Accepted Manuscript

Spectroscopic studies of the intramolecular hydrogen bonding in o-hydroxy Schiff bases, derived from diaminomaleonitrile, and their deprotonation reaction products

Anna Szady-Chełmieniecka, Beata Kołodziej, Maja Morawiak, Bohdan Kamieński, Wojciech Schilf

PII:	S1386-1425(17)30657-1
DOI:	doi: 10.1016/j.saa.2017.08.028
Reference:	SAA 15385
To appear in:	*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*
Received date:	13 March 2017
Revised date:	3 August 2017
Accepted date:	9 August 2017

Please cite this article as: Anna Szady-Chełmieniecka, Beata Kołodziej, Maja Morawiak, Bohdan Kamieński, Wojciech Schilf , Spectroscopic studies of the intramolecular hydrogen bonding in o-hydroxy Schiff bases, derived from diaminomaleonitrile, and their deprotonation reaction products, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2017), doi: 10.1016/j.saa.2017.08.028

Spectroscopic studies of the intramolecular hydrogen bonding in o-hydroxy Schiff bases, derived from diaminomaleonitrile, and their deprotonation reaction products

Anna Szady-Chełmieniecka[a], Beata Kołodziej[a*], Maja Morawiak[b], Bohdan Kamieński[b,c], and Wojciech Schilf[b]

a- West Pomeranian University of Technology, Szczecin; Faculty of Chemical Technology and Engineering; Department of Inorganic and Analytical Chemistry, Al. Piastów 42, 71-065 Szczecin, Poland
b- Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland
c- Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland
*- corresponding author

Key words

diaminomaleonitrile, Schiff bases, ^{1}H, ^{13}C, and ^{15}N NMR, ATR-FTIR, X-Ray, intramolecular hydrogen bond, deprotonation.

Abstract

The structural study of five Schiff bases derived from diaminomaleonitrile (DAMN) and 2-hydroxy carbonyl compounds was performed using ^{1}H, ^{13}C and ^{15}N NMR methods in solution and in the solid state as well. ATR-FTIR and X-Ray spectroscopies were used for confirmation of the results obtained by NMR method. The imine obtained from DAMN and benzaldehyde was synthesized as a model compound which lacks intramolecular hydrogen bond. Deprotonation of all synthesized compounds was done by treating with tetramethylguanidine (TMG). NMR data revealed that salicylidene Schiff bases in DMSO solution exist as OH forms without intramolecular hydrogen bonds and independent on the substituents in aromatic ring. In the case of 2-hydroxy naphthyl derivative, the OH proton is engaged into weak intramolecular hydrogen bond. Two of imines (salDAMN and 5-BrsalDAMN) exist in DMSO solution as equilibrium mixtures of two isomers (A and B). The structures of equilibrium mixture in the solid state have been studied by NMR, ATR-FTIR and X-Ray methods.

The deprotonation of three studied compounds (salDAMN, 5-BrsalDAMN, and 5-CH_3salDAMN) proceeded in two different ways: deprotonation of oxygen atom (X form) or of

nitrogen atom of free primary amine group of DAMN moiety (Y form). For 5-NO_2salDAMN and naphDAMN only one form (X) was observed.

Introduction

Imines (known as Schiff bases), derived from aromatic o-hydroxyaldehydes and o-hydroxyketones and primary amines, may have intramolecular hydrogen bonds between phenolic oxygen and formal imino nitrogen atom, and therefore can form dynamic equilibrium mixture of imine and enamine tautomeric forms (Fig. 1) [1-4].

Figure 1

If the proton is almost localized in the central position between the proton donor and the proton acceptor, we call such bonds as low barrier hydrogen bonds [5].

The OH···N intramolecular hydrogen bonds present in Schiff bases are specific and have important interactions, which determine chemical and physicochemical properties of investigated compounds [6-8]. The remarkable changes caused by the proton transfer from the hydroxyl oxygen atom to imine nitrogen atom are connected with the color changes known as thermochromism and photochromism [9]. These features make Schiff bases as good potential elements for constructing optical switches, molecular electronics and computing [10], and optical memory devices [11].

Our previous investigations [5, 7-8, 12] showed that position of proton in intramolecular hydrogen bond is determined by:

(i) type of substituent present in salicylaldehydes

- when acidity of OH group is increased (introducing of substituents, which are electron acceptors, for example $–NO_2$), the proton transfer from oxygen atom to nitrogen atom is promoted,
- when acidity of OH group is decreased (introducing of electron donor substituents, for example alkyl groups), the enol-imine form is promoted,

(ii) type of amine

- when an aliphatic amine is used, the proton is more effectively transferred to nitrogen atom comparing with aromatic amine,
- when an aromatic amine is used and the basicity of amine is increased (introducing of substituents, which are donors of electron, for example $–NH_2$), the proton transfer to nitrogen atom is more effective,

(iii) the phase (solution or solid)

- generally, solid phase gives rise of keto-amine form.

Substituents in salicylaldehyde ring influence not only the acidity of the phenolic group but can also strongly stabilize the polar structure of the respective compounds. This problem was intensively discussed for N-(5-nitrosalicylidene)-ethylamine in solid and in solutions as well as for other Schiff bases derived from aromatic ortho-hydroxyaldehydes [5].

We have decided to expand our research on diaminomaleonitrile (DAMN), organic π–conjugated compound with electron donor (-NH_2) and electron acceptor (-CN) substituents in molecule (Fig. 2) with high electron affinity, which features a strong intramolecular charge transfer (ICT) interaction [13-15]. Sometimes this compound is treated as a tetramer of hydrogen cyanide [16-19].

