171. Gas-Phase Basicities of Open-Chain and Cyclic Diols from Dissociations of Ammonium Adducts, Protonated Mixed Dimers and ICR Experiments. Structural and Stereochemical Effects

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Dedicated to Prof. *Tino Gäumann* on the occasion of his 60th birthday

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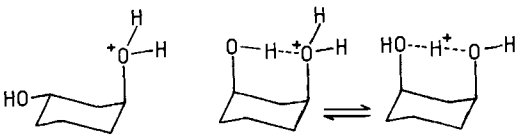
The gas-phase basicity (GB) of open-chain and cyclic diols and triols has been determined by the method of dissociation of proton-bound adducts using 1,4-butanediol and *cis*- and *trans*-1,3-cyclohexanediol as reference compounds. The GB and proton affinity (PA) of the two cyclic reference diols have been obtained in ion-cyclotron-resonance experiments. The unimolecular and the collision-activated dissociations of the ammonium adducts of the polyols allow a ranking of their GB and PA values which reflects the various structural and stereochemical effects. The possibility of internal H-bonding between the two OH groups leads to a strong increase of the PA values. The incremental effect of chain length on the PA of open-chain diols is evidenced, as well as the detailed influence of the configuration and conformation for cyclopentane- and cyclohexanediols, and -triols. These experiments also emphasized the predominant role of doubly H-bound ammonium/diol chelate conformations as opposed to singly proton-bound species.

Introduction. – The chemical ionization (CI) spectra of aliphatic diols show distinct features according to the structure and configuration of the molecular system. Internal stabilization of the product ions has been evidenced both under positive-CI [1] and negative-CI [2] conditions.



trans-**13** H^+ *cis*-**13** H^+

Due to steric requirements, the H-bridge stabilizations of the protonated species MH^+ can only occur in open-chain diols and *cis*-configurated cyclic diols but generally not in cyclic *trans*-diols as exemplified for the isomeric 1,3-cyclohexanediols **13**. Whereas *trans*-**13**H^+ is a normal oxonium ion in any molecular conformation, the *cis*-**13**H^+ epimer is stabilized by intramolecular ion solvation in a 1,3-diaxial conformation showing two possible tautomeric H-bond structures. The present work is aimed at the quantification of the structural and stereochemical effects on the stability of protonated diols and triols. For this purpose, we have used the method of proton-bound dimers which was originally

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$$M_1HM_2^+ \xrightarrow{k_1} M_1H^+ + M_2 \qquad M_1HM_2^+ \xrightarrow{k_2} M_2H^+ + M_1 \tag{1}$$

$$\ln\frac{[M_1H^+]}{[M_2H^+]} = \ln k_1/k_2 = \Delta GB/RT \tag{2}$$

developped by *Cooks* and coworkers [3] *(Eqn. 1)*. The difference in gas-phase basicity, ΔGB can be derived from *Eqn. 2*.

This procedure has already been used to obtain the relative acidities of a series of aliphatic diols [4]. Since the virtual temperature T in *Eqn. 2* is related primarily to the sampling time of the experiment [3] [4b], we have calibrated *Eqn. 2* by determining the GB values for some of the compounds in experiments conducted in an ion-cyclotron-resonance (ICR) spectrometer using equilibrium proton transfer, see *Experimental*.

A related approach to the determination of the stability of the protonated polyalcohols is based on the dissociations of ammonium adducts $M\,NH_4^+$ formed under CI(NH_3) conditions [5] using the same procedure described in *Eqn. 1* and *2* with M_2=NH_3. These investigations included both the metastable-ion (MI) and collisional-activation-dissociation (CAD) spectra. Finally the unimolecular dissociations of some disolvated ammonium adducts $M(NH_3)_2H^+$ were also investigated.

