Mannich Bases as Model Compounds for Intramolecular Hydrogen Bonding I. Solid State Structures and Molecular Calculations

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Summary. A survey of the structures and the properties of the hydrogen bonds in *ortho*-aminomethylphenols and -naphthols in the solid state is presented. The results are compared with molecular structure calculations. The solid state complexes can exist in the molecular or in zwitterionic form. In the last case, only intermolecular hydrogen bonds forming cyclic dimers or linear chains were detected.

Keywords. *Mannich* bases; Alkylaminophenol; Alkylaminonaphthol; Intramolecular hydrogen bond; Proton transfer.

Mannich-**Basen als Modelle für Intramolekulare Wasserstoffbrücken, 1. Mitt. Festkörperstrukturen und Molekülrechnungen**

Zusammenfassung. Eine Übersicht über Strukturen und Eigenschaften von Wasserstoffbrücken in *ortho*-Aminomethylphenolen und -naphtholen wird präsentiert. Die Ergebnisse werden mit Molekülrechnungen verglichen. Im Festkörper existieren diese Verbindungen in neutraler oder in zwitterionischer Form. Für den zweiten Fall können nur intermolekulare Wasserstoffbrücken nachgewiesen werden, und zwar in Dimeren oder in linearen Ketten.

Introduction

A common system for the investigation of hydrogen bonding and proton transfer is the intermolecular association between phenols and amines, because the stable hydrogen bonds of these aggregates show proton transfer depending on proton donor and proton acceptor properties which can be varied over broad ranges by different substituents. The thermodynamic and the dynamic behavior of such complexes have been studied widely using different spectroscopic [1–12] and dielectric [13–16] methods. The interpretation of the experimental results for these phenol – amine systems is sometimes difficult because of additional association and dissociation phenomena of the components and complexes themselves, concentration dependencies of the stoichiometry of adducts, and so on, which have to be determined and accounted precisely. The situation is simpler with intramolecular hydrogen bonds where most of the forementioned problems are absent. Convenient systems are the *Mannich* condensation products of substituted phenols or naphthols
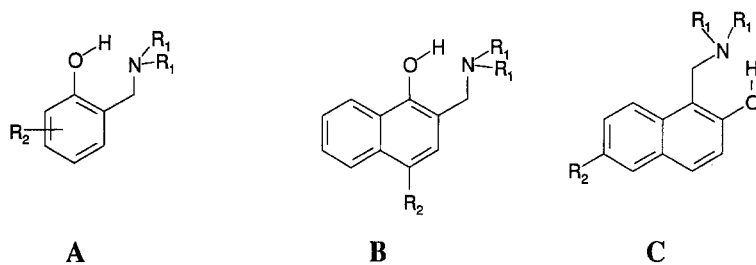
Fig. 1. *ortho-Mannich* bases of type A, B and C

with formaldehyde and secondary amines which contain a phenolic or naphtholic hydroxyl group as proton donor as well as a *ortho*-aminomethyl group as proton acceptor in the same molecule [17–19]. The favourable geometry of these *ortho-Mannich* bases leads to the formation of stable intramolecular hydrogen bonds.

In addition to the typical features of intramolecular hydrogen bonding, these systems have an extra advantage over many other intramolecular complexes: the methylene bridge joining both components prevents electronic coupling between the proton donor and the proton acceptor part of the molecule [20]. Such coupling exists *e.g.* in *o*-nitrophenols [21, 22] or salicylic acids [22] and causes substantial rearrangement of the charge [23, 24]. Also, partial compensation of charge migration in such hydrogen bonds takes place [25, 26]. The advantages of using the intermolecular complexes of the phenols and amines are preserved in the case of *ortho-Mannich* bases (see Fig. 1). They show practically the same ability for regulation of proton donor and acceptor properties [19, 27]. Nevertheless, some differences appear. The hydrogen bond is nonlinear in the intramolecularly hydrogen bonded systems, and for steric reasons the ring formed by the hydrogen bridge cannot be planar. Therefore, a careful analysis of the geometry of these compounds is necessary. Additionally, a small electronic coupling still remains and must be taken into account.

Results and Discussion

The first crystal structures of *Mannich* bases were published in 1982 [28]. The structures of 2-(N,N-diethylaminomethyl)-3,4,6-trichloro-phenol (**1**) and 2-(morpholinomethyl)-4-chloro-phenol (**2**) were determined.

