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Structure and IR spectroscopic behaviour of 2,7-dichloro-1,8-bis(dimethylamino)naphthalene and its protonated form

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ABSTRACT: X-ray diffraction and IR spectroscopic studies on the proton sponge 2,7-dichloro-1,8-bis(dimethylamino)naphthalene and its adduct with HBr were performed. It was shown that the presence of the chlorine atoms in positions 2 and 7 leads to some change of conformation with respect to the free molecule. The main factor determining the conformation remains the repulsion of the nitrogen lone electron pairs. However, the repulsion between the methyl groups and chlorine atoms causes the dimethylamino groups to be slightly less twisted compared with unsubstituted dimethylaminonaphthalene. The protonation leads to the formation of a symmetrical cation (symmetry plane passing through the C9—C10 axis) with the N···N distance equal to 2.561(3) Å. This corresponds to the situation where the barrier to the proton transfer should be very low. As in other short $[NHN]^+$ bridges, one observes the IR absorption band at about 500 cm^{-1}, assigned to the transition between the split $O_+ \rightarrow O_-$ vibrational levels. A very high frequency isotopic ratio ($\nu_H/\nu_D = 1.8$) is observed for this transition. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: proton sponge; structure; IR spectra

INTRODUCTION

The proton sponge 1,8-bis(dimethylamino)naphthalene (proton sponge, DMAN) draws continuous attention since the first publications of Alder *et al.*[1] Particularly interesting is the structure of the protonated form of DMAN (for reviews see Refs 2 and 3) where extremely short $[NHN]^+$ hydrogen bonds are formed. According to the studies performed so far, this bonding exhibits varying geometry depending on the kind of counteranion. The hydrogen bond length varies within a broad range from 2.522(1) to 2.644(2) Å.

Crystallographically symmetric $[NHN]^+$ bridges were found only in a few cases, namely in ionic adducts containing $Br^- \cdot H_2O$,[4] tetrazolate$\cdot H_2O$,[5] $(OTeF_5)^-$,[6] SCN^-,[7] 4,5-dicyanoimidazolate[8] and BF_4^-[9] anions. It is of particular interest that the shortest $[NHN]^+$ bridges are characterized by an IR absorption band of narrow width located at very low frequencies, 500 cm^{-1}. This band has been ascribed[10] to the $O_+ \rightarrow O_-$ transition between the split levels in the double minimum potential with very low energy barrier.

Recently, a number of DMAN derivatives, in particular substituted in positions 2 and 7, have been synthesized.[11] It seemed justified to choose the dichloro derivative. Owing to their considerable size, the chlorine atoms should affect the properties of both DMAN and its protonated form. The chlorine atoms in an *ortho* position do not change markedly the basicity of the DMAN molecule (in acetonitrile the pK_a of DMAN is 18.50 whereas that of the 2,7-dichloro derivative is 17.83.[12]

In this paper we report the results of x-ray diffraction studies on the 2,7-dichloro derivative of DMAN ($DMANCl_2$) and its protonated form $DMANCl_2 \cdot HBr$. The main IR characteristics are also reported.

EXPERIMENTAL

$DMANCl_2$ was synthesized as described previously[11] and crystallized from methanol; m.p. 48–50 °C. The HBr salt of $DMANCl_2$ was crystallized from acetonitrile; m.p. 230–232 °C.

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Table 1. Crystal data and structure refinement for $DMANCl_2$ and $DMANCl_2 \cdot HBr$

