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Journal of **MOLECULAR** STRUCTURE

Journal of Molecular Structure 844-845 (2007) 94-101

www.elsevier.com/locate/molstruc

NMR and X-ray studies of 2,6-bis(alkylimino)phenol Schiff bases

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Received 13 February 2007; received in revised form 16 May 2007; accepted 19 May 2007 Available online 8 June 2007

Abstract

A series of model Schiff bases – 2,6-bis(alkylimino)phenol derivatives (Me, c-Pr, c-Bu, c-Pen and Ph) – has been studied by the solution and solid state (c-Pr and Ph derivatives) NMR methods. All compounds under investigations exhibit tautomeric equilibria in which proton is distributed between two imine sites. For the whole series, the strongest intramolecular H-bond is formed by the methyl derivative. The cycloaliphatic derivatives form weaker H-bonds. Their strength is proportional to the size of the aliphatic ring. The principal components of ¹⁵N chemical shift anisotropy (CSA) tensor have been measured in the solid state for the cyclopropyl derivative. The first two principal components of the CSA tensor change in the same way with respects to hydrogen bond formation as the isotropic nitrogen chemical shift values. A relationship between the CSA principal components and structure of tautomers present in the system has been discussed. In chloroform solutions we also measured the coalescence temperatures to estimate the reaction rate and activation energy.

For the c-Pr Schiff-base derivative, the X-ray structure has been established. This compound crystallizes in the monoclinic $P2_1$ space group. There are two independent molecules in the crystal lattice. The geometry of the two moleties is very similar with the exception of some subtle changes in the intramolecular hydrogen bond and its vicinity. Although the molecules seem to be related by a glide plane, the symmetry is non-crystallographic and there is no indication of the existence of such a plane in the intensities of the reflections. We present details of the hydrogen bonds in both moieties. © 2007 Elsevier B.V. All rights reserved.

Keywords: Schiff bases; X-ray analysis; NMR studies

1. Introduction

Schiff bases are very interesting compounds because of their model character and practical applications[1,2]. Some of the Schiff bases, containing the hydroxyl group(s) at the ortho position(s), can form intramolecular hydrogen bonds. Such H-bonds have tautomeric character. The properties of such H-bonds and the correlation between structure and the proton position in the hydrogen bridge were reviewed and discussed by Filarowski [3] and Dominiak et al. [4]. Many instrumental analytical methods have

been applied for structural investigation of Schiff bases, some examples are published in: optical spectroscopy [5-7], X-ray diffraction [4,8–11], hetero nuclear NMR measurements in the liquid and in the solid state [12-17], as well as theoretical DFT calculation [18]. The Schiff bases derived from 2-hydroxy-1,3-benzenedicarboxaldehyde are even more interesting from a structural point of view since they have two equivalent basic sites and only one hydrogen bond donor. The photo- and thermochromic properties of those compounds have been investigated by Metelitsa et al. on a number of differently substituted 2-hydroxy-1,3-dialdehyde derivatives [19]. The dynamic and kinetic aspects of internal rotation of the OH group in aromatic amines 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde and derivatives have been considered by Dziembowska et al.

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^{0022-2860/\$ -} see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2007.05.029

[20]. On the basis of the line-shape analysis of proton signals they calculated the reaction rates and energy of activation for three aromatic amine derivatives.

In the present work we extend heteronuclear NMR and X-ray investigations on several model Schiff-base derivatives. We also support NMR studies by X-ray structural investigations of one of the studied compounds. Unfortunately we were unable to get single crystals of the quality suitable for single crystal X-ray investigations for the other compounds belonging to the series.

2. Experimental

2.1. Synthesis

All compounds under investigations have been synthesized by condensation of 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde with appropriate amine in methanol solution. The 1:1 mixtures of the aldehyde and amine were refluxed for about 4 h and then evaporated. The compounds crystallized from methanol solution.