For both molecules, nonplanar structures with an intramolecular hydrogen bond were found. As a parameter of the nonplanarity, the torsional angle around the
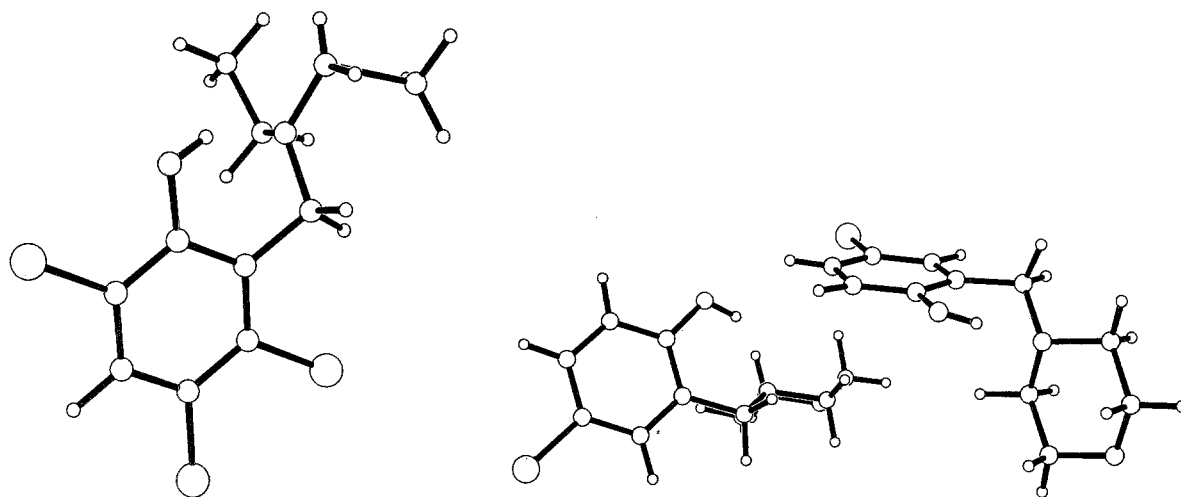
Fig. 2. a) Molecular structure of 2-(N,N-diethylaminomethyl)-3,4,6-trichlorophenol in the crystal state [27]; b) arrangement of two nonequivalent molecules of 2-(morpholino-methyl)-4-chlorophenol in the crystal [28]

C_{aryl}–C_{alkyl} bond (φ, *cf.* Fig. 6) was used. Its values were 38 and 45.8 (41.9) degrees for compound **1** and **2**, respectively (value in parenthesis concerns the second molecule in the crystal unit cell of **II**). Simultaneously performed CNDO/2 calculations gave a φ value of 28.7° [28]. Both the experiment and calculations show that the chelate ring is nonplanar and the nitrogen atom is seriously displaced from the phenyl ring plane. The CNDO/2 method gave a more planar structure, but it is known that this method generally overemphasizes the hydrogen bond strength, which leads to too flat structures in our case [31]. Molecular mechanics calculations on the geometry of the chelate ring were done by means of the atom-atom and *Lippincott-Schröder* potentials [20]. The calculations were performed as a function of the hydrogen bond strength parameter ΔH_{HB}°. This enthalphy of the complex formation was included into the recalibration procedure of the *Lippincott-Schröder* potential parameters for the linear intermolecular complexes of phenols with triethylamine. The obtained results agree with the experiment much better than those from the semiempirical CNDO/2 calculations. They show also very characteristic changes of the chelate ring structure with increasing ΔH_{HB}°. The torsional angle of 38 ± 2° was obtained as an asymptotic value for the strongest complexes. Its value increases with the decrease of the hydrogen bond strength in terms of ΔH_{HB}°. The analogous calculations for the zwitterionic forms of the intramolecular hydrogen bond, resulting from the intramolecular proton transfer, show a very similar φ dependence on ΔH_{HB}° [20].

As discussed earlier, results of the crystal structure determination seem to agree with this prediction for complex **1** with the higher $\Delta pK_a^{\#}$ value ($\Delta pK_a = 2.72$ [32]); a lower value of φ (38°) was found for compound **2** ($\Delta pK_a = -2.65$; $\varphi = 42$–47°, *cf.*

[#] ΔpK_a is defined as the difference between the pK_a value of the protonated amine component and the pK_a value of the phenolic component of the *Mannich* base
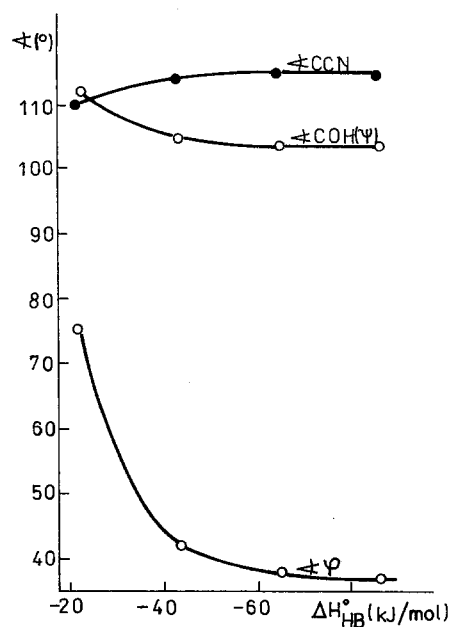
Fig. 3. Dependence of the most characteristic parameters of the chelate ring structure on the hydrogen bond strength; results of molecular mechanics calculations [20]