Figure 2

The π–conjugated system, present in DAMN molecule, is responsible for changes in reactivity of amine group [20]. In the most of aliphatic diamines, both amine groups react with carbonyls easily [21-25]. When we use the same conditions (methanolic or ethanolic solution, room or a little higher temperature, time of reaction – 1h) for reaction of DAMN with carbonyl, we obtain only mono Schiff base, even in presence of excess of carbonyl [16-17].

Diaminomaleonitrile (DAMN) is a low-cost organic compound with a high nitrogen content [26] and it is often used as versatile precursor of heterocycles [27], for example imidazoles, triazoles, porphyrazines, pyrimidines, pyrazines, diazepines, and purines. DAMN can also be used as a synthetic precursor of fluorescent dyes, jet-printing inks, hair dyes, and biologically active compounds such as insecticides and anticancer agents. [18].

Schiff base ligands derived from DAMN and aromatic aldehydes have been recently used in various fields, for example pharmacology, thermostable optical material industry, or synthesis of conjugated linear polymers [17]. Schiff base ligands based on DAMN and salicylaldehydes are taken into account for applications in Cu^{2+} and Pt^{2+} sensing [28].

It is well known that metal chelates of salicylaldehydes and diaminomaleonitrile (DAMN) derivatives are the efficient materials as an electron transporter [29].

According to the literature data the nitrogen NMR spectroscopy seems to be one of the best methods for investigations of proton position in hydrogen bonded structures [7-8, 30]. This method is very attractive for these studies because of:

(i) the sensitivity of the nitrogen chemical shift of imine atom on proton position in H-bond (from -50 to -60 ppm for pure imine form to about -240 ppm for the structure with proton transfer),

(ii) the insensitivity of the nitrogen chemical shift of formally imine atom on the substitution effects connected with different substituents in salicylaldehyde unit [7].

The general rule, used in analysis of Schiff bases having intramolecular H-bond, is: the most upfield shift of the signal of the nitrogen atom means the strongest proton transfer from oxygen atom to nitrogen site. For aliphatic derivatives without H-bonds this chemical shift is about -60 ppm, relative weak H-bond can shift this signal to about -100 ppm, and for compounds with strong proton transfer nitrogen signal can be shifted to about -240 ppm [8]. Full protonation of an imine nitrogen atom in Schiff bases gives rise to a shielding increase of about 180 ppm (about -60 ppm for pure imine form and about -230 ppm for proton transferred structure) [30].

The second parameter suitable for the structure elucidation is carbon chemical shift of formal C-OH atoms. In this case we observe opposite effect - strong proton transfer to nitrogen atom causes the downfield shift of this signal. This effect is much weaker than that observed for nitrogen chemical shift. For compounds without H-bonding the C-2 signal is located close to 155 ppm. Proton transfer process can shift it to about 175 ppm. In contrast to imine nitrogen chemical shifts, the C-2 chemical shifts are less diagnostic, since they are also affected by substituents present in phenyl ring [8].

FTIR spectroscopy is used as a suitable method as an additional source of information confirming molecule structure proposed on the base of results obtained from NMR studies. Particular attention for this class of compounds is directed to the two ranges: 3500-3300 cm^{-1} and 1770-1550 cm^{-1}, where characteristic bands are present.

In the present work we report the synthesis and structural studies in both DMSO solution and in the solid state of six known mono Schiff bases obtained from DAMN and aromatic aldehydes: benzaldehyde (benz), salicylaldehyde (sal), 5-methylsalicylaldehyde (5-CH_3sal), 5-bromosalicylaldehyde (5-Brsal), 5-nitrosalicylaldehyde (5-NO_2sal), and 2-hydroxynaphtaldehyde (naph). In previous studies [16, 17, 31-34] the structures of Schiff bases obtained from DAMN were investigated by IR, UV-VIS and ^{1}H, and ^{13}C NMR methods. Since the possibility of different types of isomers (rotamers or geometrical cis-trans isomers) should be considered [35], we applied the full set of NMR measurements together with ATR-FTIR and X-Ray experiments to describe structures of obtained compounds in details. Additionally, we performed deprotonation reactions of mentioned Schiff bases using tetramethylguanidine (TMG) as the strong base reagent. The molecular structures of Schiff bases and deprotonated species were analyzed by spectroscopic methods.

Experimental

Synthesis of Schiff bases

All compounds were obtained according to the literature method [17] slightly modified for the present reaction.

To an ethanolic solution of suitable aldehyde (2,3 mmol) an ethanolic solution of DAMN (2,3 mmol) was added.

In the case of 5-BrsalDAMN, 5-NO_2salDAMN, and benzDAMN, precipitate was formed after a while and the mixture was allowed to stand for 24 h.

In the case of naphDAMN, salDAMN, and 5-CH_3salDAMN the mixture was stirred and refluxed for 1 h, and then it was cooled to room temperature and allowed to stand for 24 h.

After 24 h the obtained precipitate was filtered out and washed by cold ethanol and dried in the air.

The authenticity and purity of obtained compounds were examined by proton NMR measurements.

Deprotonation of obtained imines

Deprotonation reactions were performed in NMR tubes by adding some excess of pure TMG to DMSO solution of appropriate Schiff base.

NMR measurements

All solution state NMR experiments were performed on Varian-Agilent 600 MHz VNMRS instrument using 5 mm inverse probehead equipped with Z-gradient coil. For signal assignment 1D proton and carbon spectra were recorded as well as 2D GHSQC, GCOSY, and GHMBC experiments. For data acquisition and spectra processing standard Varian-Agilent software was used. The proton and carbon spectra were referenced with respect to internal TMS as a standard. For nitrogen-15 external nitromethane was applied as a standard. In some cases, due to dynamic character of investigated structures no correlation for carbon atoms of CN groups was found, so suggested signal assignment was done only on the base of comparison with other compounds.