2.2. NMR

All NMR spectra were measured using a Bruker DRX 500 Avance spectrometer equipped with triple resonance TBI 5 mm inverse probehead. The chemical shifts assignments were made by analysis of standard 1D and 2D COSY, HGSQC and GHMBC spectra. The proton and carbon chemical shifts are presented with respect to internal TMS, the nitrogen spectra are referred to external nitromethane as a standard. The variable temperature experiments were performed using a BTO 2000 Variable Temperature Unit. The temperature scale was calibrated using a pure methanol sample as a standard. The solid state spectra were run using a 4 mm CPMAS Bruker probehead. The typical acquisition parameters for carbon CPMAS spectra were: spectral width 31 kHz, acquisition time 20 ms, contact time 2 ms and spin rate 9-12 kHz. To distinguish the CH_n and quaternary atoms short contact time experiments were applied. For such experiments the contact time was 40 µs. Typical spectral conditions for the nitrogen solid state spectra were: spectral width 28 kHz, acquisition time 40 ms, contact time 5 ms and spin rate 6-12 kHz. For all solid state measurements the relaxation delay was in the range 10–120 s depending on the relaxation properties of the sample. Originally the CPMAS spectra were referred to an external glycine sample and then chemical shift values were recalculated to TMS and nitromethane scale for ¹³C and ¹⁵N spectra, respectively.

2.3. X-ray data collection and structure refinement

The structure of the c-Pr Schiff base (see Figs. 1 and 2) was determined in a single-crystal X-ray diffraction experiment. The measurement was performed on a Kuma KM4CCD κ -axis diffractometer with graphite-monochro-



Fig. 1. Definition of compounds studied.

mated Mo K α radiation ($\lambda = 0.71073$ A, 50.0 kV, 40.0 mA) at liquid nitrogen temperature (100 K). The big, dark orange crystal was mounted on the glass fiber with silicon grease and positioned at 62 mm from the KM4CCD camera. 400 frames were collected at 1.5° intervals with counting time of 35 s. The multi-scan absorption correction was applied to the collected dataset. Data reduction and analysis were carried out with the Kuma Diffraction programs.

The structure was solved by direct methods using the SHELXS-97 [21] program and refinement was carried out with SHELXL-97 [22]. The refinement was based on F^2 for all reflections except those with negative intensities. Weighted R factors wR and all goodness-of-fit S values were based on F^2 , whereas conventional R factors were based on the amplitudes, with F set to zero for negative F^2 . The $F_0^2 > 2\sigma(F_0^2)$ criterion was applied only for R factors calculation and was not relevant to the choice of reflections for the refinement. The R factors based on F^2 are for both structures about twice as large as those based on F. The positions of hydrogen atoms were found exactly from the difference electron density map and isotropic temperature displacement parameters were refined for each of them. Scattering factors were taken from Tables 4.2.6.8 and 6.1.1.4 from the International Crystallographic Tables Vol.C [23].

Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 636043. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (fax: Int. code +1 223 336 033; e-mail: deposit@ccdc.cam. ac.uk).

The details of the data collection and structure refinement parameters are given in Table 1.

3. Results and discussion

The results of the carbon and nitrogen chemical shift measurements are collected in Table 2. According to our previous experience in hydrogen bond structure estimation, one can expect that the best parameters for this task could be nitrogen chemical shifts and carbon chemical shifts of atoms at the C-1 position (Fig. 1).

Unfortunately, the carbon chemical shifts of C-1 atoms are practically useless in the discussed group of



Fig. 2. Molecules I and II of the c-Pr Schiff-base in ORTEP representation. Thermal displacement ellipsoids are drawn at the 50% probability level.

Table 1

Empirical formula $C_{15}H_{18}N_2O$ Formula weight242.31	
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Crystal system, space group Monoclinic, <i>P</i> 2 ₁	
Unit cell dimensions	
a (Å) 7.0253(11)	
b (Å) 16.957(3)	
c (Å) 11.4895(19)	
α (°) 90	
β (°) 103.769(14)	
γ (°) 90	
Volume (Å ³) 1329.4(4)	
Z, calculated density (Mg/m^3) 4, 1.211	
Absorption coefficient (mm^{-1}) 0.077	
<i>F</i> (000) 520	
θ Range for data collection (°) 2.99–27.00	
Limiting indices $-8 \le h \le 8, -21 \le k \le$	21,
$-14\leqslant l\leqslant 14$	
Reflections collected/unique 11999/5543 [0.0189]	
$\begin{bmatrix} R(\text{III}) \end{bmatrix}$	
Completeness to $\theta = 27.00$ 99.90%	
Absorption correction Semi-empirical from eq	uivalents
Max. and min. transmission 0.997 and 0.987	r ²
Rennement method Full-matrix least-square	es on F
Data/restraints/parameters $5543/1/469$	
Goodness-of-fit on F^2 0.981	0.4.5
Final <i>K</i> indices $[I > 2\sigma(I)]$ $R_1 = 0.0326, wR_2 = 0.0000000000000000000000000000000000$	845
<i>K</i> indices (all data) $R_1 = 0.0467, wR_2 = 0.0000000000000000000000000000000000$	888

compounds. Using this parameter, one can only state that hydrogen bonding does exist but the proton position in the H-bond bridge remains undetermined. The other carbon chemical shifts do not provide useful structural information either. From those data we can distinguish both the bonded and non-bonded parts of the molecules but we cannot estimate the proton position. The proton signals of all investigated compounds at room temperature in chloroform are broadened indicating dynamic processes occurring in the molecules. Lowering the temperature can shift the exchange rate to coalescence and, finally, to slow down the exchange limit. This approach can provide some useful information on the dynamics of the exchange but no information about the proton position in the intramolecular hydrogen bridge.