Table 1. Comparison of the experimental and theoretical structure parameters for 2-(morpholinomethyl)-4-chlorophenol (distances in Å, angles in degrees)

Parameter	X-ray[a,[28]]	X-ray[a,[27]]	*ab initio*[b]	PM3[c]	AM1[c]
r(N$\cdots$O)	2.680(2); 2.713(2)	2.69(1); 2.71(1)	2.68	2.70	3.16
r(N$\cdots$H)	1.95(3); 1.92(3)	2.03; 1.99	1.81	1.84	2.43
r(O–H)	0.89(3); 0.85(3)	0.75(5); 0.80(5)	0.985	0.967	0.968
<COH (ψ)	115(2); 103(2)	111(4); 108(4)	109.2	107.1	109.2
<CCOH (Θ)	18; −16	−15; −23	17.4	12.8	9.0
<CCCN (φ)	−43.3(4); 46.9(5)	41.9(7); 45.8(7)	441.	36.3	62.9

[a] Two different molecules in the unit cell; [b] this work, 3-21G level, Gaussian 92 [36]; [c] this work, MOPAC 5 [37]

Table 2). The basic concept of applied molecular mechanics approach that the observed chelate ring structure is a result of the compromise between intramolecular steric repulsion and the attraction of atoms participating in the hydrogen bridge seems to be verified with this limited amount of experimental data.

Results of AM1 as well as PM3 calculations are also available [35]. In Table 1, the minimum energy geometries resulting from such semiempirical calculations [36] on 2-morpholinomethyl-4-chlorophenol are given together with *ab initio* results [37] and X-ray diffraction structures.

AM1 predicts a too weak intramolecular hydrogen bond, characterized by a very large torsional angle φ and much too long N$\cdots$O and N$\cdots$H distances, and gives a structure which is very different from the experimental one. PM3 results show a smaller dihedral angle φ than determined by the X-ray experiment but proper N$\cdots$O and N$\cdots$H distances. *Ab initio* results on a 3–21G level are in good
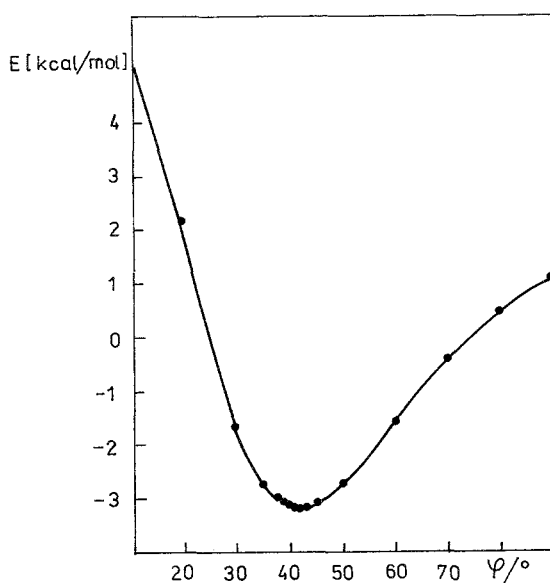
Fig. 4. Potential energy dependence on the rotation angle φ for the intramolecular complex with ΔH°_{HB} equal to $-10\,kcal/mol$; molecular mechanics results [20]

agreement with the data from the crystal structure determinations. Such a good coincidence between *ab initio* and X-ray structure is surprising because solid phase and gas phase structures are compared. In general, one can expect that *ab initio* results are more reliable than those obtained from semiempirical methods, especially in case where the molecular geometry results from a superposition of weak interactions which are rather difficult to describe. From the calculations (*cf.* Fig. 4) it can be concluded that the energy dependence of the dihedral angle has a rather flat minimum[#]; this is probably the reason for the existence of two different molecules in the crystal unit cell.

Further investigations on the solid phase structures of *Mannich* bases were performed in order to obtain more information about the influence of various factors on the molecular geometries.

In the next published structure of a *Mannich* base – 2-(N,N-dimethyl-aminomethyl)-4-nitrophenol (3) [39] – it was found that the substitution of the NO_2 group in position 4 of the phenol leads to a complete change of the structure. The hydrogen atom participating in the hydrogen bridge is located at the nitrogen atom, as can be additionally confirmed by a significant shortening of the C–O bond (to 1.283 Å). Two $NH^+ \cdots O^-$ hydrogen bonds of the length of 2.67Å form a cyclic dimer with the symmetry center, but with phenyl rings in different parallel planes (*cf.* Fig. 5).