Parameter	$DMANCl_2$	$DMANCl_2 \cdot HBr$
Empirical formula	$C_{14}H_{16}N_2Cl_2$	$C_{14}H_{17}N_2Cl_2Br$
Formula weight	283.19	364.11
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	1.5418	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Cmca*
a (Å)	9.679(2)	15.894(3)
b (Å)	12.229(2)	11.489(2)
c (Å)	13.102(3)	16.732(3)
α (°)	76.48(3)	
β (°)	82.04(3)	
γ (°)	68.72(3)	
V (Å^3)	1402.6(5)	3054.6(10)
Z	4	8
D_c (Mg m^{-3})	1.341	1.583
μ(mm^{-1})	4.020	3.029
F(000)	592	1472
Crystal size/(mm)	0.12 × 0.15 × 0.25	0.15 × 0.15 × 0.20
Diffractometer	Kuma KM4	Kuma KM4CCD
2θ range (°)	6.6–160.7	6.5–57.5
Ranges: *h*	−12 to 12	−21 to 20
k	−14 to 15	−15 to 14
l	0 to 24	−22 to 21
Reflections collected	4958	8926
Reflections unique	4958	1983
R (int)		0.0487
Data [$I > 2\sigma(I)$]/ parameters	2582/158	1882/127
Goodness-of-fit on F^2	0.928	1.174
R_1, wR_2 [$I > 2\sigma(I)$]	0.0428, 0.1113	0.0483, 0.1205
R_1, wR_2 indices (all data)	0.0928, 0.1288	0.0514, 0.1255
Extinction coefficient	0.0102(6)	0.0011(2)
Δ ρ/*e* (Å^{-3})	0.236 and −0.365	0.605 and −0.626

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $DMANCl_2$

	x	*y*	*z*	*U*(eq)[a]
Cl(11)	−0.12250(9)	0.07813(8)	0.73041(9)	0.0858(33)
Cl(12)	−0.68535(11)	−0.27568(10)	0.95115(9)	0.0944(4)
Cl(21)	−0.19029(9)	0.21118(8)	0.42103(8)	0.0760(3)
Cl(22)	0.34233(9)	0.60003(8)	0.25617(9)	0.0837(3)
N(11)	−0.2092(2)	−0.1081(2)	0.8909(2)	0.0528(6)
N(12)	−0.3960(3)	−0.2392(2)	0.95905(19)	0.0512(6)
N(21)	−0.1483(2)	0.4480(2)	0.3468(2)	0.0504(6)
N(22)	0.0404(2)	0.5780(2)	0.2725(2)	0.0534(6)
C(11)	−0.3149(3)	−0.0374(2)	0.8167(2)	0.0446(6)
C(12)	−0.2925(3)	0.0568(3)	0.7432(3)	0.0532(7)
C(13)	−0.3980(3)	0.1364(3)	0.6729(3)	0.0604(8)
C(14)	−0.5270(3)	0.1174(3)	0.6713(2)	0.0567(8)
C(15)	−0.6887(3)	0.0005(3)	0.7277(2)	0.0555(8)
C(16)	−0.7211(3)	0.0923(3)	0.7907(3)	0.0633(9)
C(17)	−0.6240(3)	−0.1681(3)	0.8666(2)	0.0542(7)
C(18)	−0.4894(3)	−0.1585(2)	0.8814(2)	0.0437(6)
C(19)	−0.4514(2)	−0.0609(2)	0.8134(2)	0.0410(6)
C(110)	−0.5545(2)	0.0186(3)	0.7386(2)	0.0447(6)
C(111)	−0.1017(3)	−0.2163(3)	0.8658(3)	0.0674(9)
C(112)	−0.1611(4)	−0.0521(4)	0.9585(3)	0.0827(11)
C(113)	−0.3466(4)	−0.3668(3)	0.9624(3)	0.0803(11)
C(114)	−0.4100(4)	−0.2054(3)	1.0580(3)	0.0722(9)
C(21)	−0.0177(2)	0.3499(2)	0.3728(2)	0.0400(6)
C(22)	−0.0225(3)	0.2369(3)	0.4138(2)	0.0498(7)
C(23)	0.1000(3)	0.1368(3)	0.4476(2)	0.0582(8)
C(24)	0.2356(3)	0.1474(3)	0.4349(2)	0.0534(7)
C(25)	0.3992(3)	0.2627(3)	0.3734(2)	0.0532(7)
C(26)	0.4229(3)	0.3658(3)	0.3300(3)	0.0584(8)
C(27)	0.3009(3)	0.4693(3)	0.3015(2)	0.0494(7)
C(28)	0.1558(3)	0.4720(2)	0.3098(2)	0.0397(6)
C(29)	0.1280(2)	0.3619(2)	0.3568(2)	0.0369(6)
C(210)	0.2525(2)	0.2589(2)	0.3880(2)	0.0409(6)
C(211)	−0.1945(3)	0.4749(3)	0.2422(3)	0.0763(10)
C(212)	−0.2651(3)	0.4791(3)	0.4274(3)	0.0772(11)
C(213)	0.0488(4)	0.6394(3)	0.1648(3)	0.0851(12)
C(214)	−0.0409(3)	0.6518(3)	0.3460(3)	0.0755(11)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The IR spectra were recorded for pellets in KBr on a Bruker FT-IR IFS 113v spectrophotometer.

