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Steric Modification of the Intramolecular Hydrogen Bond in 2-(Methylimino-phenyl-methyl)-phenols

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Summary. Three *ortho*-hydroxy *Schiff* bases (2-(methylimino-phenyl-methyl)-phenol (**1**), 4-methyl-2-(methylimino-phenyl-methyl)-phenol (**2**), 2-(benzylimino-phenyl-methyl)-phenol (**3**)) were synthesized in which the hydrogen atom in the C–C(H)=N group was substituted by a phenyl ring. Their crystal structures were determined. Strong O–H···N type intramolecular hydrogen bonds were found ($d_{ON} = 2.496(2)$ Å, $d_{OH} = 1.11(3)$ Å, $d_{HN} = 1.45(4)$ Å and $d_{ON} = 2.488(2)$ Å, $d_{OH} = 1.20(4)$ Å, $d_{HN} = 1.37(4)$ Å in **1**; $d_{ON} = 2.505(2)$ Å, $d_{OH} = 1.16(3)$ Å, $d_{HN} = 1.39(3)$ Å in **2**; $d_{ON} = 2.528(2)$ Å, $d_{OH} = 1.08(3)$ Å, $d_{HN} = 1.54(4)$ Å in **3** together with a large proton delocalization, especially in **1** and **2**. It was demonstrated that the strengthening of the hydrogen bond in comparison to related non substituted compounds results from the steric repulsion exerted by the phenyl ring.

Keywords. *Schiff* bases; Crystal structure; Proton delocalization; Short hydrogen bonds; FT-IR spectra.

Sterische Modifikation der intramolekularen Wasserstoffbrückenbindung in 2-(Methylimino-phenyl-methyl)-phenolen

Zusammenfassung. Drei *ortho*-hydroxy-substituierte *Schiff*sche Basen (2-(Methylimino-phenyl-methyl)-phenol (**1**), 4-Methyl-2-(methylimino-phenyl-methyl)-phenol (**2**), 2-(Benzylimino-phenyl-methyl)-phenol (**3**)) wurden synthesiert, in welchen das Wasserstoffatom der C–C(H)=N-Gruppe durch einen Phenylring substituiert ist. Es wurden starke Wasserstoffbrückenbindungen vom Typ O–H···N ($d_{ON} = 2.496(2)$ Å, $d_{OH} = 1.11(3)$ Å, $d_{HN} = 1.45(4)$ Å und $d_{ON} = 2.488(2)$ Å, $d_{OH} = 1.20(4)$ Å, $d_{HN} = 1.37(4)$ Å in **1**; $d_{ON} = 2.505(2)$ Å, $d_{OH} = 1.16(3)$ Å, $d_{HN} = 1.39(3)$ Å in **2**; $d_{ON} = 2.528(2)$ Å, $d_{OH} = 1.08(3)$ Å, $d_{HN} = 1.54(4)$ Å in **3**) gefunden, wobei vor allem in **1** und **2** eine beträchtliche Delokalisierung des Protons auftritt. Es konnte gezeigt werden, daß die Stärkung der Wasserstoffbrückenbindung im Vergleich zu nichtsubstituierten Verbindungen aus der sterischen Abstoßung des Phenylrings resultiert.

Introduction

The presented results are part of studies on the influence of different factors on the shape of the potential of the proton transfer reaction [1]. The problem is important

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for the explanation of the mechanism of numerous biological processes as well as of many technically useful reactions where the proton transfer is the rate determining step [2, 3].

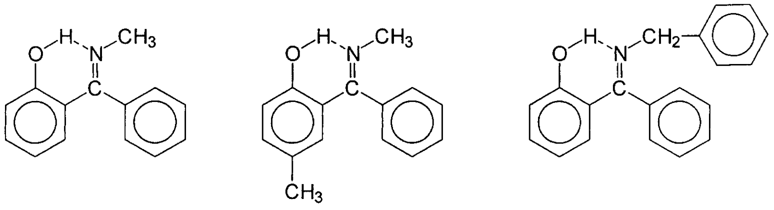
In this study we have selected *ortho*-hydroxy *Schiff* bases with phenyl substitutents at the C–C(H)=N group. These compounds appear to be of interest due to their thermochromic and photochromic properties related to intramolecular proton transfer [4] as potential materials for optical memory and optical switch devices [5]. Since only few systems with intramolecular hydrogen bonds show such properties [6], it seems important to understand the nature of the interactions and the influence of system modifications upon them with the aim to obtain materials with desired properties.

In previous investigations, the influence of two factors on the properties of intramolecular hydrogen bonds in *Schiff* bases has been analyzed. In Ref. [7] it has been shown that the formation of an intramolecular hydrogen bond in *ortho*-hydroxy *Schiff* bases is connected with an increase of the amount of the oxo resonance form. Such a type of hydrogen bond strengthening is characteristic for the so-called resonance assisted hydrogen bond [8, 9]. This effect is strongly enhanced in the form displaying proton transfer, where the amount of *ortho*-quinoic structure is estimated to be around 50%. A similar result was obtained for 5-nitro-N-salicylideneethylamine [10] which is also zwitterionic in the crystalline state.