Experimental. – The ICR experiments were conducted in the ion-trapping mode under conditions similar to those used previously [6]. Briefly, equilibrium proton-transfer reactions $M_1H^+ + M_2 \rightleftarrows M_1^+ + M_2H^+$ were observed for times up to 0.5 s. The difference $GB(M_1) - GB(M_2) = -RT\cdot\ln K_{eq}$ yielded the proton affinity difference after correcting for the entropic term considering two contributions: *a)* the translational entropy of the proton (35 kJ·mol^{-1} at the temp. of the experiment, T = 323 K) and *b)* the change in symmetry in going from the neutral to the protonated species [7]. A term accounting for internal stabilization was included in the latter contribution with values of −45, −56, and −90 J/K accompanying five-, six-, and seven-membered ring formation, respectively, in the internally H-bonded species, see [8] for further discussion on this point. These measurements provided the GBs and PAs of the reference compounds *c*-**13** and *t*-**13**. The MI and CAD experiments were performed on a double-focussing reverse-geometry mass spectrometer *ZAB-2F* fitted with a high-pressure CI source. The CI(NH_3) spectra of the diols were taken at a source temp. of 140°, a source housing pressure of 10^{-4} Torr (corresponding to ~ 0.3 Torr of NH_3 in the source). Under these conditions, the sample ions represent about 5–60% of total ionization and give rise to strong peaks of ammonium adducts $M\,NH_4^+$. The mixed diol-dimers $M_1M_2H^+$ were obtained under corresponding isobutane-CI conditions. The diols and their mixture were introduced by a cooled/heated direct probe. The CAD spectra were obtained at an He pressure which reduced the precursor ion peak to one third of the initial value, and were corrected for MI contributions. The specific rate ratios k_1/k_2 were corrected for the discrimination effect from the electron multiplier detector by division of the mass ratio$(m_1 + 1)/(m_2 + 1)$ of the dimer components [3]. In addition to the dissociation ions MH^+ and NH_4^+, the other fragmentation products $(MH - H_2O)^+$ and $(MH - 2H_2O)^+$ formed *via* single and double dehydration from MH^+ were included in the derivation of ΔGB *via Eqn. 2*. The 28 diols and 10 triols investigated are listed in the first column of *Tables 2* and *3*. The samples were available from commercial sources or from different earlier studies [1] [9].

Results and Discussion. – 1. *Thermochemical Data for* c-**13** *and* t-**13** *from ICR Experiments. Table 1* reports the basicity data determined in the ICR measurements together with data for relevant reference compounds. The substituent effect of the isolated OH group on GB of *t*-**13** is seen to be stabilizing by 23.5 kJ·mol^{-1} as given by GB(*t*-**13**) − GB(cyclohexanol, **17**). The data of *Table 1* show that the *c*-**13** epimer has a GB value similar to that of the open-chain diol **4a**: this is due to the possibility for forming a strong intramolecular H-bond in the protonated species. The smaller basicity of *c*-**13** *vs.* **4a**, ΔGB = −3 and ΔPA = −6 kJ·mol^{-1} can be interpreted as the addition of two effects

Table 1. *Basicity Data for Alcohols Determined in ICR Experiments*

M_1	M_2	GB(M_2)	ΔGr	GB(M_1)	PA(M_1)
c-**13**	**4a**	828[b])	−3	825	880
t-**13**				805.5[c])	839
4a (*1,4*-Butanediol)				828[b])	886
PrOH				767[b])	800
t-BuOH				782[b])	815
Cyclohexanol				782[d])	

[a]) Values in kJ·mol^{-1}.
[b]) All references GB values are from [7].
[c]) Determined in bracketing experiments: *t*-**13** was found to be more basic than THF (GB = 804) and less basic than Et_2O (GB = 807).
[d]) See [6].

on the stability of the protonated forms, *i.e.* firstly a negative ring-size increment ΔGB = −12.5, ΔPA = −16 kJ·mol^{-1} (from the difference between propane-/butane-α,ω-diamine), and secondly a positive structural increment ΔGB = 9.6, ΔPA = 9.6 (from cyclohexyl-/butylamine, values from [7]).

The effect of intramolecular bridging in the protonated 1,3-cyclohexanediols is reflected by the differences in the basicity data for *cis*- and *trans*-isomers, ΔGB = +19.5 kJ·mol^{-1} and ΔPA = 41 kJ·mol^{-1}. The above thermodynamic values of *c*-**13**, *t*-**13** and **4a** are used as reference points for the GB and PA interpolations on the basis of the MI and CAD in the following sections.

2. *Protonated Mixed Dimers.* The PA values derived from the unimolecular dissociation of proton-bound dimers are summarized in the *Figure*. These data confirm previous observations that 1,4-butanediol is the most basic linear homologue, slightly above 1,5-pentanediol [4a]. Furthermore, the earlier reported influence of internal H-bond formation on the basicity of the cyclohexanediol isomers [5] can now be quantified. In these cases, the stabilizing effect of internal H-bond formation is given by PA(*cis*) − PA(*trans*), and is shown to be maximum for the *cis*-1,3-epimer. This stresses the importance of the configuration at controlling the accessibility to the thermodynamically most stable structures (see [1] [5] [6]). These factors will be discussed in the light provided by the dissociations of the ammonium adducts.