X-ray measurements on $DMANCl_2$ were made on a Kuma KM4 κ-axis four-circle diffractometer using a graphite monochromated and Cu Kα radiation and for $DMANCl_2 \cdot HBr$ crystal on a Kuma KM4CCD κ-axis diffractometer using graphite monochromated and Mo Kα radiation. The $DMANCl_2 \cdot HBr$ crystal was positioned at 65 mm from the KM4CCD diffractometer; 612 frames were measured at 0.75° intervals with a counting time of 30 s each. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs. The crystallographic data and the refinement procedure details are given in Table 1.

The structures were solved by direct methods with SHELXS97[13] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97[14] program. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the Δρ maps and refined with isotropic thermal parameters. Figures were drawn by using the XP program at the Technical University of Łódz by courtesy of Professor Z. Gałdecki.

RESULTS AND DISCUSSION

The structure of $DMANCl_2$

The atomic coordinates and equivalent isotropic displacement parameters for two symmetry-independent $DMANCl_2$ molecules existing in the crystal asymmetric unit are collected in Table 2. Non-hydrogen atomic coordinates with anisotropic displacement parameters, hydrogen atom coordinates with isotropic displacement parameters and bond lengths and angles have been

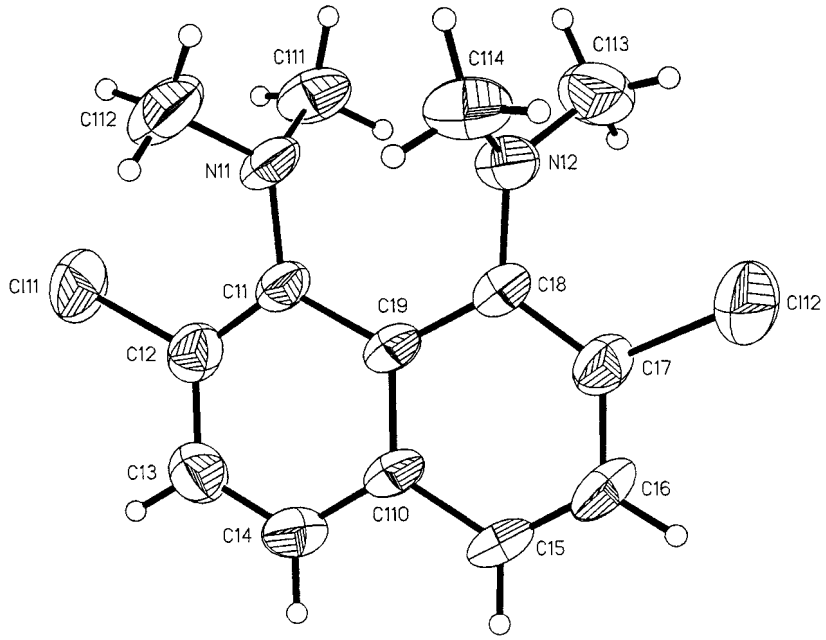

Figure 1. Structure of $DMANCl_2$ showing 50% probability displacement ellipsoids and the atom numbering scheme

