

PROTONIZATION OF THE HEXAMETHYLENETETRAMINE MOLECULE

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Protonization of the hexamethylenetetramine (HMTA) molecule was studied by means of the EHT method. The potential energy curve of the molecular pair hexamethylenetetramine-hydrogen bromide (where the relative distance of the proton between the nitrogen and the bromine atom serves as a parameter) exhibits two minima, the deeper one corresponding to the non-ionized form. In order to transfer the proton into the second minimum, *i.e.* to form a salt, an external field is necessary (*e.g.*, a crystal field). Calculations carried out for this and other models show a strong effect of an approaching proton on the electron density distribution over the atoms of the HMTA skeleton. As a result of this effect, a multiple protonization of the HMTA molecule cannot lead to the formation of stable ions. The HMTA molecule forms complexes with weak acids bound by a hydrogen bond; if no protonization occurs in this process, the HMTA molecule can combine *via* its nitrogen atoms with up to three molecules of weak acids.

Hexamethylenetetramine (formula I, further on HMTA) is one of the most interesting organic bases of medium strength¹. The highly symmetric molecule of this compound with the adamantane structure belongs to the T_d point symmetry group; its four equivalent tertiary nitrogen atoms make it possible to assume its polybasicity. However, in reality HMTA behaves as a monobasic compound which protonizes only once without decomposing. The only reason that can explain this behaviour is a change of the electron density distribution over the skeleton atoms of HMTA which accompanies the transition from the neutral form to the monovalent cation.

In this study we have investigated — by means of the quantum chemistry methods — the molecules of HMTA, HMTA hydrobromide, and several other model compounds with the aim to explain the reasons of the Brønsted monobasicity of HMTA. The interest in this problem was enhanced even more by the observation that HMTA can exhibit Lewis polybasicity.

METHODS

Calculations of quantum-chemical characteristics of molecules and ions as reported in this communication were carried out by the extended Hückel theory (EHT)² on a GE-427 computer.

Values of ionization potentials and Slater exponents were taken from conventional sources*). The value 1.75 was used for the Hoffmann constant.

Cartesian coordinates of the systems studied were obtained from the structural parameters with the use of the computer. In the HMTA molecule all C—H bonds have the same length³ ($r_{\text{CH}} = 1.008 \text{ \AA}$) and the same holds for all C—N bonds ($r_{\text{CN}} = 1.476 \text{ \AA}$); the angles CNC (107.2°) are smaller than the angles NCN (113.6°). Numbering of atoms of the HMTA molecule is given in formula I. In order to calculate the Cartesian coordinates of atoms in the molecules of 1-azabicyclo[2,2,2]octane and 1,4-diazabicyclo[2,2,2]octane (II, III), structural data from ref.⁴ were used. With III the crystal-state geometry⁴ was preferred rather than the gas-phase geometry⁵ in order to keep the consistency of the compared models. The molecule III belongs to the D_{3h} point symmetry group, while the molecule II to C_{3v} ; as a result, some eigenvalues of the molecules are doubly degenerate.

The geometry of the crystal cell of HMTA hydrobromide was studied by means of the X-ray diffraction method by Gattermayer^{6,7}. The geometry of the HMTA-H⁺ cation may be described as shown in Table I.** The local symmetry of the ion is C_{3v} , the hydrogen atom is bound to the HMTA skeleton at N(1) (see numbering in formula I). The value used for the ionization potential¹ of Br (4s) was -27.01 eV , for Br (4p) -12.44 eV . The Slater exponent for bromine was 2.054. The Cartesian coordinates of atoms were calculated from the structural parameters in Table I, the equilibrium separation of atoms in HBr was taken as 1.420 \AA . HMTA hexahydrate crystallizes from a saturated aqueous HMTA solution upon cooling to 0°C and is stable up to 13.5°C . Its structure was determined by Mak⁹ and Davidson¹⁰. The geometry of the HMTA hydrate skeleton is given in Table I.