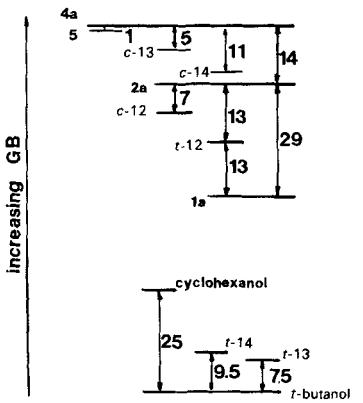


Fig. *Multiple overlapping sequence used to determine the relative PA from proton-bound dimers.* Experiments performed with the different pairs of alcohols are indicated by the arrows

Table 2. *Open-Chain Diols: MI and CAD Spectra of Ammonium Adducts* MNH_4^+, *Diol Gas-Phase Basicities*[a)][b)]

Compound *M*		MI spectrum			CAD spectrum					GB		PA	
		MH^+	NH_4^+	Σ(k)	MH^+	$(MH-H_2O)^+$	$(MH-2H_2O)^+$	NH_4^+	$\Sigma(k)$	MI	CAD	MI	CAD
1,2-Ethanediol	(**1a**)	–	0.03	0.1	0.054	0.15	0.05	1.4	5	–	802.1	–	828.5
1,2-Propanediol	(**1b**)	–	0.08	0.3	0.0701	0.42	0.14	2.9	13		801.3	–	827.6
1,2-Butanediol	(**1c**)	0.0032	0.16	0.8	0.14	0.30	0.45	3.3	18	798.8	801.7	821.4	828.5
2,3-Butanediol	(**1d**)	–	0.5	2.5	0.20	1.2	0.45	4.3	24	–	804.7	–	834.3
2-Methoxyethanol	(**1e**)	0.0055	0.021	0.1	0.37	0.24	–	1.5	8	806.3	809.7	838.1	846.0
1,3-Propanediol	(**2a**)	1.03	0.07	1.3	3.2	0.63	–	2.1	13	817.6	813.8	863.6	855.6
1,3-Butanediol	(**2b**)	3.0	0.0031	3.0	14	1.9	1.1	1.6	26	828.9	825.1	888.7	880.3
2,4-Pentanediol	(**2c**)	2.8	0.00052	2.8	21	2.9	1.6	1.4	35	833.1	827.6	898.7	886.2
1,2,3-Propanetriol	(**3**)	0.10	0.12	0.7	0.50	0.15	0.12	2.2	12	809.2	802.1	844.4	828.9
1,4-Butanediol	(**4a**)	1.5	0.0024	1.5	20	1.9	0.7	1.4	31	827.6	827.6	886.2	886.2
2,5-Hexanediol	(**4b**)	2.3	0.0022	2.3	10	2.4	1.3	0.49	18	828.5	829.7	887.8	891.2
2,5-Dimethyl-2,5-hexanediol	(**4c**)	6.5	0.011	7	15	5.6	6.3	0.40	33	826.4	834.3	882.8	901.2
1,5-Pentanediol	(**5**)	5	–	5	27	2.6	2.2	1.7	44	–	827.6	–	886.2
1.10-Decanediol	(**6**)	11	–	11	21	0.9	–	0.88	31	–	826.0	–	882.4
1,12-Dodecanediol	(**7**)	13	–	13	38	1.2	0.3	2.1	63	–	822.6	–	875.3

[a)] GB values (in $kJ \cdot mol^{-1}$; $GB(NH_3) = 821$) calculated from the dissociations of the ammonium adducts MNH_4^+ in the MI and CAD spectra. The product peak intensities are given as percentage of the MNH_4^+ precursor ($\Sigma(k)$ = corrected product ion sum). Some minor peaks are omitted. For further details see *Experimental*.

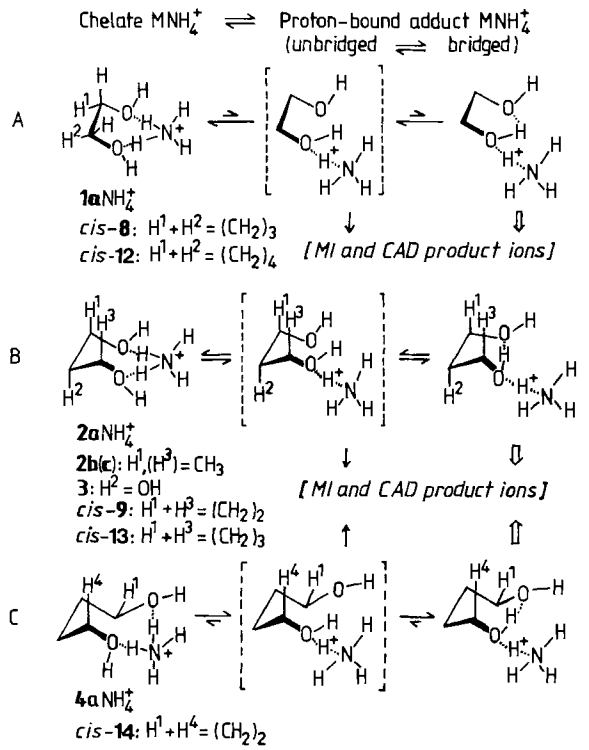
[b)] Reference values for GB interpolation: GB(*trans*-1,3-cyclohexanediol *t*-**13**) = 805.5; GB(1,4-butanediol **4a**) = 827.6.