Table 3. Selected bond lengths (Å) and angles (°) for $DMANCl_2$

N(11)—N(12)	2.761(4)	N(21)—N(22)	2.775(4)
Cl(11)—C(12)	1.735(3)	Cl(21)—C(22)	1.747(3)
Cl(12)—C(17)	1.736(3)	Cl(22)—C(27)	1.739(3)
N(11)—C(11)	1.406(4)	N(21)—C(21)	1.408(3)
N(12)—C(18)	1.402(4)	N(22)—C(28)	1.403(3)
C(11)—N(11)—C(111)		117.6(3)	
C(11)—N(11)—C(112)		119.9(3)	
C(111)—N(11)—C(112)		115.5(3)	
C(18)—N(12)—C(114)		117.4(3)	
C(18)—N(12)—C(113)		120.5(3)	
C(114)—N(12)—C(113)		114.9(3)	
C(21)—N(21)—C(211)		118.0(3)	
C(21)—N(21)—C(212)		119.0(3)	
C(211)—N(21)—C(212)		115.9(3)	
C(28)—N(22)—C(214)		118.1(3)	
C(28)—N(22)—C(213)		119.6(3)	
C(214)—N(22)—C(213)		115.6(3)	
C(12)—C(11)—N(11)		121.0(2)	
N(11)—C(11)—C(19)		121.8(2)	
C(11)—C(12)—Cl(11)		120.1(2)	
C(13)—C(12)—Cl(11)		115.9(2)	
C(16)—C(17)—Cl(12)		115.2(2)	
C(18)—C(17)—Cl(12)		119.9(2)	
C(17)—C(18)—N(12)		121.7(3)	
N(12)—C(18)—C(19)		121.6(2)	
C(22)—C(21)—N(21)		121.1(2)	
N(21)—C(21)—C(29)		122.1(2)	
C(21)—C(22)—Cl(21)		119.6(2)	
C(23)—C(22)—Cl(21)		115.8(2)	
C(28)—C(27)—Cl(22)		120.7(2)	
C(26)—C(27)—Cl(22)		115.02(19)	
C(27)—C(28)—N(22)		120.7(2)	
N(22)—C(28)—C(29)		121.6(2)	
C(210)—C(29)—C(28)		117.3(2)	

deposited at the Cambridge Crystallographic Data Centre (CCDC No. 136574-5). The molecular structure with numbering of atoms is shown in Fig. 1. Some bond lengths and angles are given in Table 3.

The geometry of the two free $DMANCl_2$ molecules is similar to that found for DMAN itself.[15] Owing to strong repulsion between the lone electron pairs, the dimethylamino groups are twisted with respect to each other in opposite directions, with corresponding torsion angles given in Table 4. Comparison with corresponding data for unsubstituted DMAN shows that chlorine atoms cause the twisting to be weaker and the molecule becomes more rigid.

The deviation of the nitrogen atoms from the naphthalene ring is 0.059(3) and 0.048(3) Å. The N · · · N distances, 2.761(4) and 2.775(4) Å, are very close to that in DMAN itself (2.792 Å). This means that the chlorine atoms in positions 2 and 7, i.e. in the direct neighbourhood of the $(CH_3)N$ groups, do not affect substantially the main structural characteristics of DMAN, and the interaction between the nitrogen atoms is more important.

Table 4. Selected torsion angles (°) for $DMANCl_2$

C(111)—N(11)—C(11)—C(19)	84.7(4)
C(112)—N(11)—C(11)—C(19)	−126.0(4)
C(114)—N(12)—C(18)—C(19)	85.1(4)
C(113)—N(12)—C(18)—C(19)	−125.9(3)
C(211)—N(21)—C(21)—C(29)	88.4(4)
C(212)—N(21)—C(21)—C(29)	−122.2(3)
C(214)—N(22)—C(28)—C(29)	86.1(4)
C(213)—N(22)—C(28)—C(29)	−123.9(4)