In Ref. [1], one more very effective way of intramolecular hydrogen bond strengthening has been detected: the steric squeezing of the hydrogen bridge in 2-(methylimino-alkyl-methyl)-phenols. An exceptionally strong effect was found in 2-(N-methyl-α-iminoethyl)-phenol where the shortest of all known O–H···N hydrogen bonds was discovered ($d_{ON} = 2.46$ Å). A detailed analysis of the geometry of this compound shows that the resonance interactions are weaker than in the compounds described in Ref. [7].

The question, however, arises to what extent the observed strengthening of the hydrogen bond results from steric repulsion. The electronic interaction of the CH_3 group can lead to an increase of N-atom basicity and consequently to a strengthening of the hydrogen bond. In order to answer this question we have synthesized derivatives of *Schiff* bases with a phenyl substitutent at the C–C(H)=N unit. Inductive interaction of the phenyl ring leads to a decrease of the negative charge on the N-atom, as inferred *e.g.* from comparing the pK_a values of quinuclidine (10.6) and benzoquinuclidine (7.78). The steric repulsion of the phenyl ring should act the same way as the methyl substituent does in previously studied compounds [1].

Three *Schiff* bases (**1**–**3**) with the phenyl substituent instead of the hydrogen atom in the C–C(H)=N group were synthesized, and their molecular structures were determined by X-ray crystallography (Scheme 1).



1 **2** **3**

Scheme 1

Results and Discussion

Final atomic coordinates of compounds **1**–**3** are given in Tables 1, 2, and 3. Molecular structures and atom labelling are displayed in Figs. 1, 2, and 3. In **1**, two non-equivalent molecules in the fundamental crystal unit cell were found.

Structural aspects

The intramolecular hydrogen bond in *Schiff* bases can be modified both by resonance and steric influence. Analysis of the bonds lengths in **1** shows some bond differentiation in the phenol ring characteristic for the participation of *o*-quinoic structure: the C1–C2 bond is extended (1.410 Å), the C1–C6 (1.390 Å) and C2–C3 (1.396 Å) bonds are distinctly longer than the C5–C6 (1.364 Å) bond, the C3–C4 and C4–C5 bonds are of equal length (1.374 Å). This picture resembles a situation in compounds with methyl substituents in the C–C(H)=N-unit [1].

According to the sequence of the C–C bonds lengths, the structure of compound **2** reveals properties of *o*-quinoic system more distinctly than that of **1**. In **2**, the C3–C4 and C4–C5 bond lengths are 1.387 and 1.397 Å. The corresponding sequence in the phenol ring of **3** is similar to **2**, also showing participation of the *o*-quinoic resonance structure. All mentioned effects are, however, less pronounced than in compounds without steric repulsion [7]. A nearly perpendicular orientation of the phenyl ring introduced in the -C–C(H)=N- moiety in structures **1**–**3** is worth mentioning. It causes a reduction of the steric repulsion of this substituent.

In discussing the influence of steric effects on the strength of the hydrogen bond in *Schiff* bases, one should compare **1**–**3** with the structures of alkyl substituted compounds [1] as well as with structurally related compounds without 'sterically demanding' substituents [7]. In this context, an increase of C3–C2–C7 angles (atoms numbering as in Fig. 2) by about 2.5° in the substituted systems should be mentioned. Simultaneously, an increase of the C10–C7=N and C7=N–C9 angles by 4° in both types of compounds with 'steric demanding' substituents is observed. On the other hand, a very pronounced decrease of the C2–C7=N angles from 121.5° in compounds without substituents to 117.9° and 117° in compounds with phenyl and methyl substituents can be observed.

One should also mention the obvious increase of the linearity of the hydrogen bridge due to steric repulsion. The OHN angles change from 142.5° in compounds without substituents [7] to 152–157° in compounds with phenyl and alkyl substituents, thus strengthening the hydrogen bond. The phenyl ring and the methyl group seem to introduce a similar steric interaction in accordance with the fact that phenyl rings are oriented almost perpendicular to the phenol ring plane. The rotation of the phenyl ring is forced by the contacts of its two *ortho* carbon atoms with the N-methyl (methylene in **3**) carbon atoms and the C3 carbon atom of the phenol ring. After rotation of the phenyl ring, all those contacts are only slightly shorter than the sum of the *van der Waals* radii. The repulsion mainly results from the interaction of the C-*ipso* atoms (C9, C10, and C8 atoms in **1**–**3**) of the phenyl ring with the N-methyl carbon atoms and the C3 atom of the phenol ring. In **1**, the C9···C8 interatomic distance is shortened by 0.7–0.65 Å with respect to the sum of the *van der Waals* radii. The C10···H3 and C10···H9c (cf. Fig. 2) distances are by