3. *Ammonium Adducts of Open-Chain Diols.* The product distributions in the dissociations of ammonium adducts were determined both in the MI and CAD spectra for 18 acylic diols and related compounds *(Table 2)*. They show strong variations in the product ion yield and fragmentation pattern. The product-ion sum $\Sigma(k)$ which represents 0.01 to 13% of the $M\text{NH}_4^+$ precursor ion intensity in the MI spectra increases to 5 to 63% in the CAD spectra, *i.e.* with higher internal energy of parent ions. Similarily, the gradual increase in each series from the C_2 to the C_{12} substrates (**1a–7**) reflects the molecular – size or degree of freedom (DOF) activation effect [10] as another general reactivity pattern in these experiments.

The ratio of the dissociation ions $M\text{H}^+/\text{NH}_4^+$ in the MI spectra shows an extremely wide dynamic range of *ca.* $2.5 \cdot 10^5$ (*cf.* **2c** and **1c** data *(Table 2)*). In the CAD spectra the substrate specificity is somewhat compromised: the values fall into a range of *ca.* $1.3 \cdot 10^3$ **4c** and **1b**.

The contributions of the dehydration peaks $(M\text{H} - \text{H}_2\text{O})^+$ and $(M\text{H} - 2\text{H}_2\text{O})^+$ spread over a large range depending on the substrate structure. The distribution pattern of $M\text{H}^+$, $(M\text{H} - \text{H}_2\text{O})^+$ and $(M\text{H} - 2\text{H}_2\text{O})^+$ in the CAD spectra of the ammonia adducts $M\text{NH}_4^+$ of the diols shows a good qualitative match with that observed in the CI spectra under isobutane conditions [1], suggesting that similar internal energy distributions in $M\text{H}^+$ ions are produced in both cases. A remarkable aspect in the ammonium adducts of

Scheme 1. *Conformational Transitions* vs. *MI and CAD Reactions of Ammonium Adducts from 1,2-, 1,3- and 1,4-Diols (A, B and C)*



diols has to be considered in addition to single H-bond formation. It consists of the possibility for additional chelate structures [5] [12], since the reactants are capable of multiple H-bonding, as depicted for the MNH_4^+ adducts of the simple 1,2-, 1,3- and 1,4-alkanediol skeletons in *Scheme 1*. The arrows point out the preferred formation of chelates (case A) or proton bound structures (case C). The range of chelating within the adduct ions influences the extent of dissociation $\Sigma(k)$ and must be considered accordingly.

The last columns of *Table 2* report the GB and PA values obtained from MI and CAD data. Similar results of diols deduced from the two kinds of spectra emphasize the importance of including the contribution of the fragment ions in the MH^+ intensity. The influence of intramolecular H-bonding, *i.e.* the stabilization of MH^+ oxonium ions shows up in the increase of PA with respect to monoalcohols of comparable size, (*e.g.* 1,2-ethanediol *vs.* propanol, see [8]). The different H-bond strengths in the protonated C_2- to C_{12}-α,ω-diols **1a**, **2a**, **4a**, **5**, **6**, and **7** can be estimated accordingly as ΔPA = 33, 56, *80*, 80, 77, and 69 kcal·mol^{-1}, respectively. (The number *80* is the value adopted for the reference diol **4a** [7].) This sequence reflects the optimal cyclization of **4a**H^+ and **5**H^+ in the favorable cyclohexane and cycloheptane chair conformations. A similar chain-length dependence is known from the protonation equilibria of α,ω-dimethyloxyalkanes [13], α,ω-aminoalcohols [8] [14] and primary and tertiary, α,ω-diamines [7] [8].