The solid state NMR measurements were run on a Bruker Avance 500 MHz spectrometer. The solid state spectra were done using 4 mm CPMAS Bruker probehead. The typical spectral condition for natural abundance nitrogen CPMAS NMR spectra were: spectral width 28 kHz, acquisition time 40ms, spin rate 6-12 kHz, contact time for spin-lock 5ms, relaxation delay 10 to 120 s depending on relaxation condition for particular sample, estimated

from carbon measurement. The typical experimental condition for carbon CPMAS were: spectral width 31 kHz, acquisition time 20 ms, contact time 2 ms, spin rate 12 kHz. To distinguish protonated and quaternary carbon atoms, the short contact time spectra with contact time 40μs were done. In SCT experiments only protonated carbon atom signals are displayed. Originally, the solid state spectra were referenced to the solid glycine sample and then the obtained chemical shifts of appropriate signals were recalculated to TMS scale for carbon, and nitromethane for nitrogen measurements, respectively.

ATR-FTIR measurements

ATR-FTIR spectra were recorded on a Bruker Alpha Fourier Transform IR (FTIR) spectrometer equipped with a platinum ATR single reflection diamond-sampling module (Bruker Optics).

The infrared spectra were collected as an average of 64 scans per sample between the wavenumber range of 4000–360 cm^{-1} at a resolution of 4 cm^{-1}, controlled by Optics User Software (OPUS) version 7.5 (Bruker Optics). Air was used as reference background spectra. The ATR diamond surface was cleaned with acetone before each sample was scanned.

X-ray structure analysis

Yellow crystals of compounds 5-CH_3salDAMN[a], 5-CH_3salDAMN[b], and brown crystals of compound benzDAMN were obtained from ethanol. Crystal data for these compounds were collected at room temperature, on Bruker X8 APEXII diffractometer using Cu-Kα radiation (λ = 1.54178 Å). Frames were integrated with the Bruker SAINT [36] software package using a narrow-frame algorithm. The structure was solved and refined using the Bruker SHELXTL Software Package [37]. Data were corrected for absorption effects using the face-indexed numerical method (SADABS) [38]. Hydroxyl group hydrogens were found from the difference electron density maps and refined with an anisotropic thermal motion model. The structure was solved by direct methods SHELXS-2014 [39] and refined with full-matrix least-squares calculations on F^2 using SHELX-2014 [39]. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, 129 Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 1528338 for 5-CH_3salDAMN[a], CCDC 1528337 for 5-CH_3salDAMN[b] and CCDC 1528336 for benzDAMN.

Results and discussion

Five Schiff bases (four imines obtained from salicylaldehyde and its derivatives, and one obtained from 2-hydroxynaphthaldehyde) and diaminomaleonitrile (DAMN) (Fig. 3 a, b) have been investigated by NMR methods in DMSO solution. The sixth Schiff base (Fig. 3 c), derivative of DAMN and benzaldehyde, was obtained in order to determine the NMR spectral data for compound, which does not have possibility to form intramolecular hydrogen bond.

Figure 3

The main subject of the study is structure investigation of possible intramolecular hydrogen bonds between formal OH group in position 2 and imine moiety. The results of NMR measurements of investigated Schiff bases are collected in Table 1. The first observation made on those data is that two compounds: 5-CH_3salDAMN and 5-NO_2salDAMN form well defined, single-component systems, whereas the other two compounds: 5-BrsalDAMN and salDAMN form two-component equilibrium systems. The molecular structures of obtained Schiff bases can be determined mainly by analysis of chemical shifts of OH, C-2, C-7, =N- and NH_2 groups. The proton chemical shift of hydroxyl group is typical for phenols, but it is not shifted enough to lowfield for intramolecular hydrogen bonds. The carbon chemical shifts for C-2 atoms are also in the range that expected for C-OH groups. For C=O groups those signals should be shifted to lowfield (170-180 ppm range).

Table 1

The analysis of nitrogen chemical shifts of imine groups is much more difficult. The typical nitrogen chemical shift value for imine without hydrogen bond is about -50 – -60 ppm. The observed δ values (-83.9 to -95.8 ppm) (Table 1) suggest that some weak hydrogen bonding should exist. Comparison of those values with nitrogen chemical shift of benzaldehyde derivative (δ_N = -83,6 ppm), which cannot form hydrogen bond (Table 2), leads to the conclusion that in the all investigated compounds derived from salicylaldehydes no hydrogen bond was found. In the case of 2-hydroxy naphthyl derivative the imine nitrogen chemical shift is -104,7 ppm (Table 3). This value suggests that naphDAMN exists in the form with weak intramolecular hydrogen bond (O-H···N). The upfield shift of imine nitrogen signal is due to substitution effect introduced by the rest of diaminomaleonitrile substituent.

Table 2

Table 3

The structure differences between forms A and B which are observed for 5-BrsalDAMN and salDAMN are the next problem. Since the all NMR data for those forms are

very similar, one can conclude that the differences are connected rather with geometry than functionality. Theoretically there are at least two possible groups of rotamers obtained by rotation around C1-C7 bond or around N-C1' bond. Some of them are presented on Figure 4 (upper trace a-c). Additionally, due to two CN and one NH_2, strongly electron-withdrawing substituents in the molecules, we have to consider the presence of cis-trans isomers (lower trace d, e).

Figure 4

Unfortunately, the observed spectral differences are so small and unspecific so we could not assign them with certainty to appropriate structures. Considering, usually lower energy activation for rotamers transformation comparing with cis-trans isomerization the last process seems to be more expected, but on the base of acquired data we cannot make final differentiation. The dynamic character of A and B systems was verified by NOESY spectra, where exchange cross peaks between appropriate positions were found, so from the NMR time scale they are slow exchange processes.