Table 1. Final atomic coordinates and equivalent thermal parameters for **1** (*esds* in parentheses)

	x/*a*	*y*/*b*	*z*/*c*	$U_{\mathrm{eq}}/U_{\mathrm{iso}}$
N11	0.5886(2)	0.1160(2)	0.3850(1)	0.0650(4)
O11	0.7002(2)	−0.1676(2)	0.4082(1)	0.0739(4)
C11	0.5274(2)	−0.1694(2)	0.4072(1)	0.0588(5)
C12	0.3836(2)	−0.0319(2)	0.3950(1)	0.0569(4)
C13	0.2062(3)	−0.0441(3)	0.3965(1)	0.0736(6)
C14	0.1704(3)	−0.1824(3)	0.4081(2)	0.0842(7)
C15	0.3131(3)	−0.3136(3)	0.4178(2)	0.0830(7)
C16	0.4888(3)	−0.3082(3)	0.4178(1)	0.0744(6)
C17	0.4230(2)	0.1155(2)	0.3802(1)	0.0573(4)
C18	0.6479(4)	0.2537(3)	0.3698(2)	0.0847(7)
C19	0.2730(2)	0.2578(2)	0.3571(1)	0.0600(5)
C110	0.2558(4)	0.3173(3)	0.2788(1)	0.0988(9)
C111	0.1150(4)	0.4462(3)	0.2577(2)	0.1120(11)
C112	−0.0065(3)	0.5167(3)	0.3134(2)	0.0845(7)
C113	0.0112(3)	0.4598(3)	0.3912(2)	0.0785(6)
C114	0.1507(3)	0.3304(3)	0.4132(1)	0.0703(6)
O21	0.3158(2)	−0.6364(2)	0.0596(1)	0.0899(5)
N21	0.1520(3)	−0.3627(2)	0.0213(1)	0.0782(5)
C21	0.3595(3)	−0.6429(3)	−0.0173(2)	0.0747(6)
C22	0.3069(3)	−0.5120(2)	−0.0756(1)	0.0695(5)
C23	0.3557(4)	−0.5279(3)	−0.1542(2)	0.0949(8)
C24	0.4545(5)	−0.6659(4)	−0.1762(2)	0.1139(10)
C25	0.5033(5)	−0.7916(4)	−0.1180(2)	0.1109(10)
C26	0.4575(4)	−0.7803(3)	−0.0406(2)	0.0962(8)
C27	0.2024(3)	−0.3657(2)	−0.0524(1)	0.0682(5)
C28	0.0470(5)	−0.2241(4)	0.0515(2)	0.0980(9)
C29	0.1604(3)	-0.2265(2)	−0.1147(1)	0.0696(5)
C210	0.2885(4)	−0.1463(3)	−0.1426(1)	0.0813(6)
C211	0.2473(5)	−0.0164(3)	−0.1996(2)	0.0919(8)
C212	0.0832(5)	0.0312(3)	−0.2294(2)	0.0927(8)
C213	−0.0434(4)	−0.0481(3)	−0.2026(2)	0.0982(9)
C214	−0.0065(4)	−0.1763(3)	−0.1450(2)	0.0895(7)
H11	0.688(4)	−0.044(4)	0.403(2)	0.148(12)
H13	0.112(3)	0.046(3)	0.393(1)	0.080(6)
H14	0.052(4)	−0.190(3)	0.408(2)	0.099(8)
H15	0.289(3)	−0.411(3)	0.425(1)	0.096(8)
H16	−0.108(4)	0.620(3)	0.299(2)	0.120(9)
H18A	0.758(5)	0.241(3)	0.325(2)	0.130(10)
H18B	0.695(5)	0.263(4)	0.418(2)	0.159(14)
H18C	0.562(5)	0.344(4)	0.360(2)	0.135(13)
H110	0.343(5)	0.259(4)	0.237(2)	0.139(11)
H111	0.117(5)	0.490(4)	0.206(2)	0.145(12)
H112	0.595(3)	−0.410(3)	0.421(1)	0.098(8)
H113	−0.077(4)	0.527(3)	0.432(2)	0.110(8)
H114	0.171(3)	0.288(3)	0.468(2)	0.101(8)
H21	0.233(4)	−0.506(4)	0.059(2)	0.135(10)
H23	0.328(3)	−0.437(3)	−0.192(1)	0.084(7)

Table 1 (*continued*)

	x/a	y/b	z/c	U_{eq}/U_{iso}
H24	0.492(4)	−0.661(3)	−0.234(2)	0.123(10)
H25	0.578(5)	−0.888(4)	−0.135(2)	0.131(10)
H26	0.491(4)	−0.869(4)	0.004(2)	0.127(10)
H28A	0.019(6)	−0.132(5)	0.017(3)	0.188(18)
H28B	0.090(6)	−0.205(5)	0.095(3)	0.181(17)
H28C	−0.073(6)	−0.239(5)	0.087(3)	0.186(16)
H210	0.402(3)	−0.178(3)	−0.122(1)	0.092(8)
H211	0.340(4)	0.045(3)	−0.218(2)	0.110(9)
H212	0.060(4)	0.119(3)	−0.273(2)	0.113(9)
H213	−0.151(4)	−0.022(4)	−0.224(2)	0.125(11)
H214	−0.093(4)	−0.240(3)	−0.129(2)	0.120(10)

0.4 Å shorter than the appropriate sum of the *van der Waals* radii. Those shortenings are almost the same in molecules **1**–**3**. Generally, the steric repulsions in **1**–**3** are almost equal and not very different from those in compounds with methyl substituents (cf. also the discussion of bond angles in Ref. [1]).