The effect of chain length in the secondary diol series (**1d**, **2c**, **4b**) is also reflected by an increase in the PA values; it is less pronounced than for α,ω-diols because of the through-bond stabilization caused by Me groups. Similar arguments account for PA behavior in the 1,3-diol group (**2a–c**, **3**). The increasing amount of fragmentation $\Sigma(k)$ is presumably due to strong changes in the ammonium chelate stability (*Scheme 1* (B)). The sudden and strong PA increase through the *C*-alkylation in **2b** and **2c** compared to **2a** may be due to a conformational control of the dissociation of these adducts. A similar stability of the chelated and proton-bound unsubstituted **2a**NH_4^+ can be assumed. Any additional Me groups R^1 or/and R^2 in part occupy the strained axial positions of the chelates **2b**NH_4^+ and **2c**NH_4^+ and, therefore, shift the equilibrium in *Scheme 1* (B) to the proton-bound conformation. As a consequence of the different chelated structures, unusually large and unknown entropic terms may accompany the dissociation thus resulting in relatively large scattering in the derived basicity data. This possibility has recently been considered in a study on the acidity of diols [4a]. The sensitivity of the MI spectra to energy effects is visualized in *Table 2*, where only diols lying in the intermediate basicity range display both dissociation products MH^+ and NH_4^+ within the available dynamic range. A generally good agreement with the diol ranking in the CAD columns is found as observed in the original approach [3]. However, the 1,3-diols **2a–c**, **3** show a significant PA increase of 8–13 kJ·mol^{-1} in the MI with respect to the CAD scale. This observation fits into the chelate preequilibria of *Scheme 1*: under the lower energy MI conditions the most stable proton-bound conformers have no possibility to isomerize to other forms (*Scheme 1* (B)) thus resulting in a higher effective PA value for the 1,3-diols. Accordingly, the long-lived 1,4-diol adducts which are assumed to exist only to a minor extent as chelates (*Scheme 1* (C)) show a smaller PA difference between MI and CAD conditions. The 1,2-diol-adduct dissociation pattern seems also to be less energy sensitive, because of the opposite conformational preference (*Scheme 1* (A)) and the smaller entropy term (compared to 1,3- and 1,4- diols) for the conversion of the acyclic to the

Table 3. *Cyclic Diols and Triols: MI and CAD Spectra of Ammonium Adducts MNH_4^+, Diol Gas-Phase Basicities*[a])[b])

Compound *M*		MI spectrum			CAD spectrum					GB		PA	
		MH^+	NH_4^+	$\Sigma(k)$	MH^+	$(MH-H_2O)^+$	$(MH-2H_2O)^+$	NH_4^+	$\Sigma(k)$	MI	CAD	MI	CAD
Cyclopentanes													
cis-1,2-Cyclopentanediol	(*c*-**8**)	0.011	0.26	1.5	0.27	0.72	0.33	1.8	12	801.3	806.7	828.5	838.9
trans-1,2-Cyclopentanediol	(*t*-**8**)	0.008	0.083	0.5	0.09	0.20	0.12	2.3	14	803.4	798.8	832.2	822.6
cis-1,3-Cyclopentanediol	(*c*-**9**)	0.65	0.060	1.0	7.9	1.1	0.2	1.4	17	831.8	818.4	853.1	861.9
trans-1,3-Cyclopentanediol	(*t*-**9**)	0.20	0.12	0.9	1.3	0.4	0.7	2.0	14	809.7	808.8	844.8	843.5
1,2,3/0-Cyclopentanetriol	(**10a**)	0.61	0.021	0.8	5.0	0.8	0.6	0.94	13	815.5	818.0	856.9	861.1
1,2/3-Cyclopentanetriol	(**10b**)	0.048	0.11	0.8	0.20	0.15	0.14	1.8	12	806.3	799.6	838.1	824.7
1,3/2-Cyclopentanetriol	(**10c**)	0.13	0.051	0.5	0.84	0.10	0.30	1.2	9	810.1	807.2	846.0	840.2
1,2,4/0-Cyclopentanetriol	(**11a**)	1.1	0.0029	1.1	9.0	0.5	2.9	0.80	15	821.4	821.0	868.2	867.8
1,2/4-Cyclopentanetriol	(**11b**)	0.049	0.083	0.6	0.29	0.21	0.28	1.4	10	807.2	803.8	839.3	833.5
1,4/2-Cyclopentanetriol	(**11c**)	0.65	0.073	1.1	2.4	0.1	0.6	1.5	13	813.0	811.3	851.5	847.7
Cyclohexanes													
cis-1,2-Cyclohexanediol	(*c*-**12**)	0.0085	0.0038	0.3	0.15	0.65	–	1.13	9	805.1	809.2	835.2	843.9
trans-1,2-Cyclohexanediol	(*t*-**12**)	0.018	0.086	0.6	0.09	0.28	0.43	1.05	8	804.7	806.3	834.7	838.5
cis-1,3-Cyclohexanediol	(*c*-**13**)	2.24	0.0011	2.2	20	1.9	3.5	1.12	35	825.0	825.0	875.7	875.7
trans-1,3-Cyclohexanediol	(*t*-**13**)	0.063	0.218	1.5	0.28	0.33	1.8	3.9	29	805.5	805.5	836.4	836.4
cis-1,4-Cyclopentanediol	(*c*-**14**)	6.7	0.024	6.9	9.9	2.0	2.4	0.56	19	820.5	826.0	866.9	877.4
trans-1,4-Cyclohexanediol	(*t*-**14**)	0.038	0.30	2.0	0.42	0.21	0.71	1.9	14	803.8	805.9	832.7	837.3
cis-5-Methyl-*cis*-1,3-cyclopentanediol	(**15a**)	1.7	0.010	1.8	19	2.2	1.0	2.6	42	819.3	818.4	864.4	862.8
trans-5-Methyl-*cis*-1,3-cyclohexanediol	(**15b**)	5.5	0.002	5.5	16	1.4	5.0	0.83	31	825.6	825.6	876.5	876.5
5-Methyl-*trans*-1,3-cyclohexanediol	(**15c**)	0.12	0.17	1.4	0.30	0.07	1.17	2.3	19	807.2	805.1	839.8	835.6
1,3,5/0-Cyclohexanetriol	(**16a**)	3,0	< 0.005	3.1	22	0.8	3.2	0.41	29	822.2	830.1	⩾ 869.9	885.7
1,3/5-Cyclohexanetriol	(**16b**)	2.9	0.15	4.0	7.1	0.5	1.0	0.27	11	814.7	826.0	854.4	877.8
Cyclohexanol	(**17**)	–	0.3	1.6	0.08	1.3	–	2.6	16	–	804.7	–	835.2