The next step of our investigations was deprotonation reaction using 1,1,3,3-tetramethylguanidine (TMG) as a strong base. The deprotonation reactions were done in NMR tube by adding slight excess of TMG and reaction products were monitored by proton spectra. The first symptom of deprotonation was the loss of well-separated, relatively sharp OH, H_2O (from solvent) and NH_2 signals. Instead of them very broad dynamic averaged signal in the range from 2 to 6 ppm was found. It means that deprotonation reaction and proton exchange processes take place in both proton reach sites: OH and NH_2 substituents. Additionally, residual water from the solvent and excess of TMG participate in the exchange processes, leading to dynamically averaged one broad signal.

The 5-NO_2salDAMN (Table 4), naphDAMN (Table 3), and benzDAMN (Table 2) after deprotonation reaction form single component systems, whereas the three remaining Schiff bases (salDAMN, 5-BrsalDAMN, and 5-CH_3salDAMN (Table 4)) in such conditions form two-component systems. The benzDAMN (Table 2) was used as a model compound, where only one position is capable for the deprotonation.

Table 4

In contrast to pure Schiff bases, the deprotonated species X and Y observed for salDAMN, 5-BrsalDAMN, and 5-CH_3salDAMN show significantly different spectral properties, which suggest that the structural differences between X and Y are larger than those found for pure Schiff bases (Table 4).

Some problem can be with the interpretation of NMR data for deprotonation of 5-BrsalDAMN. In this case the minor product has very small, about 12 % abundance, and additionally, proton signals are broadened, so only GHSQC correlation was obtained. Consequently we could not record quaternary carbon atoms signals. But, based on available data we could distinguish and interpret structures of both forms by comparing with spectral data of remaining compounds.

For the X forms of deprotonated species a few characteristic spectral effects were found:

1. C-2 atom signals are shifted downfield after deprotonation
2. C-5 signals are shifted upfield
3. C-7 signals are close to parent Schiff bases
4. Imine N signals are upfield shifted
5. C-1' signals are weakly upfield or downfield shifted.

All those effects lead to the conclusion that X forms are created by removing protons from OH group located on C-2 (Fig. 5; Tables 1 and 4).

Figure 5

The contribution of quinon (C=O) structure changes the carbon chemical shifts in positions 2 and 5, whereas positions of C-7 signals are unchanged, since in both resonance forms ($C\text{-}O^-$ and C=O) the electron structures of C-7 atoms are very similar to the parent imine. The imine nitrogen atom is slightly upfield shifted probably due to some possible weak hydrogen bonding with amine group in position 2'.

The carbon and nitrogen spectral data for Y forms show different effects than in X forms:

1. C-2 carbon signals are close to the parent imines
2. C-4 signals are upfield shifted after deprotonation reaction
3. C-5 carbon signals are close to the parent imines
4. C-7 carbon signals have strong upfield effect
5. Imine nitrogen atom signals are weakly downfield shifted
6. C-1' carbon signals have strong upfield shifts

Since the mentioned above effects are different comparing with those observed for X form we can conclude that in the case of form Y protons were removed from amine group (Fig. 6, Tables 1 and 4).

Figure 6

The negative charge created originally on nitrogen atom in position 2' can be transferred via coupled double bonds system to aromatic ring, modifying chemical shifts of entire molecules. Some small, but significant downfield shift of imine nitrogen signals to the value of -88.9 ppm and -89.3 ppm for 5-CH_3salDAMN+TMG and 5-BrsalDAMN+TMG respectively, close to those found for benzDAMN+TMG (Table 2), where only NH_2 to -NH transformation is possible, supports above conclusion of molecular structure of form Y.

For naphDAMN (Table 3) the spectral effects are a little different comparing with previously discussed. This could be due to possible delocalization of negative charge connected with quinone (C=O) structure in whole condensed rings aromatic system. In this case the upfield shift effect observed in *para* position for single ring aromatic compounds is transferred and spread out into whole condensed naphthalene system. The other effects observed after deprotonation of naphDAMN (downfield effects found on C-2, C-11 and C-1') suggest that in this case proton was removed from oxygen atom, similarly to 5-NO_2salDAMN.

The problem of isomers existence was investigated also in the solid state by CPMAS measurements. The results of those experiments were collected in Table 5.

Table 5

The first observation made on the base of those results is that three compounds: 5-CH_3salDAMN, salDAMN and benzDAMN in the solid state exist as the mixture of two forms. The analysis of chemical shifts of both forms leads to the similar conclusion as those in the DMSO solution: both forms are either rotamers or geometrical isomers. Since the differences in chemical shifts of appropriate position are small we are not able to decide what kind of isomers exists. The only one significant difference between structure in solution and the solid state is proton position in intramolecular hydrogen bridge. The upfield shift of imine nitrogen atoms of compounds capable to form hydrogen bonds indicates that in the solid state protons are more shifted, comparing with DMSO solution, to nitrogen site forming typical six-membered intramolecular unsymmetrical hydrogen bridges. For the other three compounds (5-BrsalDAMN, 5-NO_2salDAMN, and naphDAMN) only one set of signals for each compound was detected, so one can assume that in those cases no isomerization takes place.

To confirm those statements, the ATR-FTIR spectra of all Schiff bases were recorded. To verify structure conclusions obtained from NMR data, two spectral ranges were considered.