Table 5. Atomic coordinates and equivalent isotropic displacement parameters for $DMANCl_2 \cdot HBr$

	x	*y*	*z*	*U*(eq)[a]
Br(1)	0.0000	0.12369(4)	0.34943(3)	0.0538(2)
Cl(1)	−0.25260(5)	0.66690(10)	0.37551(7)	0.0682(3)
N(1)	−0.08056(15)	0.7972(2)	0.37059(13)	0.0354(5)
C(1)	−0.08000(17)	0.6711(2)	0.38010(14)	0.0335(5)
C(2)	−0.15285(19)	0.6058(3)	0.38399(18)	0.0441(6)
C(3)	−0.1510(2)	0.4845(3)	0.3942(2)	0.0519(8)
C(4)	−0.0767(2)	0.4287(3)	0.40019(18)	0.0498(8)
C(5)	0.0000	0.6138(3)	0.3856(2)	0.0322(7)
C(6)	0.0000	0.4902(3)	0.3958(2)	0.0394(8)
C(7)	−0.1136(2)	0.8623(3)	0.44079(19)	0.0461(7)
C(8)	−0.1149(2)	0.8394(3)	0.29316(18)	0.0466(7)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

The structure of $DMANCl_2 \cdot HBr$

The atomic coordinates and equivalent isotropic displacement parameters for this salt are collected in Table 5. The molecular structure with numbering of atoms is presented in Fig. 2 and selected bond lengths and angles are given in Table 6.

The $DMANCl_2 \cdot H^+$ cations in the crystalline lattice are characterized by the symmetry plane passing through the C5—C6 axis of the naphthalene ring. The nitrogen atoms are located in the naphthalene plane with a standard deviation of 0.004 Å. Therefore, we are dealing with the seventh example of a symmetrical $[NHN]^+$ hydrogen bridge in which the proton is most probably disordered in a double minimum potential similarly to the situation reported elsewhere.[3,16–18]

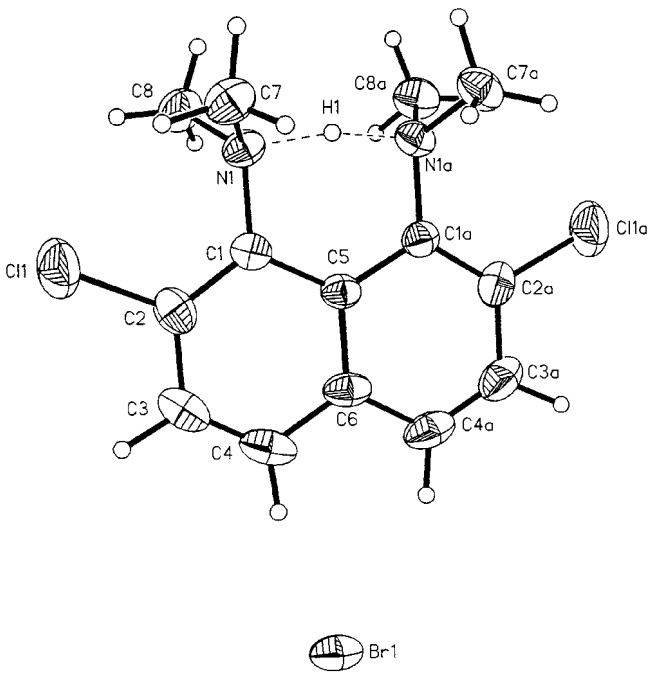

Figure 2. Structure of $DMANCl_2 \cdot HBr$ showing 50% probability displacement ellipsoids and the atom numbering scheme