It is evident that the existence of either the molecular or zwitterionic form of the hydrogen bridge in the solid state does not depend only on acidic and basic properties of the hydrogen bond. The ΔpK_a value of the 4-nitro derivative is about one unit lower than that for 2-(N,N-diethylaminomethyl)-3,5,6-trichlorophenol (1)

[#] Deviations from the energy minimum position of about $\pm 8^\circ - 10^\circ$ are caused by energies in the order of RT
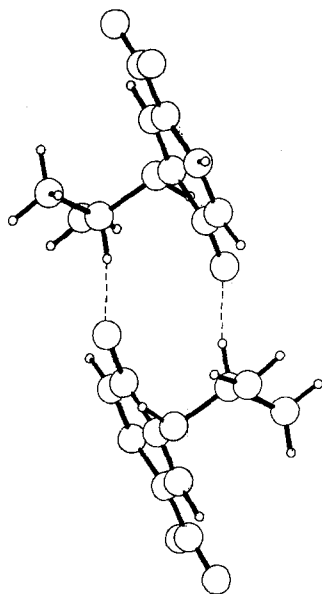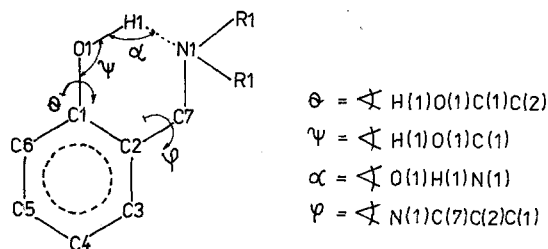
Fig. 5. Cyclic dimer structure formed by 2-(N,N-dimethylamino-methyl)-4-nitrophenol in the solid state [37]

$\Theta = \sphericalangle\ H(1)O(1)C(1)C(2)$

$\Psi = \sphericalangle\ H(1)O(1)C(1)$

$\alpha = \sphericalangle\ O(1)H(1)N(1)$

$\varphi = \sphericalangle\ N(1)C(7)C(2)C(1)$

FOR   THE   ZWITTERIONIC   FORMS:

$\Psi = \sphericalangle\ H(1)N(1)C(7)$

$\Theta = \sphericalangle\ H(1)N(1)C(7)C(2)$
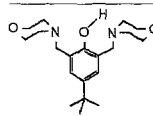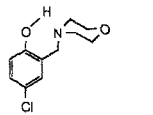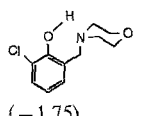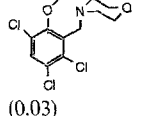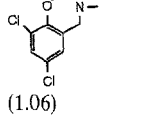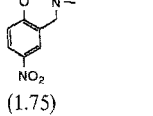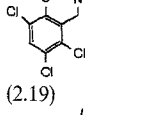
Fig. 6. Atom numbering and angles definitions in ortho-Mannich bases

which, as was shown earlier, exists in the molecular form. The large polarity of the nitro group could be responsible for the proton transfer. On the other hand, the reason of the observed effects can be decrease of the steric repulsion caused by replacing the diethylamino group in 1 by the dimethylamino substituent in 3.
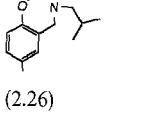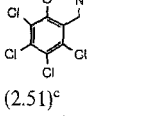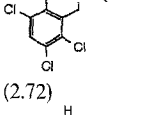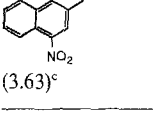
A more extensive presentation of the results of X-ray analysis is given in Table 2. For a definition of selected angles and distances see the scheme in Fig. 6. The results are ordered according to increasing values of ΔpK_a.

From the data given in Table 2 it can be recognized that the reduction of steric repulsions in 3 cannot be the deciding factor which promotes the proton transfer reaction in the solid state. The Mannich base (4), the condensation product of 2,4,5-trichlorophenol, dimethylamine, and formaldehyde, exists in the molecular form despite the higher ΔpK_a value ($\Delta pK_a = 2.19$) with respect to 3. Further increase of ΔpK_a appears to be sufficient in 2-(N,N-dimethylaminomethyl)-tetrachloro-phenol (5, $\Delta pK_a = 2.51$) to produce the zwitterionic form of a complex. As in the case of 5, the two intermolecular hydrogen bonds form a cyclic dimer, but without

Table 2. Selected distances (Å), valence, and torsion angles (degrees) for *ortho-Mannich* bases in the solid state