In the first range (3600-3000 cm^{-1}) we should observe weak or medium intensity bands assigned to stretching vibrations of N-H bonds in primary amino group (doublet). In this range broad bands which come from stretching vibrations of O-H group engaged in intramolecular hydrogen bonding could be seen but they probably overlap with bands assigned to ν (N-H) and consequently are difficult to identify. For DAMN spectrum (Suppl.Mat. IA blue line) in this range five bands are observed (3436, 3366, 3344, 3299, and 3199 cm^{-1}). In benzDAMN spectrum (Suppl.Mat. IA pink line) also five bands were recorded: two of them (3408 and 3300 cm^{-1}) are sharp and intensive, whereas the other bands (3191, 3177, and 3161 cm^{-1}) are weak and unresolved. It can be considered as a confirmation of results obtained from ^{15}N CPMAS experiment, where two signals assigned to primary amino groups were found (Table 5). The salDAMN spectrum (Suppl.Mat. IA red line) contains only three intensive bands (3415, 3303, and 3189 cm^{-1}) and one very weak band (3373cm^{-1}). It is in good agreement with CPMAS data, where carbon spectra indicate presence of isomer mixtures but in the nitrogen spectrum of salDAMN only one NH_2 signal was found. For 5-CH_3salDAMN sample (Suppl.Mat. IA green line) in this range four intensive bands were recorded (3415, 3393, 3305, and 3204 cm^{-1}) which suggests presence of two non-equivalent amine groups. Comparing this observation with NMR and X-ray data we can conclude that this compound exists as the mixture of two geometrical isomers, probably cis and trans.

On the Fig. IB the ATR-FTIR spectra of remaining compounds (5-BrsalDAMN, 5-NO_2salDAMN and naphDAMN) are presented. On the base of NMR data (only one isomer detected for each compound) one can expect fewer number of bands in this region. In fact, for all those compounds only sets of three intensive bands were recorded (5-BrsalDAMN: 3396, 3297, and 3195 cm^{-1}; 5-NO_2salDAMN: 3402, 3303, and 3202 cm^{-1}; naphDAMN: 3466, 3337, and 3191 cm^{-1}).

The second interesting region (1680-1600 cm^{-1}) is characteristic for strong bands caused by stretching vibrations of double bonds: C=C, C=N and strong or medium intensity bands of scissoring vibrations single bond N-H. The IR spectra (Suppl. Mat. IIA and IIB) have strong absorption bands (1630-1603 cm^{-1}) which can be assigned to following vibration:

1. C=N stretching vibrations of the Schiff base functional group (1690-1590 cm^{-1}[40]),
2. C=C stretching vibrations for cis isomers (1680-1600 cm^{-1} [41]),
3. N-H scissoring vibrations close to 1615 cm^{-1} [41],
4. C=C skeletal vibrations (1650-1430 cm^{-1} [41].

It is very likely that some of those bands can overlap [40]. The band assignment of this region was done on the base of literature data [29, 31, 34, 42-49] and is presented in Table 6.

Table 6

The 1680-1600 cm^{-1} range for DAMN derivatives usually is assigned to C=N vibration, however the strong band close to 1625 cm^{-1} (5-BrsalDAMN, 5-NO_2salDAMN, 5-CH_3salDAMN, salDAMN) can be assigned to stretching vibration of aliphatic cis C=C bond coupled with aromatic ring. For isomer trans those vibrations are in the same region but are less intensive [50]. So, those bands are not diagnostic to distinguish cis and trans isomers in the mixture.

For benzDAMN and naphDAMN compounds strong bands at 1607 and 1603 cm^{-1} respectively, were recorded. They can be assigned to stretching vibrations of imine C=N bonds and to stretching vibrations of C=C bonds in aromatic rings. In the naphDAMN spectrum the additional 1615 cm^{-1} band was found, which was assigned to scissoring vibration of non-bonded amino group [41].

From the ^{13}C CPMAS NMR (Table 5) measurements we know that salDAMN derivative exists as the mixture of two isomers (double signals of aliphatic carbon atoms). In the IR spectrum of this compound in this range is the band of 1623 cm^{-1} with the shoulder on the left side, which suggests overlapping of two signals from different isomers. In the IR spectra of remaining compounds we do not observe such shoulders.

Crystal data and selected geometrical parameters for the X-Ray investigated crystal structures of 5-CH_3salDAMN[a], 5-CH_3salDAMN[b], and benzDAMN are summarized in Tables 7-8.

Table 7

Table 8

The X-Ray structure analysis of 5-CH_3salDAMN[b] and benzDAMN revealed, that the asymmetric part of the unit cell contains two independent molecules I and II. View of the molecules with numbering of the atoms is shown in Figure 7.

Figure 7

The bond lengths and angles in benzDAMN are identical to (Z)-2-Amino-3-[(E)-benzylideneamino]but-2-enedinitrile [51], while 5-CH_3salDAMN[a] and 5-CH_3salDAMN[b] are close related to structures of 2-Amino-3-[(*E*)-(2-hydroxy-3-methylbenzylidene)amino]but-2-enedinitrile [52] and (2*Z*)-2-Amino-3-{[(1*E*)-(4-hydroxyphenyl)methylene]-amino}but-2-enedinitrile [53]. However, in both cases the observed geometry of the nitrile groups is identical to that which we can see in compounds 5-CH_3salDAMN[b] and benzDAMN. The arrangement of the nitrile groups observed in 5-CH_3salDAMN[a] was not previously described in

the literature. This is example of polymorphism. Two different conformations were observed in crystals from the same sample. 5-CH_3salDAMN crystallized in two different shapes as a needle and plate.

There are two types of intramolecular hydrogen bonds in Schiff bases, which may be stabilized either in keto-amine (N—H···O hydrogen bond) [54] or phenol-imine (N···H— O hydrogen bond) tautomeric forms [55-56]. The present X-Ray investigation shows that the 5-CH_3salDAMN[a] and 5-CH_3salDAMN[b] are Schiff bases which exist in the phenol-imine form in the solid-state.