Table 6. Selected bond lengths (Å) and angles (°) for $DMANCl_2 \cdot HBr$

Cl(1)—C(2)	1.739(3)
N(1)—C(1)	1.458(3)
N(1)—C(8)	1.487(4)
N(1)—C(7)	1.488(3)
N(1)—H(1)	1.292(8)
C(1)—N(1)—C(8)	114.9(2)
C(1)—N(1)—C(7)	114.5(2)
C(8)—N(1)—C(7)	113.3(2)
C(2)—C(1)—N(1)	122.6(3)
C(5)—C(1)—N(1)	117.9(2)
C(1)—C(2)—Cl(1)	122.8(2)
C(3)—C(2)—Cl(1)	115.4(2)
C(1)—N(1)—H(1)	96(3)
C(8)—N(1)—H(1)	112(2)
C(7)—N(1)—H(1)	104(2)
N(1)—C(7)—H(4)	108(2)
N(1)—C(7)—H(5)	109(2)
N(1)—C(7)—H(6)	103(2)
N(1)—C(8)—H(7)	114(3)
N(1)—C(8)—H(8)	105(2)
N(1)—C(8)—H(9)	108(2)

The $[NHN]^+$ hydrogen bond length of 2.561 Å is comparable to those found for other crystallographically symmetrical $DMAN \cdot H^+$ cations. The NHN bridge is only slightly bent with an angle of 164.7(2)°, similarly as in all other symmetrical $DMAN \cdot H^+$ cations reported so far. Therefore, one can conclude that also in the $DMANCl_2 \cdot H^+$ cation the influence of the chlorine atoms on the bridge geometry is negligibly small.

The packing of the $DMANCl_2 \cdot HBr$ adduct in the crystalline lattice is of some interest. According to symmetry requirements, the Br^- anion is located in the symmetry plane of the cation. It is located in cavities formed by 10 hydrogen atoms from the CH_3 groups and C—H bonds in positions 4 and 4a of the naphthalene rings as shown in Fig 3. The contact distances between the bromine anion and hydrogen atoms are in the range 2.88–3.05 Å and are comparable to the sum of van der Waals radii. It is interesting that Br^- anions are in contact with H atoms and not with carbon atoms or with the π-electron system. The DMAN rings are antiparallel and tilted by 27.6°.

IR spectra of $DMANCl_2 \cdot HBr$

A characteristic feature of the shortest $[NHN]^+$ bridges in protonated DMAN is the IR absorption band of NHN stretching vibrations located at extremly low frequency in the region of 500 cm^{-1}. We ascribed it to the $O_+ \rightarrow O_-$

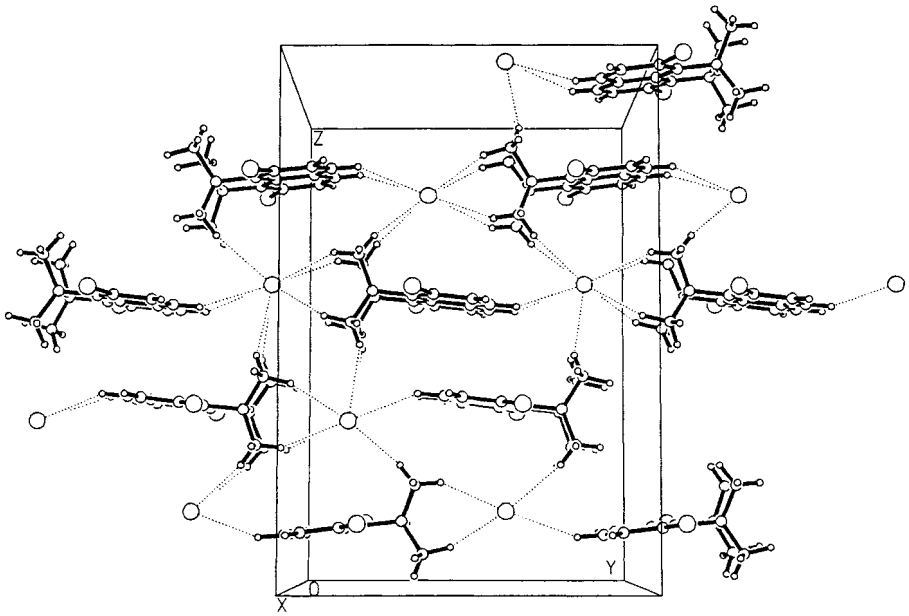

Figure 3. Arrangement of $DMANCl_2 \cdot H^+$ and Br^- ions in the crystalline lattice

transition, i.e. between the split levels in the double minimum potential.[10]