RESULTS

The quantum-chemistry characteristics calculated with the use of the EHT method for the molecules I—III are given in Tables II and III. The tables show the values of LFMO, HOMO, and some other molecular orbitals as well as the results of the Mulliken population analysis^{13–16}. From the calculated data the mutual interaction of the nitrogen atoms in the HMTA molecule can be inferred which are not sufficiently isolated by a single CH_2 group. This interaction shows itself even in the value of pK_a to the first degree ($\text{pK}_a = 6.2$) which, in comparison with other aliphatic amines, is relatively small¹. In the molecule of 1,4-diazabicyclo[2,2,2]octane the mutual interaction between nitrogen atoms is screened off by two CH_2 groups. Also, high value of the net atomic charge on the carbon atoms of the HMTA molecule is remarkable (in comparison with the values for carbon atoms of the other two bases) which shows a strong interaction between nitrogen and carbon atoms in the HMTA molecule. This interaction is also indicated by the values of orbital charges of the carbon atoms in HMTA. Several authors assume for the sake of simplicity that all angles in the HMTA molecule are tetrahedral¹⁶. Our calculations carried out for this structure show that it is rather improbable (see values of the total energy in Table II).

* The values of ionization potentials: H (1s) = -13.6 eV ; C (2s) = -19.2 eV ; C (2p) = -11.79 eV ; N (2s) = -25.79 eV ; Slater exponents for H = 1.000; C = 1.625, and N = 1.950.

** Valence angles and interatomic distances were calculated by Rybiář⁸ from the Cartesian coordinates of atoms reported by Gattermayer^{6,7}.

Problems of the protonization of the HMTA molecule can be demonstrated on its hydrobromide. According to the results of crystallographic analysis⁶⁻⁸ the distance between the bromine atom and the N(1) atom is 3.1 Å; the HBr molecule lies on the corresponding three-fold symmetry axis of the HMTA molecule which goes through the N(1) atom. Values of the total energy were calculated by the EHT method for 24 different separations H—N(1), while the Br—N(1) separation was kept constant. By plotting this energy vs the internuclear separation H—N(1) a potential curve was found with two minima at 1.7 Å and 0.7 Å (Fig. 1); the former minimum is deeper and corresponds to the non-ionized state of the HMTA system. For this particular separation H—N(1) further models with the variable separation Br—N(1) were considered; the results are in Table IV. The changes in the potential energy curve caused by shifts of the heavy atoms could be interesting mainly from the point of view of solving the energetics of the hydrogen bond N...H...Br. In connection with the problem under study we did not pursue this aspect any more, mainly because it can be in principle estimated from the results reported elsewhere^{17,18}.

HMTA hexahydrate belongs to the clathrate compounds; its specificity is the participation of the chemical interaction (hydrogen bonds) in stabilizing the crystal structure. The geometry of its molecule is described in ref.^{9,10}. It is based on non-planar ten-membered rings consisting of ten water molecules with oxygen atoms in the apexes. The HMTA molecules form the cross-bonds among these rings (Fig. 2), each one rendering three nitrogen atoms to form bonds with hydrogens of the water cyclodecamers.

A direct calculation of the HMTA hexahydrate molecule did not seem promising. Therefore, we used a model in which we let to approach three free protons to the HMTA molecule along the three-fold symmetry axes of the molecule going through the atoms N(1), N(2), and N(3). In principle, this model may be simplified further by letting to approach one isolated proton along the symmetry axis going through

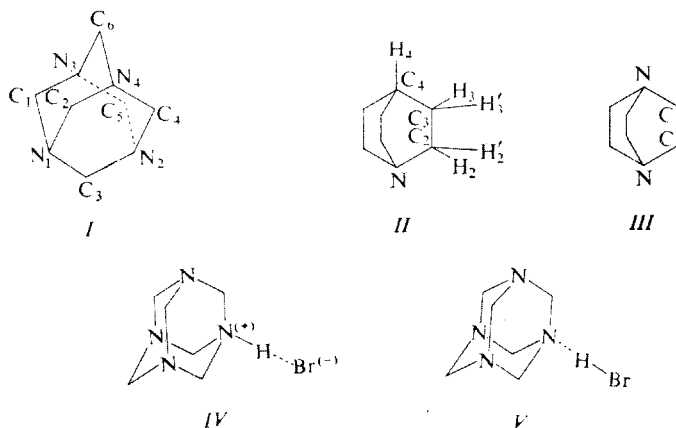


TABLE I

Differences in Internuclear Distances (Å) and Valence Angles (°) Values of Skeletons of Molecules of Hexamethylenetetramine and its Derivatives