An intramolecular O1—H1···N1 hydrogen bond, a characteristic hydrogen bond for Schiff bases, leads to the formation of a S(6) six-membered ring (Figure 8). Details of the hydrogen bonds are given in Table 9.

Figure 8

Table 9

In case of benzDAMN in both independent molecules the benzene rings and diaminomaleonitrile moieties are anti with respect to azomethine C=N bonds. In the crystal structure, intermolecular N—H···N hydrogen bonds (Table 9) connect the molecules into ribbons in one direction (Figure 9).

Figure 9

The differences between conformations of molecules 5-CH_3salDAMN[a], 5-CH_3salDAMN[b] and benzDAMN are illustrated in Figure 10, showing the overlay of all molecules by fitting of C=N in azomethine. The conformations of these molecules are described the torsion angles φ_2 = C2–C1–C7–N1 and φ_3 = C7–N1–C8–C9, which are of 2.6(3)° for 5-CH_3salDAMN[a], -1.8(5)° and -1.2(5)° for 5-CH_3salDAMN[b], 0.9(2)° and 2.5(2)° for benzDAMN and 2.2(3)° for 5-CH_3salDAMN[a], 0.7(5)° and -0.4(4)° for 5-CH_3salDAMN[b], 5.6(2)° and -2.9(2)° for benzDAMN, respectively.

Figure 10

Conclusions

On the basis of proton, carbon and nitrogen NMR data it was found that all investigated compounds obtained from salicylaldehydes exist in DMSO solution as OH forms without intramolecular hydrogen bonds. In the case of 2-hydroxy naphthyl derivative, the proton was engaged into weak intramolecular hydrogen bond. The upfield shifts of imine nitrogen atoms observed in the solid state indicated that in this phase unsymmetrical intramolecular hydrogen bonds are present.

Additionally, in some imines derived from DAMN (salDAMN and 5-BrsalDAMN), it is observed that two-component (A and B) are in equilibrium mixtures.

All the investigated imines were deprotonated by reaction with tetramethylguanidine (TMG). Deprotonation reaction of imine derivatives of DAMN occurs in two different ways. For three DAMN derivatives (salDAMN, 5-CH_3salDAMN, and 5-BrsalDAMN) deprotonation products form two-component (X and Y) mixtures. In contrast to parent imines (equilibrium mixture of cis and trans isomers), structures of deprotonated forms (X and Y) differ significantly. In form X, deprotonation takes place on oxygen atom, whereas in form Y, proton is subtracted from NH_2 group of diaminomaleonitrile residue. Two other derivatives (5-NO_2salDAMN and naphDAMN) form only one deprotonation product, where the proton is removed from OH group.

References

1. A. Filarowski, M. Lopatkova, P. Lipkowski, M. Van der Auweraer, V. Leen, W. Dehaen *J. Phys. Chem. B* **119** (2015) 2576-2584

2. H. Houjou, H. Shingai, K. Yagi, I. Yoshikawa, K. Araki *J. Org. Chem.* **78** (2013) 9021-9031

3. I. Król-Starzomska, A. Filarowski, M. Rospenk, A. Koll, S. Melikova *J. Phys. Chem. A* **108** (2004) 2131-2138

4. T. Hökeleka, Z. Kılıç, M. Işıklan, M. Toy *J. Mol. Struct.* **523** (2000) 61-69

5. K. Pyta, P. Przybylski, W. Schilf, B. Kołodziej, A.Szady-Chełmieniecka, E.Grech, B. Brzeziński *J. Mol. Struct.* **967** (2010) 140-146

6. A.A. Hoser, W. Schilf, A. Szady Chełmieniecka, B. Kołodziej, B. Kamieński, E. Grech, K. Woźniak *Polyhedron* **31** (2012) 241-248

7. W. Schilf, B. Kamieński, K. Užarević *J. Mol. Struct.***1031** (2013) 211-215

8. W. Schilf, B. Kamieński, A. Szady-Chełmieniecka, B. Kołodziej, E. Grech, D. Zarzeczańska, A. Wcisło, T. Ossowski *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **109** (2013) 47-54

9. A. Filarowski, T. Głowiak, A. Koll *J. Mol. Struct.* **484** (1999) 75-89

10. A. Jiménez-Sánchez, N. Farfán, R. Santillan *J. Phys. Chem. C* **119** (2015) 13814-13826

11. E. Tas, I. Ucar, V.T. Kasumov, A. Kilic, A. Bulut *Spectrochim. Acta Part A* **68** (2007) 463-468

12. W. Schilf, B. Kamieński, A. Szady-Chełmieniecka, E. Grech *J. Mol. Struct.* **743** (2005) 237-241

13. T.G. Jo, J. Na, J.J. Lee, M.M. Lee, S.Y. Lee, C. Kim *New J. Chem.* **39** (2015) 2580-2587

14. G.J. Park, H.Y. Jo, K.Y. Ryu, C. Kim *RSC Adv*. **4** (2014) 63882-63890

15. R. Sheng, P. Wang, Y. Gao, Y. Wu, W. Liu, J. Ma, H. Li, S. Wu *Org. Lett.* **10** (2008) 5015-5018

16. J. Yang, R. Shi, P. Zhou, Q. Qiu, H. Li, *J. Mol. Struct.* **1106** (2016) 242-258

17. A. Guha, J. Adhikary, T.K. Mondal, D. Das *Indian Journal of Chemistry* **50** (2011) 1463-1468

18. Y. Kubota, T. Shibata, E. Babamoto-Horiguchi, J. Uehara, K. Funabiki, S. Matsumoto, M. Ebihara, M. Matsui *Tetrahedron* **65** (2009) 2506-2511