Searching in the crystallographic base data set did not show structures directly related to those discussed here, but revealed three structures [11] which can be discussed with respect to an influence of substituents on the properties of the hydrogen bond: 4-((4-chlorophenyl)-(5-fluoro-2-hydroxyphenyl)-methyleneamino)-butanamide [12], 2,2′-(2,2-dimethyl-1,3-propanediyl-*bis*-(nitrilophenylmethylidene))-diphenol [13], and 2,2′-((1,2-ethanediyl)-*bis*-(nitrilo-(phenyl)-methylidyne))-bisphenol [14], all of them containing phenyl substituents in the C=N–C moiety. Similar shortenings of distances and changes of angles as discussed here have been observed for these compounds.

In **1** there are two independent molecules in the crystal unit cell. The hydrogen bond is different in both molecules (Table 2). In the first molecule it is longer ($d_{ON} = 2.496$ Å) than in the second one ($d_{ON} = 2.488$ Å). (Table 4). In the second molecule, the proton is located more in the center of the hydrogen bridge ($d_{OH} = 1.20$ (4) Å, $d_{H\cdots N} = 1.37$ (4) Å). The difference results from the interactions of these molecules with their surroundings in the crystal lattice. The probable reason for these differences is the larger non-planarity of the chelate ring in the first molecule compared to the second one. In the first molecule the torsional angles amount to H1–O1–C1–C2 = 4.1° and O1–C1–C2–C7 = 2.3° when the related angles in the second molecule are kept at 0°. An increase of C8···C9 (2.911 Å) and C3···C9 (2.947 Å) distances weakens forces squeezing on the hydrogen bridge in the first molecule of **1**.

It the case of **2**, the chelate ring is also non-planar like in the first molecule of **1** (H1–O1–C1–C2: 4°, N1–H1–O1–C1: 12.9°). The N···O distance is 2.505 Å, which is somewhat longer than in the first molecule of **1** (2.496 Å); this can be explained as a result of methyl substitution in *para*-position of the phenol ring.

The hydrogen bond in **3** is the weakest one of the three compounds studied. $d_{NO} = 2.528$ Å, $d_{OH} = 1.08$ Å and $d_{H\cdots N} = 1.54$ Å indicative of a hydrogen bond with localized proton. The chelate ring is here also non-planar, but the main reason of the hydrogen bond weakening is the introduction of the N-benzyl substituent instead of the N-methyl moiety.

Table 2. Final atomic coordinates and equivalent thermal parameters for **2** (*esds* in parentheses)

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
O1	0.2547(1)	0.0924(1)	0.4477(1)	0.0650(4)
N1	0.5108(2)	0.1715(1)	0.5013(1)	0.0514(4)
C1	0.2657(2)	0.0574(1)	0.3396(2)	0.0521(4)
C2	0.3923(2)	0.0786(1)	0.3080(2)	0.0465(4)
C3	0.3968(2)	0.0364(1)	0.1956(2)	0.0546(4)
C4	0.2809(2)	−0.0243(2)	0.1125(2)	0.0626(5)
C5	0.1560(2)	−0.0412(2)	0.1456(2)	0.0660(5)
C6	0.1478(2)	−0.0015(2)	0.2553(2)	0.0618(5)
C7	0.5154(2)	0.1455(1)	0.3933(2)	0.0457(4)
C8	0.2883(3)	−0.0680(2)	0.0089(2)	0.0937(8)
C9	0.6225(2)	0.2402(2)	0.5907(2)	0.0634(5)
C10	0.6346(2)	0.1852(1)	0.3480(2)	0.0486(4)
C11	0.7803(2)	0.1483(2)	0.4015(2)	0.0660(5)
C12	0.8897(2)	0.1946(2)	0.3640(2)	0.0838(7)
C13	0.8540(3)	0.2768(2)	0.2763(2)	0.0820(7)
C14	0.7097(3)	0.3114(2)	0.2209(2)	0.0778(6)
C15	0.6004(2)	0.2654(2)	0.2564(2)	0.0637(5)
H1	0.373(3)	0.131(2)	0.494(3)	0.122(9)
H3	0.487(2)	0.050(2)	0.178(2)	0.059(5)
H5	0.068(3)	−0.088(2)	0.089(2)	0.090(7)
H6	0.053(2)	−0.015(2)	0.279(2)	0.078(6)
H8A	0.295	−0.009	−0.061	0.141
H8B	0.200	−0.110	−0.052	0.141
H8C	0.375	−0.114	0.010	0.141
H9A	0.573(3)	0.296(2)	0.625(2)	0.090(7)
H9B	0.677(4)	0.195(3)	0.663(3)	0.141(12)
H9C	0.683(3)	0.285(2)	0.548(2)	0.095(7)
H11	0.799(2)	0.091(2)	0.466(2)	0.074(6)
H12	0.981(3)	0.159(2)	0.404(3)	0.120(10)
H13	0.937(3)	0.312(2)	0.251(3)	0.108(8)
H14	0.692(3)	0.374(2)	0.156(3)	0.112(9)
H15	0.485(3)	0.287(2)	0.210(2)	0.093(7)
H9A	0.573(3)	0.296(2)	0.625(2)	0.090(7)
H9B	0.677(4)	0.195(3)	0.663(3)	0.141(12)
H9C	0.683(3)	0.285(2)	0.548(2)	0.095(7)

Spectroscopic characteristics of the hydrogen bond

IR investigations support the conclusions resulting from the X-ray studies that the hydrogen bonds in **1** and **2** are very strong and the proton is located nearly in the centre of the hydrogen bridge. As a proof, a wide absorption band between 3200 and 800 cm^{-1} in **1** and **2** is observed, which shifts to low frequencies after cooling to liquid nitrogen temperature. The wide absorption above 2500 cm^{-1} decreases at low temperatures, whereas the absorption below 1800 cm^{-1} increases (Fig. 4).