Compound (ΔpK_a)	$r(N{\cdots}O)$	$r(O{-}H)$	$r(N{\cdots}H)$	$r(C{-}O)$	ψ	Θ	φ	α	Ref. (R^a)
(−3.50)	2.682(1)	0.87(4)	1.94(4)	1.374(3)	112.8	−19.7	35.9	142(3)	[33] (0.065)
(−2.65)	2.680(2)	0.89(3)	1.95(3)	1.356(3)	115(2)	18(2)	−43.3(4)	138(3)	[29] (0.042)
	2.713(2)	0.85(3)	1.92(3)	1.364(3)	103(2)	−16(2)	46.9(5)	155(2)	b
	2.69(1)	0.75(5)	2.03	1.354(6)	111(4)	−15	41.9(7)	147	[28]
(−1.75)	2.71(1)	0.80(5)	1.99	1.359(6)	108(4)	−23	45.8(7)	150	b
	2.652(2)	0.84(3)	1.91(3)	1.355(3)	108(2)	−6(2)	41.5(6)	147(3)	[30] (0.037)
(0.03)	2.649(2)	0.89(2)	1.83(2)	1.342(3)	104(2)	−14(3)	49.8(3)	154(2)	[30] (0.027)
(1.06)	2.651(3)	1.00(4)	1.70(4)	1.352(5)	102(2)	−15(3)	41.3(4)	156(3)	[30] (0.044)
(1.75)	2.667(2)	1.71(2)	0.97(2)	1.283(3)	110.7	64.9(4)	−81.9(5)	169(2)	[39] (0.032)
(2.19)	2.567(3)	1.10(4)	1.59(4)	1.339(3)	106(2)	4.4(12)	−31.1(4)	145(33)	[30] (0.044)
(2.26)	2.620(9)	1.03(9)	1.65(9)	1.341(8)	105(4)	−11(3)	36.4(9)	156(7)	[34] (0.062)
	2.614(3)	0.97(3)	1.78(3)	1.343(3)	114(2)	11(2)	−35.7(3)	141(3)	[30] (0.051)
(2.51)c	2.637(4)	1.67(4)	1.00(4)	1.278(4)	109.7	−41.2	−75.4(4)	163(4)	[34] (0.043)
	2.640(4)	1.61(5)	1.05(5)	1.279(4)	116(2)	35.3	−75.3(4)	168(4)	[29] (0.044)
(2.72)	2.58(1)	0.90(6)	1.76(6)	1.355(5)	107(4)	19	38.0(7)	152	[28]
(3.63)c	2.76	1.90	0.87	1.285	108.7	74.1	105.3	170.0	[40]

a Final values of the residual indices in structure solving; b two nonequivalent molecules in the unit cell; c for the ionic structures, $r(N{\cdots}O)$ and $r(O{-}H)$ as well as α are defined for atoms belonging to two different molecules
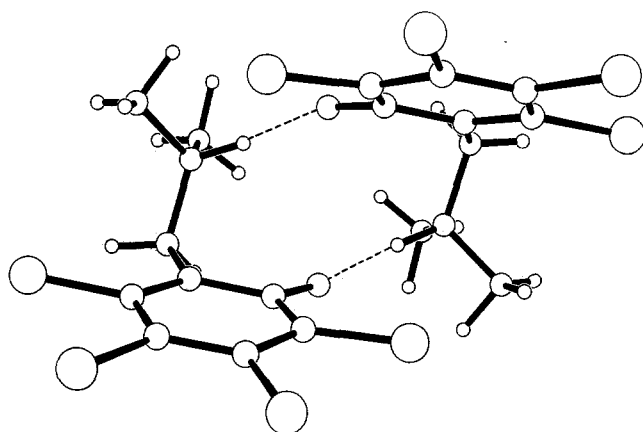
Fig. 7. Cyclic dimer structure of 2-(N,N-dimethylaminomethyl)-tetrachlorophenol [28]
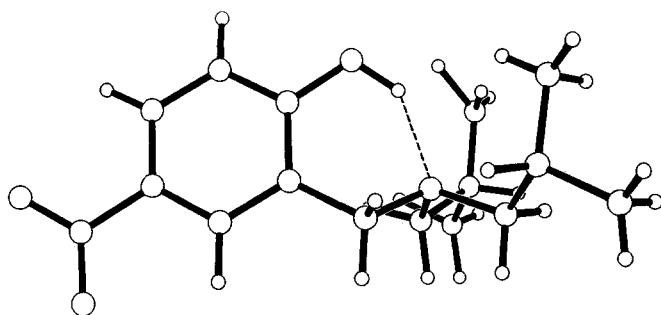

Fig. 8. Structure of 2-(N,N-diisobutylaminomethyl)-4-nitrophenol [28]

a symmetry center (cf. Fig. 7). Two molecules are related by a C_2 symmetry axis. Such a conformation can also be used as an example of cyclic dimers with non zero dipole moment in solution [41].

It is interesting to mention that the shortest hydrogen bond was found in the molecular form of 4 (O $\cdots$ N = 2.567 Å). Ionization of the hydrogen bond in 5 leads to an increased O $\cdots$ N distance (≈ 2.64 Å).