The first approximation of the proton position in the Hbridge can be achieved by examination of the nitrogen chemical shifts. When the values of this parameter are in the range from -70 to -100 ppm, this indicates that the molecule can exist as the OH structure with a relatively weak hydrogen bond to the nitrogen atom. The Schiff bases with the proton transferred to the nitrogen site are characterized by nitrogen chemical shifts close to -200 ppm (the lowest observed value is about -240 ppm). The nitrogen chemical shift by itself is not a very precise measure of the proton position. A much better approximation can be achieved by investigations of the difference between chemical shifts of the pure (no Hbond at all) OH compounds and the ones from the Hbonded structure. Generally, it is very difficult to find a good reference compound for the non-bonded structure. It is much easier in the discussed group of compounds, because in the same molecules we have both the bonded and nonbonded structural Schiff molecular fragments. For the exact estimation of the proton position in intramolecular hydrogen bonds, it is necessary to consider the existence and strength of the interactions with the solvent. In chloroform solution such interactions (weak hydrogen bonds) do exist and can cause measurable effects of an upfield shift of the values of the nitrogen chemical shift. Those effects are in the range of a few ppms and they depend on the basicity of the investigated nitrogen site.

The best approximation of the structure without intermolecular H-bonds are solid state spectra of reference compounds where the intermolecular hydrogen bonds with solvent cannot take place. For the aliphatic derivatives, two nitrogen chemical shift values in the solid state for imines without hydrogen bonds are available: -47.9 ppm for the cyclopropyl derivative and -47.2 ppm for the cyclopentyl compound (the average value -47.55 ppm).

Table 2 Carbon and nitrogen chemical shifts of compounds under investigation

	Me	c-Pr	c-Pr solid state	c-Bu	c-Pen	Ph	Ph solid state
C1	160.0	157.5	157.2	160.4	159.9	159.7	160.4 ^a
C2	118.6	119.1	119.4	118.3	118.3	119.4	118.0
C3	134.3	133.2	133.4	134.1	133.9	136.2	b
C4	127.5	128.1	126.9	127.3	127.4	128.6	b
C5	130.0	128.8	130.1	130.1	130.3	131.0	b
C6	123.1	123.3	123.6	123.4	123.7	123.6	124.1
C7	165.9	162.8	163.7	161.9	162.4	162.4	160.4 ^a
C8	158.5	154.7	152.6	154.1	154.5	156.0	154.8
$\Delta \delta = \delta_{\rm C2} - \delta_{\rm C6}$	-4.5	-4.2	-4.2	-5.1	-5.4	-4.2	-6.1
$\Delta \delta = \delta_{\rm C3} - \delta_{\rm C5}$	4.3	4.4	3.3	4.0	3.6	5.2	
$\Delta \delta = \delta_{\rm C7} - \delta_{\rm C8}$	7.4	8.1	11.1	7.8	7.9	6.4	5.6
N–H	-103.8	-74.8	-73.3	-86.6	-83.4	-86.6	-92.1
-N=	-72.7	-53.3	-47.9	-50.2	-47.2	-61.8	_
$\Delta \delta = \delta_{\rm NH} - \delta_{-\rm N=}$	-31.1	-21.5	-25.4	-24.4	-36.2	-24.8	_
$\Delta \delta_{\rm R} = \delta_{\rm NH} - \delta_{-\rm N=REF}$	-56.2	-27.2	-25.7	-39.0	-35.8	-32.9	_
CH ₃		20.7	21.3	20.3	20.5	20.3	19.4
C1′		40.6	42.1	60.7	69.5		
		42.6		63.0	72.6		
C2′		9.9	10.3	30.5	34.6		
			8.9				
C3′				15.6	24.6		

 $\delta_{-N = REF}$ reference nitrogen chemical shift for Schiff base without intermolecular H-bond with solvent. For aliphatic compounds $\delta_{-N = REF} = -47.6$ ppm (the average value for aliphatic derivative in the solid state where intermolecular H-bonds with solvent does not exist). For the aromatic derivative it is the value obtained for Ph–CH=N–Ph in DMSO solution; $\delta_{-N = REF} = -53.7$ ppm (Annual Reports on NMR Spectroscopy, Vol. 11B).