Table 3. Final atomic coordinates and equivalent thermal parameters for **3** (*esds* in parentheses)

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
N1	0.1434(1)	0.1420(2)	0.4477(1)	0.0575(3)
O1	0.1195(1)	−0.1107(2)	0.3352(1)	0.0649(3)
C1	0.2160(1)	−0.0892(2)	0.3458(1)	0.0494(3)
C2	0.2764(1)	0.0406(2)	0.4048(1)	0.0442(3)
C3	0.3760(1)	0.0524(2)	0.4117(1)	0.0525(4)
C4	0.4144(1)	−0.0569(3)	0.3621(1)	0.0629(4)
C5	0.3538(1)	−0.1820(3)	0.3037(1)	0.0660(5)
C6	0.2560(1)	−0.1988(2)	0.2959(1)	0.0610(4)
C7	0.2351(1)	0.1630(2)	0.4558(1)	0.0461(3)
C8	0.3020(1)	0.3038(2)	0.5138(1)	0.0471(3)
C9	0.3278(1)	0.4579(2)	0.4778(1)	0.0665(5)
C10	0.3922(2)	0.5840(3)	0.5321(2)	0.0782(5)
C11	0.4317(1)	0.5559(3)	0.6218(1)	0.0739(5)
C12	0.4057(1)	0.4043(3)	0.6586(1)	0.0670(5)
C13	0.3403(1)	0.2787(2)	0.6049(1)	0.0565(4)
C14	0.0943(1)	0.2621(3)	0.4922(1)	0.0674(5)
C15	−0.0022(1)	0.3292(2)	0.4251(1)	0.0562(4)
C16	−0.0914(1)	0.2605(3)	0.4243(1)	0.0698(5)
C17	−0.1803(2)	0.3244(4)	0.3625(2)	0.0873(7)
C18	−0.1793(2)	0.4541(4)	0.3029(2)	0.0949(8)
C19	−0.0915(2)	0.5229(4)	0.3035(2)	0.0936(7)
C20	−0.0029(2)	0.4615(3)	0.3642(1)	0.0749(5)
H1	0.107(2)	−0.016(3)	0.382(2)	0.106(7)
H3	0.421(1)	0.142(2)	0.453(1)	0.059(4)
H4	0.484(1)	−0.049(3)	0.370(1)	0.078(5)
H5	0.382(1)	−0.263(3)	0.268(1)	0.075(5)
H6	0.210(1)	−0.283(3)	0.257(1)	0.070(5)
H9	0.302(2)	0.475(3)	0.414(1)	0.089(6)
H10	0.409(2)	0.696(3)	0.503(2)	0.110(8)
H11	0.481(2)	0.645(3)	0.660(2)	0.103(7)
H12	0.434(1)	0.376(3)	0.722(1)	0.084(6)
H13	0.319(1)	0.170(3)	0.632(1)	0.071(5)
H14A	0.135(1)	0.361(3)	0.518(1)	0.070(5)
H14B	0.081(2)	0.185(3)	0.542(2)	0.106(7)
H16	−0.091(2)	0.176(3)	0.469(1)	0.084(6)
H17	−0.242(2)	0.272(4)	0.368(2)	0.120(8)
H18	−0.241(2)	0.506(4)	0.258(2)	0.130(9)
H19	−0.092(2)	0.621(4)	0.258(2)	0.132(10)
H20	0.061(2)	0.505(3)	0.363(2)	0.109(8)

All those features show the existence of a strong hydrogen bond in **1** with a large proton delocalization. The increase of the low frequency absorption upon lowering of the temperature may be connected with an increase of the amount of molecules with stronger hydrogen bonding.

Compound **3** shows a ν(OH) absorption with a maximum at 2600 cm^{-1} (Fig. 5).