An interesting result occurs in the case of 2-(N,N-diisobutylaminomethyl)-4-nitro-phenol. This compound, containing a 4-nitro substituent similar to 3, exists in a structurally different molecular form due to increased steric repulsion. Figure 8 illustrates the shielding of the hydrogen bridge from the environment by the isobutyl chains.

2-(N,N-diethylaminomethyl)-1-naphthol shows an intramolecular hydrogen bond of medium strength [40]. The hydrogen bond again is not coplanar with the aromatic ring, and the proton is bound to the oxygen atom with a distance of 1.35 Å for the C–O bond in agreement with other structures of phenol derivatives [42–44]. By comparison with structures containing a weaker proton acceptor (morpholine instead of piperidine as base), an enhanced N $\cdots$ O distance of the hydrogen bond is observed together with an increased angle φ which is caused by a minor flattening of the chelate ring formed by the hydrogen bond.

Changing from phenols as proton donors to naphthols, the hydrogen bond strength is increased due to the enhanced proton donor ability, and therefore the ring with the hydrogen bond is flattened again. Substitution of the phenyl ring at the
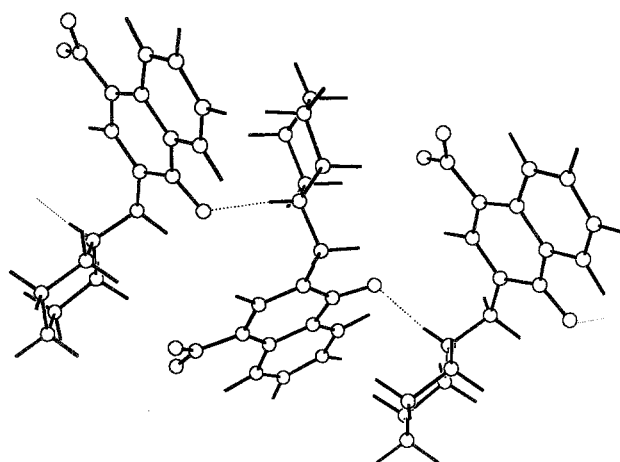
Fig. 9. Hydrogen bonded chain formed in the crystal structure of the zwitterionic form of 2-(piperidinomethyl)-4-nitro-1-naphthol [38]
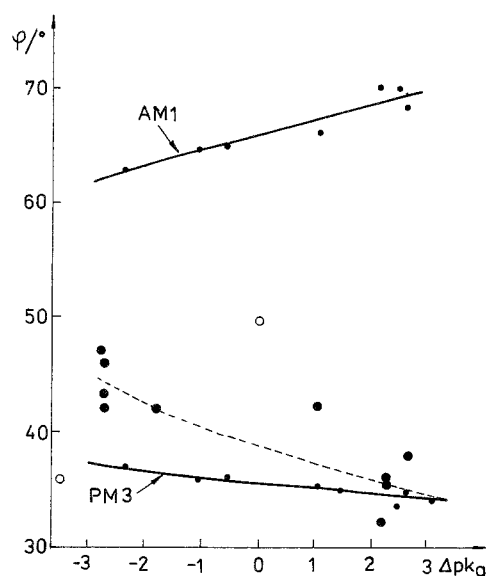

Fig. 10. Dependence of the torsional angle N1-C7-C2-C1 (φ) in molecular crystals of *Mannich* bases on ΔpK_a in comparison with the results of AM1 and PM3 calculations

methylene bridge between proton donor and amine increases the hydrogen bond strength, too. Influenced by a steric interaction of the phenyl ring, the angle φ is drastically reduced [40].

In 2-(piperidinomethyl)-4-nitro-1-naphthol, a zwitterionic hydrogen bond is formed. The intermolecular hydrogen bonds of a length of 2.76 Å form chains in the crystal (*cf.* Fig. 9) [40].

One can try to correlate the results of the X-ray structure with the predictions of the theoretical methods. The most sensitive parameter on the hydrogen bond strength modification is the dihedral angle φ (*cf.* Fig. 3). However, this parameter can be additionally influenced by the surrounding. Results of the molecular mechanics calculations show, for example, that the crystal packing forces in the order of RT (0.6 kcal/mol) are sufficient to shift φ from its optimal value by $\pm 8°-10°$ (*cf.* Fig. 4).