^a Overlapping signals.

^b Unresolved pattern of overlapping signals from three aromatic rings.

For the aromatic X=Ph derivative, this procedure cannot be applied since the signal of the nitrogen atom without H-bond was missing in the nitrogen-15 solid state spectrum. This was probably due to a severe broadening of this signal or very inconvenient relaxation properties of this compound. In this case, it was necessary to use the model compounds for the structure without Hbond. The best approximation seems to be the phenyl[1-phenylmethylidene]-amine in DMSO solution $\delta_{-N=REF} = -53.7$ ppm. The results of such calculations are collected in Table 3.

The effects of hydrogen bond formation on the nitrogen chemical shifts are presented by two parameters $\Delta \delta = \delta_{\rm NH} - \delta_{-\rm N=}$ and $\Delta \delta_{\rm R} = \delta_{\rm NH} - \delta_{-\rm N=REF}$. The first one is a simple difference between the nitrogen chemical shifts of bonded and non-bonded atoms and it suggests that in all compounds the intramolecular H-bonds are very similar. However, the observed effects are generated by concerted action of both intra and intermolecular hydrogen bond interactions with solvent moieties. The effects of intermolecular hydrogen bonding can be removed by application of second parameter $\Delta \delta_R = \delta_{NH} - \delta - N_{=REF}$. Then it appears that the strongest intramolecular H-bond is formed by the methyl derivative. The cycloaliphatic derivatives form weaker H-bonds the strength of which is proportional to the size of the aliphatic ring. The hydrogen bond strength of the aromatic derivatives is studied using the cyclopropyl and cyclobutyl derivatives. This means that the cyclopropyl ring does not force the proton to transfer from the oxygen atom to the nitrogen, which is in contrast to the linear aliphatic chains or larger aliphatic rings (cyclobutyl or cyclopentyl).

Table 4 contains a comparison of the principal components of the chemical shift anisotropy (CSA) tensor of compounds containing intramolecular hydrogen bonds. For all, except one, presented compounds, the principal compo-

Table 3	
The principal components of CSA tensor	

	c-Pr OH	<i>i</i> -Pr	c-Pr H-bond	Me H-bond	Me H-bond	Me NH	Me NH
$\delta_{\rm Iso}$	-47.9	-62.6	-73.3	-85.4	-90.4	-235.3	-237.4
$\delta_{11} = \delta_t$	204	139.5	165	198.1	188.0	-104.1	-105.1
$\delta_{22} = \delta_r$	-12	-11.0	-62	-81.6	-86.6	-246.2	-253.2
$\delta_{33} = \delta_{\perp}$	-335	-316.4	-324	-372.7	-372.5	-355.6	-354.0

c-Pr OH, cyclopropyl derivative in the OH form without H-bond; *i*-Pr, isopropyl naphtyl derivative in OH form with very weak H-bond [14]; c-Pr H-bond, cyclopropyl derivative in OH form with H-bond; Me H-bond, N-methyl derivative in OH form with H-bond [14]; Me NH, N-methyl derivative in NH form [14].

Table 4 Activation energies and exchange rates of investigated compounds calculated from proton NMR data

	Me	c-Pr	c-Bu	c-Pen	Ph
H7–H8					
$\Delta \delta_{\rm H}$ [Hz]	235	221	260	255	187
$k_{\rm co}$ [1/s]	521	490	577	566	415
$T_{\rm co}$ [K]	275	274	280	290	293
ΔG^+	52.8	52.8	53.6	55.7	57.2
H4–H6					
$\Delta \delta_{\rm H} [{\rm Hz}]$	310	282	365	335	348
$k_{\rm co}$ [1/s]	688	626	810	743	772
$T_{\rm co}$ [K]	279	279	287	295	303
ΔG^+	53.4	53.2	54.2	56.2	57.7

nents δ_t and δ_r change in the same way as the isotropic nitrogen chemical shift values.