Bond	HMTA . . HBr ^{a,b}	HMTA . 6 H ₂ O ^{a,c}	HMTA . . 2 Br ₂ ^{a,d}
N(1)—C(1)	+0.061	-0.009	-0.044
N(1)—C(2)	+0.061	+0.013	-0.044
N(1)—C(3)	+0.061	-0.009	+0.089
N(2)—C(3)	-0.031	-0.009	+0.089
N(2)—C(4)	+0.131	+0.013	-0.044
N(2)—C(5)	+0.131	-0.009	-0.044
N(3)—C(1)	-0.031	-0.009	+0.042
N(3)—C(5)	+0.131	-0.009	+0.042
N(3)—C(6)	+0.131	+0.013	-0.039
N(4)—C(2)	-0.031	-0.023	+0.042
N(4)—C(4)	+0.131	-0.023	+0.042
N(4)—C(6)	+0.131	-0.023	-0.039
Valence angle			
N(1)—C(1)—N(3)	-2.6	-1.6	+0.4
N(1)—C(2)—N(4)	-2.6	-0.6	+0.4
N(1)—C(3)—N(2)	-2.6	-1.6	-9.6
N(2)—C(4)—N(4)	-6.6	-0.6	+0.4
N(2)—C(5)—N(3)	-6.6	-1.6	+0.4
N(3)—C(6)—N(4)	-6.6	-0.6	-14.5
C(1)—N(1)—C(2)	+2.8	+0.8	-8.2
C(1)—N(1)—C(3)	+2.8	+0.8	+17.8
C(1)—N(3)—C(5)	+3.8	+0.8	-1.2
C(1)—N(3)—C(6)	+3.8	+0.8	-11.2
C(2)—N(1)—C(3)	+2.8	+0.8	+17.8
C(2)—N(4)—C(4)	+3.8	+0.8	-1.2
C(2)—N(4)—C(6)	+3.8	+0.8	-11.2
C(3)—N(2)—C(4)	+3.8	+0.8	+17.8
C(3)—N(2)—C(5)	+3.8	+0.8	+17.8
C(4)—N(2)—C(5)	-0.2	+0.8	-8.2
C(4)—N(4)—C(6)	-0.2	+0.8	-11.2
C(5)—N(3)—C(6)	-0.2	+0.8	-11.2

^a Relative to the values³ of internuclear distances C—N in HMTA 1.476 Å and bond angles N—C—N 113.6° and C—N—C 107.2°; ^b values of internuclear distances and valence angles calculated by Rybiář⁸ from the results of X-ray diffraction as published by Gattermayer^{6,7}; ^c ref.^{9,10}; ^d ref.^{11,12}.

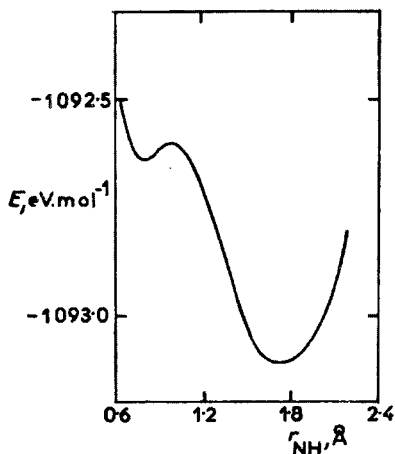


FIG. 1

Potential Curve Showing Changes of the Calculated Value of Total Energy of Hexamethylenetetramine in Dependence on the Position of Proton between the Atoms N (I) and Br (r_{NH} = 3.100 Å)

The distance r_{NH} plotted as a parameter.

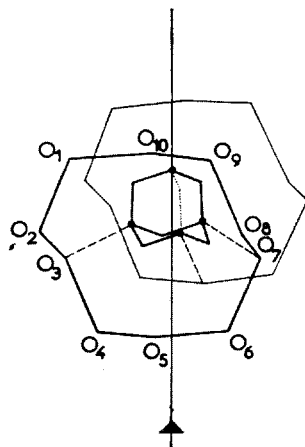


FIG. 2

Schematic of the Hexamethylenetetramine Hexahydrate Structure (from ref.^{9,10})

Ten-membered rings formed by water molecules (oxygen atoms in apexes of decahedrons), in the hexamethylenetetramine molecule nitrogen atoms are indicated as well as directions of hydrogen bonds which form bonds among water cyclodecamers.

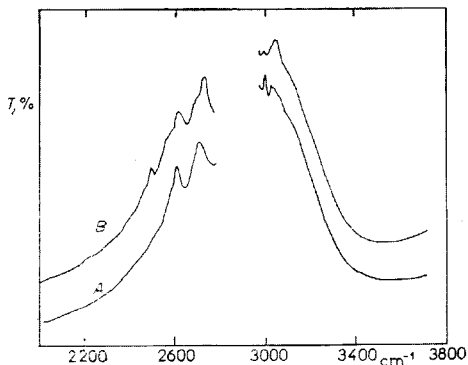


FIG. 3

Region of Stretching Vibrations of X—H Bonds from Infrared Spectra of Hexamethylenetetramine Molecular Compounds with Phenol (A); with 2-Methylphenom (B)

Measured in Nujol suspension, region of Nujol absorption left out.