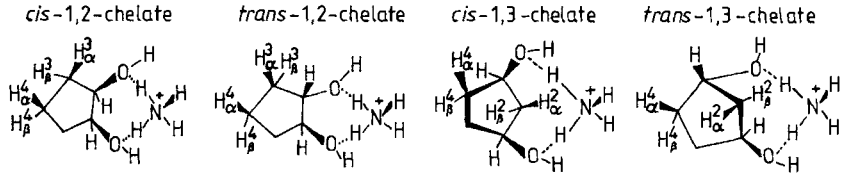
[a]) GB values obtained as in *Table 2*.

[b]) References values: GB(*trans*-1,3-cyclohexanediol *t*-**13**) = 805; GB (*cis*-1,3-cyclohexanediol *c*-**13**) = 825.

1,2-bridged adducts, thus largely suppressing the lower PA contributions from acyclic MH^+ ions.

4. *Ammonium Adducts of Cyclopentane Diols and Triols.* The main features of the discussion on open-chain diols also apply to the results on the ammonium adducts of cyclopentane and cyclohexane diols and triols given in *Table 3*. The major interest is now on the effect of the carbocyclic skeleton and of the configuration in these two classes of cyclic polyols. The increasing degree of alkyl substitution in the vicinal ethane, 1,3-butane and *cis*-1,2-cyclopentanediols (**1a**, **1d**, *c*-**8**) is nicely documented by their rising PAs of 762, 834, and 839 kJ·mol^{-1}. However, the ranking is different in the 1,3-diol series **2a**, **2c** and *c*-**9** (PAs: 856, 878 and 862 kJ·mol^{-1}), as the rigidity of the cyclopentane ring has an opposite effect. The internal 1,3-bridge in the proton-bound conformation of the *c*-**9**NH_4^+ adduct is somewhat weakened and furthermore its chelate conformation is entropically favoured (*Scheme 1* (B)) in comparison to the acyclic stronger base **2c**. The geometry of the *trans*-configurated 1,2- and 1,3-cyclopentanediols (*t*-**8** and *t*-**9**) does not allow internal H-bridging as reflected by the negative PA increments of −16.3 and −18 kJ·mol^{-1}*vs.* the *cis*-epimers. The absolute PAs of the *trans*-isomers of **8** and **9** correspond to the expected values of cyclic monoalcohols (cyclohexanol **17**) with the additional effects of remote OH groups which are incapable of transannular interactions. The more complex cyclopentanetriols **10** and **11** have a multitude of H-bond constellations in their ammonium adducts MNH_4^+ *(Scheme 2)* underlying the PA behaviour. The four prototypes of the ammonium chelation are the *cis*-1,2-, *trans*-1,2-,*cis*-1,3-, and *trans*-1,4-chelates of the respective cyclopentanediols **8** and **9**. As MNH_4^+ molecular models show, the symmetric *trans*-triols **10c** and **11c** and the all-*cis*-triols **10a** and **11a** can accommodate two competing chelate types, the latter triols also including a triply coordinated ammonium association complex. Three different competing chelate types are accessible for the chiral *trans*-triols **10b** and **11b**. *Scheme 2* also notes the number, type and relative strength of the internal H-bridges in the individual chelate conformations. These bridged species are the

Scheme 2. *Ammonium-Chelate Conformations of Cyclopentane Diols and Triols.* Additional 1,2- and 1,3-H-bridges in triol chelates; (), (()) = increasing strain. Triple NH_4^+ coordination is also possible with all-*cis*-**10a** and **11a**.