The third component δ_{\perp} , does not follow this relation. First of all, the amplitude of this component is much smaller then the other ones and, hence, it is much less sensitive to structural differences. This component describes the electron density along the direction perpendicular to the nitrogen atom environment. This means that the hydrogen bond formation does not affect the electron density distribution in this direction. The only compound which behaves differently (c-Pr) has the methyl substituent on the Schiff carbon atom. The methyl group in this position causes some steric effects promoting the OH structure and can disturb electron distribution at the nitrogen atom neighborhood. Generally, one can say, that the principal components δ_t and δ_r are far more sensitive to H-bond formation compared with the isotropic value.

In all our previous investigations of H-bonding in Schiff bases at room temperature, we always observed a proton exchange process – very fast on the NMR time scale. In contrast to this, in the proton spectra of 4-methyl-2,6-bis-(alkylimino)-phenol derivatives, a severe dynamic broadening was observed. Previously, the dynamic of proton exchange in Schiff bases was investigated in a few arylimino derivatives. Dziembowska et al. [20], using line-shape analysis found that activation energy for those compounds is in range from 47.2 to 49.5 kJ/mol and only slightly depends on the substituent in the phenyl ring.

In the present work, we measure the coalescence temperature to estimate the reaction rate and activation energy. The results of these measurements are collected in Table 4. For all compounds the reaction rates and ΔG^+ values were calculated for two temperatures at which coalescence was observed for two pairs of proton signals: H7–H8 and H4–H6, respectively. The results of such calculations show that the activation energies calculated on the basis of the coalescence temperature of protons H4–H6 are slightly higher then those obtained from the H7–H8 data. The differences are on an acceptable low level. The most interesting conclusion from comparison of our and published data is a systematic difference in the activation energies calculated by both methods. This may be a consequence of the approximate character of our calculations based on the coalescence temperature measurement. The second source of difference could be error in temperature measurement in both series of experiments. The precise temperature measurements can be crucial in standard experiments using different probe head and temperature control units. However one can state that activation energies for all the aliphatic compounds are very close and slightly lower than those calculated for the aromatic compound.

3.1. Structural results

The structural picture of H-bond interactions in a model c-Pr Schiff base is quite a complex one. The c-Pr Schiff base crystallizes in the monoclinic $P2_1$ space group. There are two independent molecules in the crystallographic asymmetric part of the unit cell and all the atoms occupy general positions. The geometry of the two moieties is very similar, some subtle changes are present only in the case of the intramolecular hydrogen bond and its vicinity. Otherwise, the molecules seem to be related by a glide plane, although the symmetry is non-crystallographic and there is no indication of the existence of such a plane in the intensities of the reflections.

The general structure of the molecule I and II is presented in the Fig. 2.

The central aromatic ring is planar and shows only slight bond alternation, with the C1–C2 bond significantly longer (1.410 Å vs. 1.39 Å on the average). There is an intramolecular hydrogen bond between the hydroxyl group and one of the Schiff-base nitrogen atoms, denoted further as N1, and therefore a pseudo-six membered ring is formed. The N1 and the Schiff-base C7 atoms are located in the plane of the main aromatic ring. The cyclopropyl substituent connected with the N1 atom appears in the trans position with respect to the Schiff-base carbon atom. In the case of the other cyclopropyl substituent, it is located in the *cis* position with respect to the C11 Schiff-base carbon atom. The substituent is slightly distorted with respect to the main aromatic ring, so that C14 lies in the plane defined by the main aromatic ring, whereas the C12 atom, connecting the cyclopropyl moiety with the rest of the molecule, is well out of that plane.

The main differences between the molecules are manifested in the geometry of the intramolecular hydrogen bonds. The H-bond is responsible for many of the properties of the Schiff-base and the crystal structure gives us means to analyze the two different kinds of H-bonds in the same structure and similar crystal environment. Additionally, the geometrical information from that particular structure is valuable because there are no intermolecular interactions in the structure, in which the atoms constituting the H-bonds might have been involved.

In the case of the molecule I, the H1O hydrogen position is better defined. The H1O atom is located closer to the O1 oxygen and in the plane formed by the other members of the pseudo-six membered ring (i.e.



Fig. 3. c-Pr Schiff base – difference electron density maps prepared in O1–C1–C2–C7–N1 plane with the H-bond hydrogen included for molecule I (a) and molecule I (b) or excluded for molecule I (c) and molecule I (d) during the calculation of the map coefficients.