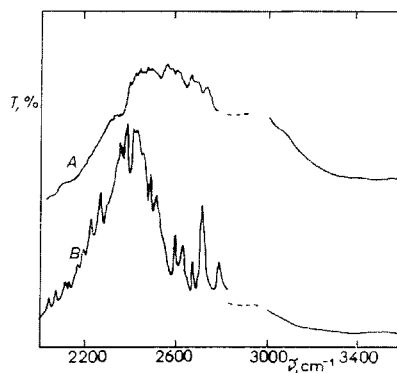


FIG. 4

Region of Stretching Vibrations of X—H Bonds from Infrared Spectra

A HMTA with 4-nitrophenol compound; B HMTA hydrobromide. Measured in Nujol suspension, region of Nujol absorption left out.

TABLE II

Quantum-Chemical Characteristics Calculated by the EHT Method for Molecules of Hexamethylenetetramine (HMTA), 1-Azabicyclo-[2,2,2]octane (*II*), and 1,4-Diazabicyclo[2,2,2]octane-*(III)*

Orbital	HMTA	HMTA ^a	<i>II</i>	<i>III</i>
LFMO, HOMO and total energy, eV				
LFMO	-6.728	-6.779	-7.093	-7.626
HOMO	-13.184	-13.152	-12.436	-12.656
	-13.184	-13.152	-12.644	-12.728
	-13.184	-13.152	-12.644	-13.188
	-13.706	-13.696	-12.766	-13.188
	-13.706	-13.696	-13.219	-13.200
	-13.696	-13.706	-13.219	-13.200
	-14.510	-14.423	-13.431	-13.733
$E_{\text{LFMO}} - E_{\text{HOMO}}$	6.372	6.456	5.342	5.031
Total energy	-959.381	-958.802	-731.790	-756.088
Atoms	HMTA	HMTA ^a	<i>II</i>	<i>III</i>
Overlap population				
N C(2)	0.411	0.408	0.388	0.387
C(3) C(4)	—	—	0.686	—
C(2) C(3)	—	—	0.669	0.684
C(2) H(2)	0.817	0.820	0.814	0.812
C(3) H(3)	—	—	0.804	0.812
C(4) H(4)	—	—	0.821	—
Net atomic charges				
N	-1.778	-1.770	-1.781	-1.778
C(2)	1.011	1.014	0.414	0.408
C(3)	—	—	-0.216	—
C(4)	—	—	-0.033	—
H(2)	0.087	0.083	0.089	0.092
H(3)	—	—	0.100	—
H(4)	—	—	0.081	—

^a Calculations carried out for HMTA molecule assuming all angles CNC and NCN are equal and tetrahedral.

TABLE III

Orbital Charges for Hexamethylenetetramine (HMTA), 1-Azabicyclo[2,2,2]octane (*II*), and 1,4-Diazabicyclo[2,2,2]octane (*III*) Molecules

Orbital	HMTA	HMTA ^a	<i>II</i> ^b			<i>III</i>
			(2)	(3)	(4)	
H(1s)	0.913	0.913	0.910	0.900	0.919	0.908
N(2s)	1.886	1.886	—	1.885	—	1.885
(2p _x)	1.496	1.505	—	1.904	—	1.915
(2p _y)	1.764	1.751	—	1.496	—	1.489
(2p _z)	1.630	1.628	—	1.496	—	1.489
C(2s)	1.210	1.210	1.320	1.419	1.412	1.321
(2p _x)	0.980	0.980	0.830	0.899	0.922	0.831
(2p _y)	0.288	0.288	0.448	0.905	0.849	0.454
(2p _z)	0.510	0.510	0.987	0.992	0.849	0.986

^a Calculations carried out for HMTA molecule assuming all angles CNC and NCN are equal and tetrahedral; ^b in view of low symmetry of the molecule *II*, values of orbital charges for hydrogen and carbon atoms in positions 2,3 and 4 differ (numbering see formula *II*).

N(1). Both models correspond in the described form to the C_{3v} point symmetry group. For the one-proton model we obtained potential with a minimum at 1.3 Å (separation H—N(1)), if the HMTA skeleton was described by the geometry of HMTA hydrobromide. Under these geometrical assumptions and for the separation 1.3 Å we solved the three-proton problem. The results on both these models are summarized in Table V. This calculations bear out an interesting finding, namely a strong effecting of the carbon atoms in the vicinity of the protonized nitrogen.