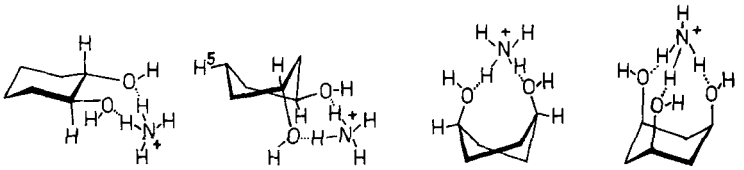
Diols: *cis*-**8**NH_4^+ *trans*-**8**NH_4^+ *cis*-**9**NH_4^+ *trans*-**9**NH_4^+

Triol·NH_4^+	OH	H-bridges 1,2	1,3	OH	H-bridges 1,2	1,3	OH	H-bridges 1,2	1,3	OH	H-bridges 1,2	1,3
10a (1,2,3/0)	H^3_α	1	1	–	–	–	H^2_α	2	0	–	–	–
10b (1,2/3)	H^3_β	0	0	H^3_α	((1))	0	–	–	–	$H^2_{\alpha,\beta}$	0	0
10c (1,3/2)	–	–	–	H^3_β	0	((1))	H^2_β	0	0	–	–	–
11a (1,2,4/0)	H^4_α	0	2	–	–	–	H^4_α	1	1	–	–	–
11b (1,2/4)	H^4_β	0	0	–	–	–	–	–	–	H^4_β	(1)	0
11c (1,4/2)	–	–	–	$H^4_{\alpha,\beta}$	0	(1)	H^4_β	0	0	H^4_α	0	0

key parent structures for the unimolecular and collision-activated dissociations. The bridge strengths and the kinetic contributions of the respective conformers determine the PA values of the triols in the ammonium adduct experiments. Thus, the 1,3-bridged all-*cis*-isomers **10a** and **11a** have high PAs similar to *cis*-1,3-cyclopentanediol *c*-**9**. In line with this, the strained 1,3-bridged *trans*-1,2-chelates of **10c** and **11c** lead to PAs in the range of *trans*-1,3-cyclopentane (*t*-**9**), whereas the strained 1,2-bridged *trans*-chelates of **10b** and **11b** resemble the *trans*-1,2-diol *t*-**8**.

5. *Ammonium Adducts of Cyclohexanediols.* Analogous stereochemical effects as above are also observed on the PA values in the cyclohexanediol group. The CAD data show PAs near 836 kJ · mol^{-1} for the monoalcohol prototype cyclohexanol (**17**) and for all 1,2-, 1,3- and 1,4-isomeric *trans*-diols **12**–**15**. For the *cis*-configuration, the PA increments due to internal solvation are 8, *39*, 40, and 41 kJ · mol^{-1} for *c*-**12**, *c*-**13**, *c*-**14**, and *c*-**15b**, respectively. (The number *39* is adopted from the ICR experiments.) The 1,3-diaxial steric interference of the *cis*-5-methyl group in the *cis*-1,3-diol **15a** decreases its PA against the *trans*-5-epimer **15b** by 14 kJ · mol^{-1} closely to the expected value of 15 kJ · mol^{-1} [14]. The additional ion solvation by the *cis*-5-hydroxy group in the protonated all-*cis*-1,3,5-triol **16aH**$^+$ stabilizes the latter by 8 kJ · mol^{-1} with respect to the *trans*-5-epimer **16b**. The cyclohexanediol PAs in the MI column of *Table 3* are generally very similar to the CAD data: the slightly lower values for the 1,2- and 1,4-isomeric diols **12** and **14** can be rationalized similarly to the cyclopentanediol results (conformational control of the MH^+/NH_4^+ ratio under different MI/CAD energetics, *vide supra*). However, the 1,3/5-triol **16b** shows a large PA deficit (23.4 kJ · mol^{-1}) in the MI spectrum of MNH_4^+. This may reflect the preference for less basic MH^+ contributions through the

Scheme 3. *Ammonium-Chelate Conformations of Cyclohexane Diols and Triols.* For *cis*-**12** and *cis*-**13** see *Scheme 1.*



unbridged *trans*-1,3 chelate which involves a strained twist conformation *(Scheme 3)* suitable for the MI energy window. Such twist-type chelates are not accessible in the MNH_4^+ ions of the exclusively *cis*-1,3-configurated species *c*-**13**, **15a**, **15b**, and **16a** which show unchanged PAs.

Further experimental evidence for the sterically controlled ammonium chelate formation is found for the analogous *trans*-diol *t*-**13** which apparently includes quite large portions of chelate twist conformers. This conclusion is indirectly supported by the high CAD product yield as compared with the *trans*-1,4-diol *t*-**14** and the *trans*-5-methyl-1,3-diol **15c** in which either the longer 1,4-distance or the 5-methyl hindrance opposes the formation of a *trans*-chelate. The MNH_4^+ adducts for *t*-**14** and **15c** are mainly simple proton-bound conformers characterized by lower cross sections for CAD.