Figure 10 presents the dependence of the crystallographic φ values on ΔpK_a in comparison with the results of AM1 and PM3 calculations. The AM1 method
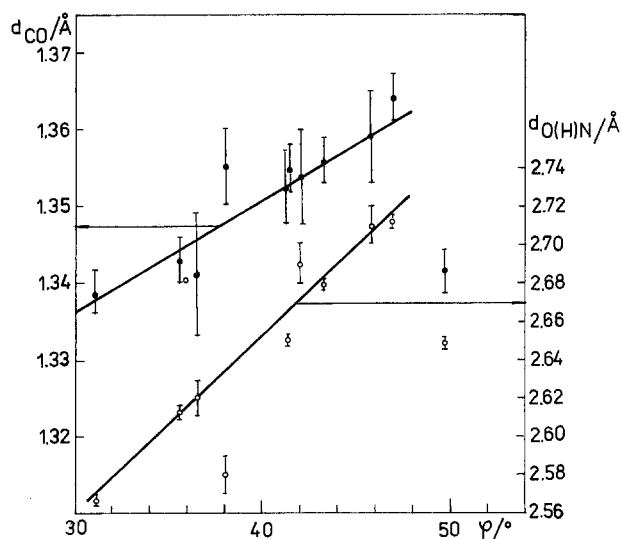
Fig. 11. Internal correlation between the parameters of the chelate rings in *ortho-Mannich* bases which are especially strongly related to the hydrogen bond strength

predicts all dihedral angles much too high, as a consequence of too large calculated hydrogen bond lengths. A much better agreement of the experimental values with the PM3 results, particulary in the range of stronger hydrogen bonds, can be mentioned. However, a too small slope of this dependence is described by the PM3 method. The experimental data show a spread of φ values in the correlation with ΔpK_a, probably caused by crystal packing effects. An attempt was done to detect these structures which are influenced by the crystal forces to a large extent. The φ parameter was therefore correlated with the length of the C–O bond and the O $\cdots$ N distance. Both parameters depend also significantly on the hydrogen bond strength, but they may be assumed to be less dependent on the shape of the molecule and for this reason on crystal packing effects.

Figure 11 shows a surprisingly good correlation of C–O bond lengths and O $\cdots$ N distances with φ for the majority of the experimental structures except for two geometries with serious displacement from the correlation lines exceeding the average standard deviations as well as a standard deviations calculated for these correlations.

These points, indicated in Fig. 10 as open circles, belong to complexes with morpholine substitution. This bulky moiety can be influenced in a serious way by the crystal packing conditions. Inspecting the remaining points, shown as a black circles in Fig. 10, one can find some tendency of φ to decrease with increasing ΔpK_a which has been suggested earlier by molecular mechanics calculations [20].

In Table 2, the results of independent determinations of the structure for three *ortho-Mannich* bases are presented. Generally, the differences in obtained values of related parameters are within the limits of standard deviations. Especially large deviations are visible in the case of α values (the bending angle of the hydrogen bridge) as a result of the high uncertainty of the location of the H atoms.

Conclusions

In the present paper, the structure of the hydrogen bond in *ortho-Mannich* bases, using the direct crystallographic information and the results of molecular calcula-

tions on different level, is discussed. All these sources show stable, bent intramolecular OH–N hydrogen bonds forming nonplanar chelate rings. A general trend (the stronger the hydrogen bond, the more planar the structure) was proved. Semiempirical AM1 and PM1 methods used in the hydrogen bond structure description behave in a different way. The PM3 method gives rational values of the NCCC torsional angle ($\varphi = 33°-36°$) which differ from the experimentally determined ones no more than 10°, generally predicting more planar structures than obtained from X-ray determinations.

Values of the torsional angle ($\varphi = 65°-70°$) and the O$\cdots$N distances obtained with the AM1 procedure are distinctly too high. The PM3 gives generally too short hydrogen bonds, but the deviation from the experiment is considerably smaller than in the case of AM1. *Ab initio* procedures at a rather low level (HF/3-21G) determines the most accurate structure; the agreement with the crystal structure data is better than it could be expected, taking in account the possible deformations resulting from crystal packing forces.

Performed correlations and analyses demonstrate that in most cases there exists an internal consistency of different parameters dependent on the strength of the hydrogen bond, leading to the conclusion that the structure of *Mannich* bases of molecular form in the crystal state is mainly determined by internal properties of the complexes. Only in the case of two compounds containing the morpholine ring more serions deviations were found.

Mannich bases with ΔpK_a values higher than 1.7 can exist in the zwitterionic form in the solid state. The form of the hydrogen bond does not depend exclusively on the hydrogen bond strength. Existence of high polar substituents like the nitro group facilitates the proton transfer, whereas the extension of N-chains, increasing the steric repulsion, makes this process more difficult.

Determined structures of individual molecules as well as observed tendencies in the whole group of compounds can be useful in discussing dielectric, spectroscopic, and thermodynamic properties of *ortho-Mannich* bases – the model compounds for intramolecular hydrogen bonding.