DISCUSSION

As it follows from the geometry of HMTA hydrobromide, the protonization leads to a significant change in bond-lengths and skeleton angles, in comparison with the neutral molecules. Thus, *e.g.*, all three bonds between N(1) and C(1), C(2), and C(3) are extended by 0.06 Å, and all bonds C—N in the six-membered ring opposing the protonized nitrogen are longer by as much as 0.131 Å. As HMTA belongs to the cage-type molecules, these changes result in the over-all deformation of the molecule. Similar deformations of the skeleton were found in studying^{11,12} the geometry of the charge-transfer complex HMTA.2 Br₂ of the C_{2v} symmetry group¹⁹.

It follows from the infrared spectra²⁰ that HMTA hydrobromide in the crystalline state is of ionic nature. The proton is bound by a covalent bond to the N(1) atom and by a strong hydrogen bond to the Br⁻ anion (formula IV). In connection with this the finding that the quantum-chemical calculation shows a larger stability of the non-ionic form in which the hydrogenbromide proton is bound by a hydrogen bond to N(1) of the HMTA molecule (formula V) seems rather surprising. However, a similar result comes from quantum-chemical *ab initio* calculations of simpler systems H₃N.HF (ref.²¹) and H₃N.HCl (ref.¹⁷). Both in our case and in the cases

TABLE IV

Quantum-Chemical Characteristics Calculated by the EHT Method for Hexamethylenetetramine Hydrobromide with Varying Distance Nitrogen-Bromine (r_{NBr}) and Nitrogen-Proton (r_{NH})

$r_{\text{NBr}}, \text{Å}$	3.05	3.10	3.15	3.10
$r_{\text{NH}}, \text{Å}$		1.70		0.70
Overlap population				
N(1) C(1)	(.000) ^a	0.357	(.000) ^a	0.376
N(2) C(3)	(.000)	0.419	(.000)	0.424
N(2) C(4)	(.001)	0.326	(.000)	0.326
C(1) H(1)	(.000)	0.813	(.000)	0.819
C(4) H(4)	(.000)	0.808	(.000)	0.808
C(4) (H4')	(.000)	0.804	(.000)	0.804
N(1) Br	-(.004)	-0.046	(.004)	-0.042
N(1) H	-(.007)	0.018	(.006)	0.482
Br H	(.029)	0.451	(.018)	0.024
Net atomic charges				
N(1)	-(.005)	-1.850	(.005)	-1.540
N(2)	-(.003)	-1.862	(.000)	-1.861
C(1)	-(.001)	1.030	(.000)	1.008
C(4)	-(.001)	1.034	(.000)	1.034
H(1)	(.000)	0.091	(.000)	0.089
H(4)	(.000)	0.121	(.000)	0.121
H(4')	(.001)	0.119	(.001)	0.119
H	-(.006)	0.503	(.029)	0.719
Br	(.000)	-0.526	(.025)	-0.974
LFMO		-8.517		-8.517
HOMO		-12.438		-12.398
Total energy (eV)	(.067)	-1 093.091	(.042)	-1 092.642

^a In parentheses differences of parameter values are given related to the values for the model with $r_{\text{NBr}} = 3.10 \text{ Å}$.

TABLE V
Quantum-Chemical Characteristics Calculated by the EHT Method for HMTA Molecule
Approached by One or Three Isolated Protons

Atoms	HMTA ... H ⁺	HMTA ... 3 H ⁺
Overlap population		
N(1) C(1)	0.365 (-0.046) ^a	0.430 (0.019) ^a
N(2) C(2)	0.326 (-0.085)	0.427 (0.016)
N(2) C(1)	0.421 (0.010)	0.394 (-0.017)
C(1) H(1)	0.815 (-0.002)	0.819 (0.002)
C(2) H(2)	0.808 (-0.009)	0.808 (-0.009)
C(2) H(2')	0.804 (-0.013)	0.538 (-0.279)
N(1) H ⁺	0.408	—
N(2) H ⁺	—	-0.022
Net atomic charges		
N(1)	-1.479 (0.299) ^a	-1.731 (0.047) ^a
N(2)	-1.862 (-0.084)	-1.730 (0.048)
C(1)	1.022 (0.011)	1.014 (0.003)
C(2)	1.033 (0.022)	1.365 (0.354)
H(1)	0.090 (0.003)	0.083 (-0.004)
H(2)	0.121 (0.034)	0.124 (0.037)
H(2')	0.119 (0.032)	0.217 (0.130)
H ⁺	0.631	0.420

^a In parentheses differences of values of calculated parameters are given related to the values for HMTA molecule.