19. M. Takahashi, T. Iwamoto *J. Inorg. Nucl. Chem.* **43** (1981) 253-256

20. J. Clayden, N. Greeves, S. Warren, P. Wothers *Organic Chemistry* vol. 1, Oxford University Press 2001

21. S. Kedy, N. Almhna, F. Kandil *Arabian J. Chem.* **8** (2015) 93-99

22. K. Mohammadi, S.S. Azad, A. Amoozegar *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **146** (2015) 221-227

23. M.A.S. Omer, J.-C. Liu, W.-T. Deng, N.-Z. Jin *Polyhedron* **69** (2014) 10-14

24. S. Naskar, S. Naskar, R.J. Butcher, S.K. Chattopadhyay *Inorg. Chim. Acta* **363** (2010) 404-411

25. U. Casellato, S. Tamburini, P. Tomasin, P.A. Vigato *Inorg. Chim. Acta* **357** (2004) 4191-4207

26. Z.-J. Liua, W.-C. Wanga, D.-Z. Yanga, S. Wanga, L.-Y. Daib, Z.-L. Yang *Ceramics International* **42** (2016) 3411-3417

27. A. Yahyazadeh, F. Hossaini *E-Journal of Chemistry* **4** (2007) 376-380

28. J. Cheng, Y. Zhang, X. Ma, X. Zhou, H. Xiang *Chem. Commun.* **49** (2013) 11791-11793

29. W. Zhang, X. Jin, X. Yu, J. Zhou, G. Tang, D. Peng, J. Hu, C. Zhong *J. Organomet. Chem.* **749** (2014) 26-33

30. W. Schilf, B. Kołodziej, E. Grech *J. Mol. Struct.* **791** (2006) 93-97

31. H. Khanmohammadi, V. Arab, K. Rezaeian, G.R. Talei, M. Pass, N. Shabani, *J. Mol. Struct.* **1129** (2017) 169-178

32. D. Mandal, D. Chakraborty, V. Ramkumar, D.K. Chand, *RSC Adv.* **6** (2016) 21706-21718

33. S.A. Lee, J.J. Lee, J.W. Shin, K.S. Min, C. Kim *Dyes and Pigments* **116** (2015) 131-138

34. V. Kumar, R.K. Mishra, S. Shukla, R. Mishra, M. Singh, I. Tiwari, K. Thapliyal, K.K. Upadhyay *J. Mol. Struct.* **1047** (2013) 66-72

35. C-W. Lin, P.-T. Chou, Y.-H. Liao, Y.-C. Lin, C.-T. Chen, Y.-C. Chen, C.-H. Lai, B.-S. Chen, Y.-H. Liu, C.-C. Wang, M.-L. Ho *Chem.Eur.J.* **16** (2010) 3770-3782

36. Bruker, 2004, APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA

37. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Crystallogr.*, **64** (2008), 112

38. Bruker, 2008, SADABS. Bruker AXS Inc., Madison, Wisconsin, USA

39. G. M. Sheldrick, SHELXL-2014. Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany (2014)

40. J. Coates *Encyclopedia of Analytical Chemistry* vol. 12, pp. 10815-10837, John Wiley & Sons Ltd., Chichester 2000

41. B. Stuart *Infrared Spectroscopy. Fundamentals and Applications*, John Wiley & Sons Ltd., 2004

42. A. Yahyazadeh, V. Azimi *Eur. Chem. Bull.* **2** (2013) 453-455

43. V.B. Devi, R.K.B. Singh *IJSR* **2** (2013) 312-318

44. H. Khanmohammadi, K. Rezaeian, A. Abdollahi *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.***139** (2015) 405-412

45. M.Kr. Paul, Y.D. Singh, N.B. Singh, U. Sarkar *J. Mol. Struct.* **1081** (2015) 316-328

46. J. Hu, X. Jin, D. Peng, Q. Xie, Y. Liu, Y. Liao, C. Zhu, C. Zhong *Res. Chem. Intermed.* **41** (2015) 8327-8342

47. J. Zhang, G. Dai, F. Wu, D. Li, D. Gao, H. Jin, S. Chen, X. Zhu, C. Huang, D. Han *J. Photochem. Photobiol. A: Chemistry* **316** (2016) 12-18

48. I. Sheikshoaie, S.Y. Ebrahimipour, N. Lotfi, J.T. Mague, M. Khaleghi *Inorg. Chim. Acta* **442** (2016) 151-157

49. M. Kalhor, Z. Seyedzade *Res. Chem. Intermed.* DOI 10.1007/s11164-016-2829-8

50. R.M. Silverstein, F.X. Webster, D.J. Kiemle *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, Inc. 2005

51. G. Varsha, V. Arun, M. Sebastian, P. Leeju, D. Varghese, K.K.M. Yusuff, *Acta Cryst.*, **E65** (2009), o919

52. E.S. Aazam, O. Büyükgüngör, *Acta Cryst.* **E68** (2012), o1406

53. V.V. Nesterov, M.Yu. Antipin, V. N. Nesterov, B.G. Penn, D.O. Frazier, T.V. Timofeeva, *Crystal Growth & Design*, **4** (2004), 521 – 531