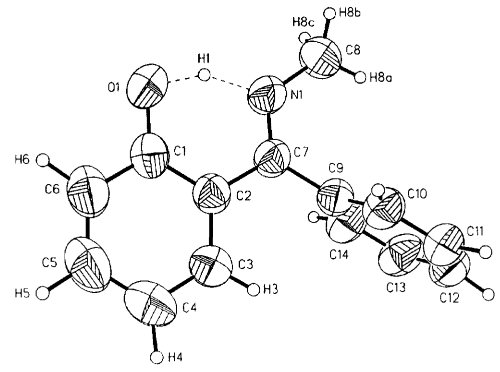


Fig. 1. Molecular structure and atoms labelling system of **1**

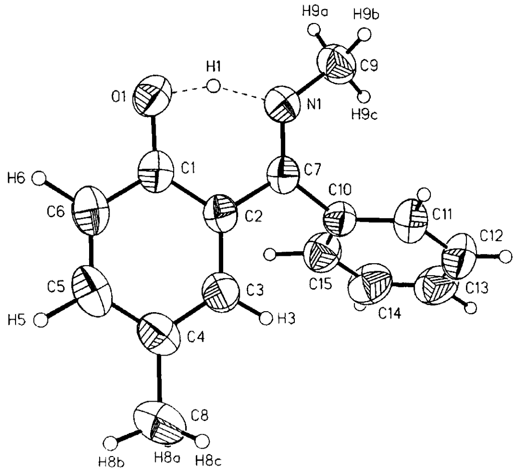


Fig. 2. Molecular structure and atoms labelling system of **2**

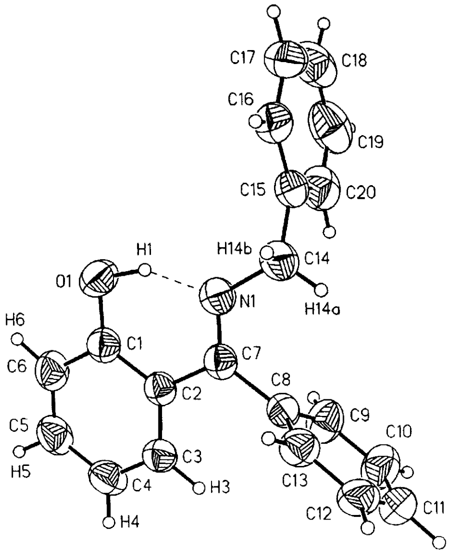


Fig. 3. Molecular structure and atoms labelling system of **3**

Table 4. Selected bond lengths (Å) and angles (°) in the pseudoaromatic chelate rings of **1–3** (*esds* in parentheses)

	Hydrogen bond	OH	ON	HN	α(OHN)	β(COH)	γ(C7NH1)	δ(C9NH)
1	O···H···N	1.11(3)	2.496(2)	1.45(4)	152(3)	103(2)	104(1)	132(1)
		1.20(4)	2.488(2)	1.37(4)	152(3)	103(2)	106(1)	131(1)
2	O···H···N	1.16(3)	2.505(2)	1.39(3)	157(3)	99(1)	103(1)	134(1)
3	O–H···N	1.08(2)	2.528(2)	1.54(2)	150(2)	99(1)	103(1)	134(1)

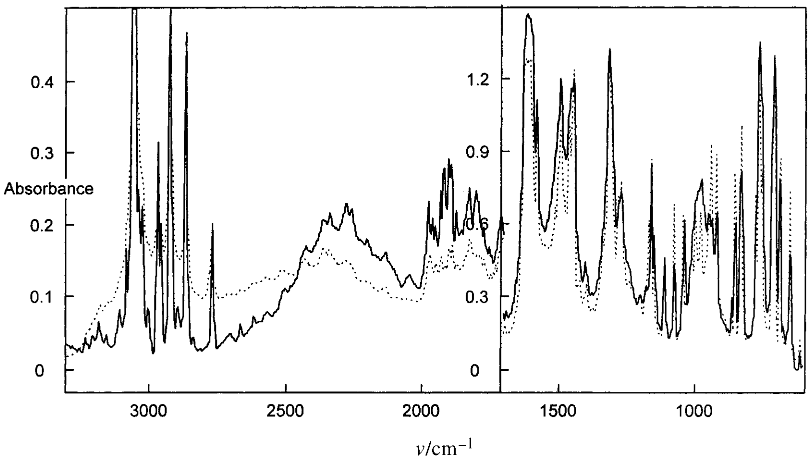


Fig. 4. Solid film FT-IR spectra of **1** at room (dottet lines) and at liquid nitrogen (thick lines) temperatures

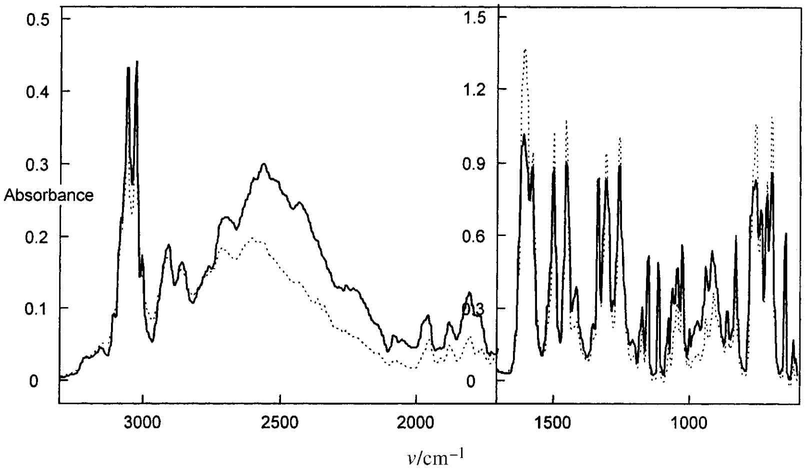


Fig. 5. Solid film FT-IR spectra of **3** at room (dotted lines) and liquid nitrogen (thick lines) temperatures

A temperature decrease does not enhance the absorption below1800 cm^{-1}. These spectroscopic features are in full agreement with the crystallographic determinations which show a rather localized proton in **3** resulting from replacing the N-methyl group by an N-benzyl moiety.