The various occurence of *trans*-chelates is also underlined by very strong $M\text{NH}_4^+$ peaks in the CI(NH_3) spectra [5] of the *trans*-diols **8**, **9**, **12**, and **13** (56, 66, 51, and 54% of the substrate ions) but not of the *trans*-diols **14** and **15c** (19 and 9%) under comparable conditions. A direct experimental proof of the existence of the chelate conformation in the *trans*-**13** NH_4^+ ions is given in the following paragraph by the dissociation experiments with the $M(NH_3)_2H^+$ cluster ions.

6. *Disolvated Ammonia Adducts* $M(NH_3)_2H^+$ *of Cyclic Diols. Table 4* shows the MI and CAD spectra of the ammonia cluster adducts $M(NH_3)_2H^+$ of the *cis*- and *trans*-1,3- and 1,4-cyclohexanediols **13** and **14**, respectively. The kinetic approach was applied to calculate the mixed pair proton affinities (MPPA) [8] of the neutral ammonia adducts $M\text{NH}_3$ on the basis of *Eqn. 3*:

$$M(NH_3)_2H^+ \rightarrow M\text{NH}_4^+ + \text{NH}_3 \quad (3a)$$

$$M(NH_3)_2H^+ \rightarrow MH^+ + 2\,\text{NH}_3 \quad (3b)$$

$$M(NH_3)_2H^+ \rightarrow \text{NH}_4^+ + M + \text{NH}_3 \quad (3c)$$

By considering *Eqns. 3a* and *3b*, PA ($M\text{NH}_3$) values were obtained with reference to PA (M). For *c*-**13**NH_3 and *c*-**14**NH_3 they read 911 and 915 kJ·mol^{-1} for the MI and 895 kJ·mol^{-1} each for the CAD data. The solvation energies calculated as the difference between MPPA and the average PA of the two mixed base pairs (867 and 862 kJ·mol^{-1}) are in the expected order of 30–50 kJ·mol^{-1} [7]. According to the CAD spectra the epimeric *trans*-**13**NH_3 and *trans*-**14**NH_3 base pairs show somewhat lower MPPAs of 882 and 873 kJ·mol^{-1} in agreement with the reduced internal solvation possibilities. The additional solvation strength of 9 kJ·mol^{-1} in the *trans*-1,3-compared to the *trans*-1,4-species can be interpreted as the outcome of a 1,3-chelate formation in *t*-**13**NH_3 with a second H-bond, whereas *t*-**14**NH_3 must have a singly H-bound conformation.

Table 4. *MI and CAD Spectra of Ammonia Clusters* $M(NH_3)_2H^+$ *of Cyclohexanediols, Gas-Phase Proton Affinity of* $M\text{NH}_3$ *Adducts*[a])

Cyclo-hexane-diol *M*	MI spectra				PA ($M\text{NH}_3$)	CAD spectra						PA ($M\text{NH}_3$) *vs. M*	PA ($M\text{NH}_3$) *vs.* NH_3
	$M\text{NH}_4^+$	MH^+	$(NH_3)_2H^+$	NH_4^+		$M\text{NH}_4^+$	MH^+	$-H_2O$	$-2H_2O$	$(NH_3)_2H^+$	NH_4^+		
c-**13**	4.06	0.14	–	–	911.2	8.34	0.77	0.13	0.32	0.126	0.116	895.4	886.6
c-**14**	4.79	0.018	–	–	914.6	5.01	0.56	0.12	0.17	0.110	0.089	895.4	883.7
t-**13**	2.42	–	0.0048	0.0020	–	6.79	0.009	0.009	0.070	0.171	0.142	882.0	882.0
t-**14**	1.01	–	0.162	–	–	3.03	0.029	0.007	0.061	0.41	0.147	872.8	872.4

[a]) PA values obtained as in *Table 3*.

The PA ($M\text{NH}_3$) values can also be obtained by considering *Eqns. 3a* and *3c*, yielding the values reported in the last conlumn of *Table 4*. A good match is found for the *trans*-compounds, whereas the values for the *cis*-isomers are lowered by *ca.* 8–12.5 kJ·mol^{-1} with respect to the PA ($M\text{NH}_3$) *vs. M* values. This results from the possibility of consecutive dissociation of $M\text{NH}_4^+$ which overestimates the contribution of *Eqn. 3c*. Such an effect is in accordance with the preferred formation of internally proton-bound adducts for *c*-**13** and *c*-**14** as depicted in *Scheme 1*.

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