In Fig. 4, the low-frequency part of the IR spectrum of $DMANCl_2 \cdot HBr$ is shown. The position of the intense, relatively narrow band with a maximum at 494 cm^{-1} (centre of gravity at 530 cm^{-1}) is comparable to those of other symmetrical $DMAN \cdot H^+$ cations and particularly in the symmetrical 4,5-dicyanoimidazolate adduct.[10] The only difference is that except for the weakly marked window at 565 cm^{-1} we do not observe deep Evans holes characteristic of other $DMAN \cdot H^+$ cations. The formation of Evans holes was ascribed to the coupling of protonic with CNC bending vibrations which modulate the potential for the proton motion.[19] The presence of the chlorine atoms in positions 2 and 7 probably renders the molecule more rigid and changes the dynamics of the dimethylamino groups. Deuteration shifts the ν(NHN) band to 290 cm^{-1} and the frequency isotopic ratio is 1.8, in agreement with the correlation for very short NHN hydrogen bonds reported previously.[20]

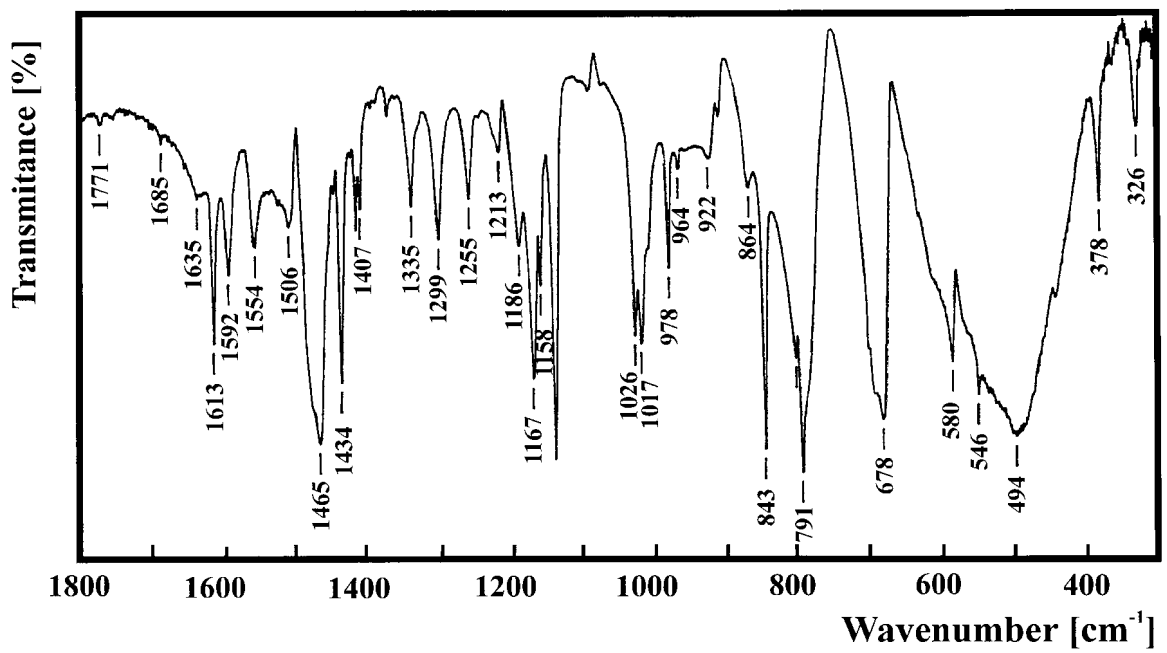

Figure 4. IR spectrum below 1800 cm^{-1} (KBr pellets) for $DMANCl_2 \cdot HBr$

The spectrum shows in addition some broad absorption of lower intensity in the range 1400–1700 cm^{-1}. The explanation of the origin of this absorption needs further studies. No absorption was detected above 1800 cm^{-1} apart from the C—H bands.

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