TABLE VI
Prepared Molecular Compounds of Hexamethylenetetramine with Phenols and Their Characteristics

Phenol	pK _a ^a	Component ratio HMTA : phenol	% N	
			calc.	found
Non-substituted	9.98	1 : 3	13.26	13.44
2-Methyl	10.28	1 : 3	12.06	11.90
4-Methyl	10.14	1 : 3	12.06	12.16
4-Nitro	7.15	1 : 1	25.08	24.91
2,4,6-Trinitro	0.71	1 : 1	26.55	26.71

^a Dissociation constants of phenols from ref.²⁷.

cited above^{17,21} the effect of an external field was not taken into consideration in the calculations. The proton shift towards the nitrogen atom is thus a result of forces acting within the crystal, while in the isolated system the non-ionic form is more stable.

In verifying the correctness of the quantum-chemical calculations the matrix experiment can be used. The infrared spectra of $H_3N.HCl$ studied in a cooled matrix of solid nitrogen²² unambiguously exclude the existence of the ionic structure. In the nitrogen matrix the interaction partners, *i.e.* the molecules NH_3 and HCl , are exposed solely to the action of the neighbouring nitrogen molecules and this does not favour the salt formation. Of course, in the crystalline state and in solutions of polar liquids only the form $(NH_4)^+Cl^-$ exists.

If an activation by external field is necessary to protonize the HMTA molecule by an acid as strong as HBr , with weak acids the protonization does not have to be taken into consideration. Therefore, in the HMTA hexahydrate molecule only non-ionic structures would be present whose stability would stem from the hydrogen bonds between water molecules and HMTA nitrogen atoms. It is known that a proton-acceptor molecule rehybridizes only slightly when forming a hydrogen bond. Therefore, the influence of three protons attacking three nitrogen atoms of each HMTA molecule in the hexahydrate does not cause larger internuclear separation and valence angle changes than up to about 1.5%.

Phenols which form complexes with a variety of compounds²³ *via* hydrogen bonds, form molecular compounds with HMTA, too. The compounds of HMTA with phenol²⁴, alkylphenols²⁵, polyfunctional phenols (pyrogallol²⁶) were studied more in detail. The ratios in which these compounds are formed vary, but most frequently they are 1 : 3.

We prepared molecular compounds of HMTA with five phenols of a gradually differing acidity under such conditions that only stable equilibrium compounds could be formed. Their analysis showed that weak phenols formed complexes of the 1 : 3 type, while strongly acidic phenols formed complexes of the 1 : 1 type (Table VI). The compounds of the former type are evidently stabilized by hydrogen bonds and thus three phenol molecules can attach to the HMTA molecule. However, as soon as the phenol acidity increases to the point that the nitrogen atoms in the HMTA molecule can be protonized, the stoichiometry changes to 1 : 1. The difference between these two types of molecular compounds is clearly visible in their infra-red spectra: the 1 : 3 complexes exhibit a strong absorption of the $\nu(O-H)$ vibration in the region above 3000 cm^{-1} (Fig. 3), while the 1 : 1 complexes show an absorption of the $\nu(N^+-H)^*$ vibration at about 2600 cm^{-1} (Fig. 4). For com-

* The band in the region above 3000 cm^{-1} was ascribed to the $O-H$ bond vibration, as the $\nu(N^+-H)$ vibration can occur in this region only exceptionally, *e.g.*, in the spectra of salts with anions of the $MHal_n^-$ type (M is boron or a rare metal, Hal is fluorine or chlorine); these compounds were not investigated in this study.

parison, Fig. 4 shows also the spectrum of HMTA hydrobromide with the characteristic absorption $\nu(\text{N}^+—\text{H})$.

The results presented here show a possibility of using the stoichiometry of HMTA molecular compounds in determining the mechanism of their component interaction, assuming the interaction is of the acid–base type. The calculation of the two-minima potential indicates that the proton tunnelling effect in HMTA hydrobromide plays a role. With the help of the tunnel effect the structure of the $\nu(\text{N}^+—\text{H})$ band of this hydrobromide could be explained; in its interpretation²⁰, all the existing theories of hydrogen bonding have failed.

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