Conclusions

Our studies clearly demonstrate that the phenyl rings in **1**–**3** introduce roughly the same steric effects as methyl substituents. Hydrogen bonds are much shorter and stronger than in nonsubstituted compounds, but are weaker in compounds with a phenyl substituent instead of an alkyl group. An important influence of the planarity of the chelate ring formed by intramolecular hydrogen bonds has been demonstrated which depends on crystal packing conditions. Replacement of the N-methyl group by the N-benzyl moiety reduces the strength of the hydrogen bridge. The results demonstrate that 'external' squeezing forces not only shorten the hydrogen bridge, but also lead to pronounced spectroscopic effects characteristic for the strong hydrogen bonds.

As a general conclusion one can state that steric effects comprise very effective means to modulate the potential of the proton transfer reaction. More detailed studies on the shape of the potential are in progress.

Experimental

Synthesis of compounds **1**–**3** from stoichiometric mixtures of the corresponding salicylaldehydes and amines in methanol was performed according to Ref. [15]. After recrystallization from methanol solid yellow products were obtained which were studied by X-ray diffraction at room temperature (293(2) K). Details of data collection and refinement are given in Table 5. Unit cell parameters and orientation matrices were calculated using least-squares techniques. Intensities were collected using a KUMA KM4 diffractometer in the ω-2θ scan with graphite monochromated CuK_α radiation. The intensities of three standard reflections, monitored after every 100 intensity scans, gave no evidence of crystal decay. The data were corrected for *Lorentz* and polarization effects. No absorption correction was applied.

The structures were solved by direct methods using SHELXS-86 [16] and refined by full-matrix least-squares on all F^2 using SHELXL-93 [17]. The positions of hydrogen atoms were located from the difference *Fourier* synthesis. Only the hydrogen atoms of the 4-methyl group in **2** were placed in the geometrically calculated positions with the isotropic thermal factors taken as 1.2 U_{eq} of the neighbouring heavier atoms. Several cycles of refinement of the coordinates and anisotropic thermal parameters for the non-hydrogen atoms were performed. The scattering factors of neutral atoms were taken from Ref. [18]. The X-ray data have been deposited at the Cambridge Structural Data Centre (deposition Nos.: 129666 to 129668).

Vibrational spectra were obtained with an FT-IR Avatar 360 spectrophotometer at a resolution of 1 cm^{-1} in CCl_4 solutions and as solid films crystallized between KBr windows. ^{1}H NMR spectra (δ, ppm relative to internal *TMS*) were measured on a Bruker AMX-300 spectrometer (293 K). UV/Vis spectra were recorded on a Varian Cary 1 spectrophotometer, mass spectra on a Hewlett-Packard HP 5890 II instrument combined with a HP 5971 A mass spectrometer instrument.

Compound **3** has already been described [19, 20]; m. p.: 95°C Refs. ([19, 20]: 90°C).

2-(Methylimino-phenyl-methyl)-phenol (**1**; $C_{14}H_{13}NO$)

Recrystallization from methanol afforded yellow crystals. M.p.: 80°C; MS: *m/z* = 210 (M-1), 194, 181, 167, 152, 134, 118, 91, 77, 65, 51; IR (CCl_4): ν = 3082 (m), 3063 (m), 3026 (m), 2956 (m), 2956 (m), 2923 (m), 2866 (m), 2598 (s, broad, OH), 1613 (s), 1601 (m), 1579 (m), 1496 (m), 1453 (m), 1412 (l), 1401 (l), 1334 (m), 1310 (m), 1259 (m), 1005 (m), 911 (l), 709 (m), 699 (m), 685 (l), 647 (l), 552 (l), 538 (l), 486 (l), 465 (l), 449 (l) cm^{-1}; UV/Vis ($CH_3(CH_2)_4CH_3$): λ_{max} = 323 nm;

