between $3000\text{--}1800\text{ cm}^{-1}$ with two submaxima situated at 2640 and 2520 cm^{-1} . This absorption is similar both in position and its shape to that found in the spectra of CNP with triethylamine (TEA) in 1,2-dichloroethane, acetone and acetonitrile solutions (see Fig. 5(C)). The fact that the absorption is shifted towards higher wavenumbers in solvents with higher dielectric constant (acetone and acetonitrile) confirms the ionic character of the interaction [17].

The pronounced changes comparing with the parent

molecules spectra were observed below 1700 cm^{-1} . Four of the product bands, namely: 1325 , 1142 , 995 and 782 cm^{-1} are especially meaningful as the structure of the complex is concerned. The features at 1325 and 1142 cm^{-1} are assigned to the in-plane bending motion $\delta(\text{NH}^+)$ and out-of-plane deformation $\gamma(\text{NH}^+)$, respectively. In the solution spectra of the corresponding Mannich base [44] the $\delta(\text{NH}^+)$ mode was found to be coupled with other motions and appeared at 1340 , 1265 and 1227 cm^{-1} while the $\gamma(\text{NH}^+)$ vibration was situated at 935 cm^{-1} . The considerably higher position of the latter mode in argon matrix (1142 cm^{-1}) is in agreement with the known fact that the intramolecular hydrogen bonds are weaker than the intermolecular ones formed between the parent molecules. Two bands observed at 995 and 782 cm^{-1} are attributed to the asymmetric and symmetric $\nu(\text{C}_3\text{N}^+)$ vibrations of the protonated TMA. These frequencies are close to those found for an ionic complex formed between trifluoroacetic acid and TMA in argon matrices (994 and 800 cm^{-1} , respectively) [3]. The corresponding bands for free amine in solid argon have been observed at 1038 ($\nu_{\text{as}}(\text{C}_3\text{N})$) and 824 cm^{-1} ($\nu_{\text{s}}(\text{C}_3\text{N})$).

Several other product bands observed in the spectra of CNP/TMA/Ar matrices are due to the stretching

and deformation phenol ring vibrations (1602 , 542 and 460 cm^{-1}), asymmetric and symmetric stretching modes of nitro groups (1572 and 1352 cm^{-1}) and to the perturbed stretching $\nu(\text{C}-\text{Cl})$ mode (751 cm^{-1}) of CNP bonded to TMA. All these perturbed phenol modes are shifted by $8\text{--}20\text{ cm}^{-1}$ comparing with the corresponding vibrations of CNP. This confirms relatively strong perturbation of the phenol ring after the formation of the ionic complex with proton transferred to the amine.

The most intriguing are the results obtained for matrices containing phenol of the intermediate strength (PCP) and TMA. Pentachlorophenol-N-base complexes have been studied both in solid and solutions [17,20]. In solutions these systems exist in tautomeric equilibrium with different degree of proton transfer depending on the base and solvent which consequently leads to different spectroscopic characteristics. In a series of the crystalline PCP-N-bases complexes a characteristic evolution of the protonic absorption was observed [17]. For molecular hydrogen bonds and for complexes with proton transferred to the base a broad absorption was observed in the $3200\text{--}1800\text{ cm}^{-1}$ region due to the $\nu(\text{OH}\cdots\text{N})$ or $\nu(\text{NH}^+\cdots\text{O}^-)$ vibrations, respectively. In the inversion region an additional broad absorption appeared in the low wavenumber range with a maximum between $650\text{--}950\text{ cm}^{-1}$. Simultaneously, the relative intensity of the broad high frequency band decreased.

The results obtained here for PCP-TMA system isolated in argon matrices indicate that complex formation gives rise to two broad protonic absorptions appearing between $3000\text{--}1600\text{ cm}^{-1}$ with a maximum at ca. 2300 cm^{-1} and between $950\text{--}400\text{ cm}^{-1}$. The high frequency feature is similar in position to that observed for PCP-TEA in our solution spectra (see Table 4) and may be assigned to the $\nu(\text{NH}^+\cdots\text{O}^-)$ mode of the ionic complex with proton transferred to the amine molecule [17]. The low frequency absorption exhibits a complex structure accompanied by several Evans holes (see Fig. 4). The maximum intensity of this absorption occurs at ca. 740 cm^{-1} . Such a low frequency absorption has been observed for the crystalline PCP-4-methylpyridine complex [17] and is characteristic for symmetric or pseudosymmetric hydrogen bonds in solid phase (see for example [45]). In matrices, the absorption with the maximum between $750\text{--}700\text{ cm}^{-1}$ was observed for

pseudosymmetric $\text{O}\cdots\text{H}\cdots\text{Cl}$ or $\text{N}\cdots\text{H}\cdots\text{Cl}$ hydrogen bonds [5,13]. In our opinion, the appearance of the broad absorption between $900\text{--}400\text{ cm}^{-1}$ in the spectra of PCP-TMA suggests, on the bases of the earlier observations, that the pseudosymmetric complex is present in argon matrices in addition to the ion pair.