Acknowledgements

References

[1] Schuster P, Zundel G, Sandorfy C (eds) (1976) The hydrogen bond. North-Holland Publishing Comp, Amsterdam New York Oxford
[2] Baba H, Matsuyama A, Kokubun H (1960) Spectrochim Acta **25A**: 1709
[3] Scott R, dePalma D, Vinogradov SN (1968) J Phys Chem **72**: 3192
[4] Scott R, R Vinogradov R (1969) J Phys Chem **73**: 1890
[5] Romanowski H, Sobczyk L (1975) J Phys Chem **79**: 2535
[6] Bron J, Simmons EL (1976) J Phys Chem **80**: 1854
[7] Ivin KJ, McGarvey JJ, Simmons EL, Small R (1973) J Chem Soc Faraday I **69**: 1016

[8]   Socrates G (1970) Trans Faraday Soc **66**: 1052
[9]   Fritsch J, Zundel G (1981) J Phys Chem **85**: 556
[10] Murthy ASN, Reddy AR (1981) Spectrochim Acta **37A**: 805
[11] Oncescu T, Oancea A-M, DeMaeyer L (1983) J Phys Chem **87**: 2593
[12] Dega-Szafran Z, Szafran M (1987) J Chem Soc Perkin Trans II: 897
[13] Ratajczak H, Sobczyk L (1969) J Chem Phys **50**: 556
[14] Nouwen R, Huyskens P (1973) J Mol Struct **16**: 459
[15] Hawranek JP, Oszust J, Sobczyk L (1972) J Phys Chem **76**: 2112
[16] Debecker G, Huyskens P (1971) J Chim Phys **68**: 287
[17] Sucharda-Sobczyk A, Ritter S (1978) Polish J Chem **52**: 1555
[18] Schreiber VM, Koll A, Sobczyk L (1978) Bull Acad Pol Sci Ser Sci Chim **26**: 651
[19] Haslinger E, Wolschann P (1980) Monatsh Chem **111**: 563
[20] Koll A (1983) Bull Soc Chem Belg **92**: 313
[21] Iwasaki F, Kawano Y (1978) Acta Cryst **B34**: 1286
[22] Eda B, Ito K (1956) Bull Chem Soc Japan **29**: 524
[23] Eda B, Ito K (1957) Bull Chem Soc Japan **30**: 164
[24] Koll A, Ratajczak H, Sobczyk L (1970) Rocz Chem **44**: 825
[25] Brzezinski B, Zundel G (1980) Chem Phys Lett **75**: 500
[26] Brzezinski B, Zundel G (1982) J Phys Chem **86**: 5133
[27] Koll A, Rospenk M, Sobczyk L (1981) J Chem Soc Faraday Trans I **77**: 2309
[28] Robien W, Völlenkle H, Wolschann P (1982) Z Phys Chem **130**: 123
[29] Glowiak T, Koll A (unpublished results)
[30] Koll A, Glowiak T (to be published)
[31] Schuster P (1976) In: Schuster P, Zundel G, Sandorfy C (eds) The hydrogen bond – recent developments in theory and experiments, vol II. North Holland, Amsterdam, p 116
[32] Serjeant EP, Dempsey B (1979) Ionisation constants of organic acids in aqueons solution. Pergamon Press, NY; Perrin DD (1972) Dissociation constants of organic bases in aqueous solution. Butterworths, London
[33] Shanmuga Sundara Raj S, Ponnuswamy MN, Shanmuga G, Kandaswamy M (1993) J Cryst Spectr Res **23**: 607
[34] Slowikowska J, Beagley B, Pritchard RG, Wozniak K (1994) J Mol Struct **317**: 99
[35] Szemik-Hojniak A, Koll A (1993) J Photochem Photobiol A: Chem **72**: 123
[36] Gaussian 92/DFT, Revision F.3, Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Wong MW, Foresman JB, Robb MA, Head-Gordon M, Replogle ES, Gomperts R, Andres JL, Raghavachari K, Binkley JS, Gonzalez C, Martin RL, Fox DJ, Defrees DJ, Baker J, Stewart JJP, Pople JA (1993) Gaussian, Inc, Pittsburgh, PA
[37] Stewart JJP (1989) J Comput Chem **10**: 221; MOPAC 5. QCPE No 455 (1989)
[38] Karpfen A, Koll A, Parasuk W, Wolschann P (in preparation)
[39] Koll A, Glowiak T (1985) J Cryst Spectr Res **15**: 411
[40] Völlenkle H, Wolschann P (unpublished results)
[41] Koll A, Rospenk M, Stefaniak L, Wójcik J (1994) J Phys Chem **7**: 171
[42] Anderson EK, Anderson IKG (1975) Acta Cryst **B31**: 387
[43] Kagawa T, Kawai R, Kashino S, Haisa M (1976) Acta Cryst **B32**: 3171
[44] Iwasaki F, Kawano Y (1977) Acta Cryst **B33**: 2455
[45] Kohler P, Huyskens P (1976) Adv Mol Relax Processes **8**: 125