Table 5. Data collection and processing parameters

Compound	**1**	**2**	**3**
Formula	$C_{14}H_{13}NO$	$C_{15}H_{15}NO$	$C_{20}H_{17}NO$
Molecular weight	211.25	225.28	287.35
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Cell constants	25 ref., $22.6<2\theta<48.3$	25 ref., $22.6<2\theta<46.5$	25 ref., $24.4<2\theta<48.7$
Crystal system	triclinic	monoclinic	monoclinic
a (Å)	7.673(2)	9.603(2)	14.394(3)
b (Å)	9.381(2)	12.272(2)	7.342(2)
c (Å)	17.543(4)	11.360(2)	16.048(3)
α (deg)	77.53(3)	–	–
β(deg)	80.02(3)	111.28(3)	110.40(3)
γ(deg)	72.11(3)	–	–
Cell volume (Å^3)	1165.5(5)	1247.5(4)	1589.6(5)
Formula units/unit cell	4	4	4
D_{cal}(Mg$\times$m^{-3})	1.204	1.200	1.201
Max. crystal dimensions (mm)	0.20×0.20×0.25	0.20×0.20×0.20	0.25×0.25×0.25
Scan width (deg)	variable	variable	variable
No. of stand. ref. and int.	3 (100 ref.)	3 (100 ref.)	3(100 ref.)
Reflections measured	4724	2612	3484
2θ range (deg)	5.2–160.0	10.1–160.64	7.1–160.4
Range of h, k, l	−9/1, −11/10, −22/21	0/12, −15/15, −13/12	0/18, 0/9, −20/19
Reflections observed ($F_o>4\cdot\sigma$ (F_o))	2761	1788	3456
No.of parameters varied	394	204	268
GOF	1.066	1.033	1.018
$R_1=\Sigma(\lvert F_o\rvert-\lvert F_c\rvert)/\Sigma(\lvert F_o\rvert)$	0.0459	0.0464	0.0406
$wR_2=(\Sigma(wF_0^2-F_0{}^2)^2)/\Sigma(w(F_0^2)\,^2))^{1/2}$	0.1327	0.1223	0.1013
Function minimized		$\Sigma w(\Delta F^2)^2$	
Largest feature final diff. map (e$\cdot$Å^{-3})	0.145 and −0.121	0.207 and −0.156	0.145 and −0.132

^{1}H NMR (300 MHz, δ, $CDCl_3$): $\delta=15.88$ (1H, s, O-H), 3.16 (3H, s, N-CH_3), 6.5–7.5 (9H, m, C_6H_4, C_6H_5) ppm.

4-methyl-2-(methylimino-phenyl-methyl)-phenol (**2**; $C_{15}H_{15}NO$)

Recrystallization from methanol afforded yellow crystals. M.p.: 110°C; MS: $m/z=224$ (M-1), 210, 195, 180, 165, 148, 133, 118, 104, 77, 63, 51; IR (CCl_4): $\nu=3083$ (m), 3062 (m), 3024 (m), 2952 (m), 2922 (m), 2866 (m), 2597 (s, broad, OH), 1615 (s), 1600 (m), 1584 (s), 1490 (m), 1444 (l), 1404 (l), 1336 (m), 1296 (m), 1241 (m), 1034 (l), 887 (m), 705 (m), 699 (l), 664 (l), 546 (l), 480 (l) cm^{-1}; UV/Vis ($CH_3(CH_2)_4CH_3$): $\lambda_{max}=334$ nm; ^{1}H NMR (300 MHz, δ, $CDCl_3$): 15.61 (1H, s, O-H), 2.11 (3H, s, 4-CH_3), 3.13 (3H, s, N-CH_3), 6.5–7.5 (8H, m, C_6H_3, C_6H_5) ppm.

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References

[1] Filarowski A, Koll A, Głowiak T (1999) J Mol Struct **484**: 75

[2] Lussier LS, Sandorfy C, Le-Thanh Hoa, Vocelle D (1987) J Phys Chem **91**: 2282

[3] Jensen NP, Chang MP (1984) Chem Abstr **99**: 13947u (Eur Pat Appl EP 81782 A 1, 22.07.1983)

[4] Hadjoudis E (1990) In: Bouas-Laurent H, Dürr H (eds) Photochromism Molecules and Systems. Elsevier, Amsterdam

[5] Sekikawa T, Kobayashi T, Inabe T (1997) J Phys Chem **A 101**: 644

[6] Koll A, Wolschann P (1999) Monatsh Chem **130**: 983

[7] Filarowski A, Koll A, Głowiak T, Majewski E, Dziembowska T (1998) Ber Bunsenges Phys Chem **102**: 393

[8] Gilli G, Bellucci F, Ferretti V, Bertolasi V (1989) J Am Chem Soc **111**: 1023

[9] Gilli P, Bertolasi V, Ferretti V, Gilli G (1994) J Am Chem Soc **116**: 909

[10] Krygowski TM, Woźniak K, Anulewicz R, Pawlak D, Kolodziejski W, Grech E, Szady A (1997) J Phys Chem **101**: 9399

[11] Allen FH, Davies JE, Galloy JJ, Johnson O, Kennard O, Marcrae CF, Mitchell EM, Mitchell GF, Smith JM, Watson DG (1991) J Chem Inf Comput Sci **31**: 187

[12] Pascard BC, Kaplan J-P, Raizon B, Mompon B (1982) Acta Cryst **B38**: 3131

[13] Corden JP, Errington W, Moore P, Phillips PR, Wallbridge MGH (1996) Acta Cryst **C52**: 3199

[14] Corden JP, Errington W, Moore P, Wallbridge MGH (1997) Acta Cryst **C53**: 486

[15] Kristek F, Klicnar J, Vetesnik P (1971) Collect Czech Chem Commun **38**: 3608

[16] Sheldrick GM (1990) Acta Crystallogr Sect **A 46**: 467

[17] SHELXL 93. Crystal Structure Refinement, Department of Inorganic Chemistry, Univ of Göttingen, German

[18] International Tables for X-Ray Crystallography, vol 4 (1974) Kynoch Press, Birmingham, UK

[19] Al-Sayyab AF, Lawson A, Stevens JO (1968) J Chem Soc **C**: 411

[20] Mal S, Norula JL, Rawat MSM (1982) Indian J Chem **21B**: 120

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