The possibility of the simultaneous presence of two kinds of PCP-TMA complexes in argon matrix requires some further comments. Mainly PCP monomers were isolated at the studied conditions so the presence of the 2:1 $(\text{PCP})_2\text{-TMA}$ complexes may be excluded. On the other hand, due to the steric obstacles around the nitrogen atom, interaction between phenol and tertiary amines do not lead to 1:2 phenol-(amine)₂ complexes [46]. So, we must assume that 1:1 complexes between PCP and TMA exist both in ionic ($\text{N}-\text{H}^+\cdots\text{O}^-$) and pseudosymmetric ($\text{O}\cdots\text{H}\cdots\text{N}$) form. The possible explanation of this phenomenon is the presence of two different matrix sites and the sensitivity of the intermolecular potential of PCP-TMA complex to the surrounding matrix cage [47].

There are many new features in the PCP/TMA/Ar spectra appearing below 1000 cm^{-1} however the analysis of these results is not straightforward. For the ionic complex the $\nu_{\text{as}}(\text{C}_3\text{N}^+)$ and $\nu_{\text{s}}(\text{C}_3\text{N}^+)$ modes should occur at similar positions as those observed for the CNP-TMA complex (995 and 782 cm^{-1} , respectively). A weak shoulder at 996 cm^{-1} in the PCP/TMA/Ar spectra might be attributed to the $\nu_{\text{as}}(\text{C}_3\text{N}^+)$ however an alternative assignment for this band is possible: the perturbed vibration of the PCP ring $\phi(\text{C}-\text{C}-\text{C})$ (989 cm^{-1} for free PCP in argon). Another product band at 746 cm^{-1} is situated too far from the position expected for the $\nu_{\text{s}}(\text{C}_3\text{N}^+)$ (782 cm^{-1} in CNP-TMA complex). A complicated absorption pattern observed between $950\text{--}400\text{ cm}^{-1}$ does not allow for precise assignment of the bands. The multiple components of this absorption and three transition windows (situated at 840 , 732 and 630 cm^{-1}) most probably arise from resonance interactions of the broad $\nu(\text{O}\cdots\text{H}\cdots\text{N})$ band with internal modes (or their overtones) of the PCP, TMA subunits. Recently, ab initio calculations performed for complexes of HCl with 4-X-pyridines have shown that several bands below 1300 cm^{-1} arise from the proton motion in the $\text{Cl}\cdots\text{H}\cdots\text{N}$ bridge coupled to internal modes of the pyridine ring [48].

5. Concluding remarks

Three substituted phenols of different proton-donor ability allowed us to study three types of hydrogen bonded complexes of phenol with trimethylamine in argon matrices. The first complex between TCP and TMA exhibits strong molecular hydrogen bond O–H...N between neutral molecules. The strongest phenol, CNP, forms with TMA an ionic N–H⁺...O[−] hydrogen bond. Both these complexes are characterized by protonic $\nu(\text{O–H}\cdots\text{N})$ or $\nu(\text{N–H}^+\cdots\text{O}^-)$ absorption in the 3000–1800 cm^{−1} region. The third complex PCP–TMA is characterized by two broad features situated between 3000 and 1600 cm^{−1} and 950–400 cm^{−1} due to the $\nu(\text{N–H}^+\cdots\text{O}^-)$ and $\nu(\text{O}\cdots\text{H}\cdots\text{N})$ modes, respectively showing that two forms of the 1:1 complex are present in solid argon.

The obtained results allow us to conclude that a continuous transition from the molecular through pseudosymmetric proton shared to the proton transfer hydrogen bond takes place in the studied matrix isolated systems. Such continuous changes have been already postulated for hydrogen bonded complexes in the gas phase and for other systems in low temperature matrices [49,50]. The fact that two forms of 1:1 PCP–TMA complex are observed at the studied conditions indicates high sensitivity of the hydrogen bond potential to the changes of the surrounding matrix environment.

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