O1-C1-C2-C7-N1), with the H1O-O1-C1-C2 torsion angle $0.78(11)^{\circ}$. The isotropic thermal displacement factor of the H1O atom has a value of $0.031(5) \text{ Å}^2$ which shows, that the position of the hydrogen atom is well

defined. In the molecule I, the H1OD hydrogen is located significantly further from the O1D oxygen and out of the O1D–C1D–C2D–C7D–N1D plane, with the H1OD–O1D–C1D–C2D torsion angle $-8.44(10)^{\circ}$. The

 Table 5

 Selected bond lengths and valence angles in the vicinity of intramolecular H-bond

Bonds (Å)	Molecule I	Molecule II	Angles (°)	Molecule I	Molecule II
H10–01	0.878(20)	0.983(33)	N1-H10-O1	149.86(205)	144.08(312)
01–C1	1.349(5)	1.352(5)	H10-01-C1	107.31(139)	108.66(197)
C1–C6	1.398(11)	1.394(11)	O1-C1-C2	121.08(16)	121.22(16)
C1–C2	1.410(6)	1.410(6)	O1–C1–C6	119.17(16)	119.09(16)
C2–C3	1.397(5)	1.390(5)	C1-C2-C7	121.03(19)	121.16(19)
C2–C7	1.448(11)	1.448(11)	C1–C2–C3	119.32(17)	119.37(17)
C7–H7	0.928(21)	1.041(23)	C2-C7-H7	114.39(129)	118.24(119)
C7-N1	1.273(6)	1.275(6)	C2-C7-N1	122.39(18)	122.01(17)
N1-H1O	1.795(22)	1.729(36)	C7–N1–C8	118.14(16)	119.00(16)
N1-C8	1.42(1)	1.418(10)	C7–N1–H1O	98.10(69)	100.87(112)
N101	2.592(3)	2.590(3)			



Fig. 4. Crystal packing for the c-Pr Schiff-base along the *X*-axis (a), *Y*-axis (b) and *Z*-axis (c).

isotropic thermal displacement factor of the H1OD atom has a value of 0.087(5) Å², nearly three times higher than the same parameter measured for the H1O atom and twice as high as the parameters for the other H atoms in the structure. This indicates a significant amount of thermal motion or possibly the partial transfer of the proton to the N1D atom. However, the difference electron density maps (Fig. 3) prepared for both molecules with omission of the H atoms involved in the H-bond as well as without it look rather similar and there is no strong indication that a proton transfer form oxygen to nitrogen might take place in the molecule **II**. Nevertheless, the differences in the location and behavior of the H atoms in the two H-bonds influence also the geometry of the adjacent part of the molecule. A comparison of the more important geometrical parameters is presented in Table 5.

The packing of the c-Pr molecules in the crystallographic unit cell reveals a nice illustration of the non-crystallographic symmetry in the structure. It is shown in Fig. 4. Both in the case of the view along the X and Z crystallographic directions the molecules I and II seem to be related by a plane – an a glide plane. Closer analysis of the distances, however reveals that the translation needed to transform molecule I into II is not 1/2 of the a crystallographic unit.

The molecules \mathbf{I} and \mathbf{II} form layers perpendicular to the crystallographic Y direction each consisting of molecule \mathbf{I} or \mathbf{II} . The central aromatic rings in a single layer are oriented parallel to one another so that the hydrogens from the cyclopropyl moiety are oriented toward the central aromatic ring of the next molecule of the same kind. Short contacts appear also between the carbons from the cyclopropyl moieties and the hydrogens from the aromatic ring that belongs to the molecule of the different kind.

In conclusion we have presented structural (for c-Pr) and NMR spectroscopic properties for a series (Me, c-Pr, c-Bu, c-Pen, Ph) of model Schiff bases – 2,6-bis(alkylimino) phenol derivatives. It appears that the strongest intramolecular H-bond is formed by the methyl derivative. The cycloaliphatic derivatives form weaker H-bonds with strength proportional to the size of the aliphatic ring. For the cyclopropyl derivative we were able to measure a slow rotated solid state spectrum and calculate the principal components of chemical shift anisotropy tensor (CSA). We found out that the first two principal components of the chemical shift anisotropy (CSA) tensor change in the same way as the isotropic nitrogen chemical shift values. We also measured the coalescence temperature to estimate the reaction rate and activation energy.

For the c-Pr Schiff-base derivative, the X-ray structure has been established. It appears that there are two independent molecules in the crystal lattice. The geometry of the two moieties is very similar with the exception of some subtle changes in the intramolecular hydrogen bond and its vicinity. Although the molecules seem to be related by a glide plane, the symmetry is non-crystallographic and there is no indication of the existence of such a plane in the intensities of the reflections. We present details of the hydrogen bonds in both moieties.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc. 2007.05.029.

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