54. T. Hökelek, Z. Kiliç, M. Isiklan, M. Toy, *J. Mol. Struct.* **523** (2000), 61 – 69

55. M. Odabaşoğlu, C. Albayrak, O. Büyükgüngör, *Acta Cryst.* **E61** (2005), o425 – o426

56. E.S. Aazam, O. Büyükgüngör, *Acta Cryst.* **E66** (2010), o2587 – o2588

57. K. Užarević, M. Rubćić, V. Stilinović, B. Kaitner, M. Cindrić, *J. Mol. Struct.* **984** (2010) 232

Table 1. **Results of NMR measurements of Schiff bases in DMSO solution.**

compound / position	5-CH_3salDAMN		5-BrsalDAMN				salDAMN				5-NO_2salDAMN	
			A 72%		B 18%		A 80%		B 20%			
	^1H	$^{13}C/^{15}N$	^1H	$^{13}C/^{15}N$	^1H	$^{13}C/^{15}N$	^1H	$^{13}C/^{15}N$	^1H	$^{13}C/^{15}N$	^1H	$^{13}C/^{15}N$
C-1	-	121.5	-	124.4	-	122.9	-	121.7	-	120.4	-	122.6
C-2	-	156.7	-	157.8	-	157.5	-	158.6	-	158.5	-	163.6
C-3	6.80	116.8	6.86	119.1	6.87	119.3	6.90	116.85	6.90	116.9	7.08	117.5
C-4	7.11	134.4	7.41	135.6	7.43	135.0	7.29	133.7	7.29	132.9	8.15	128.3
C-5	-	128.5	-	112.0	-	111.2	6.85	119.8	6.85	120.0	-	140.8
C-6	7.83	129.1	8.29	130.4	7.82	131.5	8.01	129.3	7.62	130.7	8.92	124.3
C-7	8.52	153.2	8.47	150.2	8.40	150.7	8.56	153.2	8.42	153.5	8.52	149.8
OH	10.1	-	10.6	-	11.1	-	10.4	-	11.1	-	11.9	-
N	-	-93.8	-	-87.0		-89.1		-92.9		-95.8	-	-83.9
C-1’	-	104.0	-	103.7		103.9		103.9		103.95		103.6
C-2’	-	126.3		127.2		128.4		126.4		126.4		127.8
1’-CN	-	114.4		114.3		114.2*		115.0		113.7		114.3
2’-CN	-	115.0		114.9		113.6*		114.4		112.4		114.9
NH_2	7.80	-292.4 91Hz	8.00	-290.3 91Hz	8.1	-292.9 92Hz	7.81	-	8.00	-	8.17	-288.0 91Hz
CH_3	2.2	20.5	-	-		-						

***- assignment can be reversed**

For NH_2 nitrogen signals the line widths are specified in second row

Table 2. **NMR data for benzDAMN and deprotonation reaction product in DMSO solution.**

compound / position	benzDAMN		benzDAMN + TMG	
	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$
C-1	-	135.9	-	139.9
C-2	8.00	129.6	7.88	128.6
C-3	7.45 ov.	129.2	7.39 ov.	129.1
C-4	7.45 ov.	131.9	7.39 ov.	130.8
C-5	-	-	-	-
C-6	-	-	-	-
C-7	8.23	155.5	8.1	151.1
OH	-	-	-	-
N		-83.6		-80.2
C-1’		103.1		99.6
C-2’		127.4		126.1
1’-CN		114.8		117.1*
2’-CN		114.2		116.8*
NH_2	7.92	-290.8 91.8Hz	-	-

ov.- overlapped signals

*- assignment can be reversed

Table 3. **NMR data for naphDAMN and its deprotonation product in DMSO solution.**

compound / position	naphDAMN		naphDAMN + TMG	
	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$
C-1	**-**	**110.8**	**-**	**110.9**
C-2	**-**	**160.3**	**-**	**179.1**
C-3	**7.20**	**119.0**	**6.41**	**128.6**
C-4	**8.60**	**122.5**	**7.34**	**135.8**
C-5	**7.85**	**129.4**	**7.33**	**128.2**
C-6	**7.59**	**129.1**	**7.24**	**127.9**
C-7	**7.40**	**124.5**	**6.88**	**119.9**
C-8	**7.97**	**135.7**	**9.20**	**124.4**
C-9	**-**	**132.2**	**-**	**135.4**
C-10	**-**	**128.4**	**-**	**120.0**
C-11	**9.22**	**155.5**	**9.11**	**159.2**
C-1'	**-**	**104.4**		**111.8**
C-2'	**-**	**125.6**		**124.9**
1'-CN	**-**	**114.6**		**115.7***
2'-CN	**-**	**115.2**		**117.9***
OH	**11.9**	**-**		**-**
=N-		**-104.7**		**-127.5**
NH_2	**7.88**	**-292.3 (91.3Hz)**	**-**	**-**

*- assignment can be reversed

Table 4. **NMR data for deprotonation products in DMSO solution.**

compound / position	5-CH_3salDAMN + TMG				5-BrsalDAMN + TMG				salDAMN + TMG				5-NO_2salDAMN +TMG	
	X 65%		Y 35%		X 88%		Y 12%		X 66%		Y 34%			
	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$	^{1}H	$^{13}C/^{15}N$
C-1	-	121.75	-	121.6	-	124.6		124.6	-	122.3	-	122.2	-	122.5
C-2	-	162.2	-	155.45	-	173.5	-		-	166.6	-	157.6	-	179.3
C-3	6.57	118.7	6.62	116.2	6.10	125.9	6.50	120.3	6.52	120.0	6.70	118.8	6.11	123.1
C-4	6.90	133.6	6.84	129.5	6.84	135.6	7.01	131.3	7.0	132.4	7.01	128.6	7.74	128.8
C-5	-	124.3	-	127.3	-	102.2		106.8	6.40	114.5	6.70	116.4	-	130.5
C-6	7.53	128.2	7.02	128.8	7.75	129.7	7.39	129.5	7.64	128.6	7.2	128.5	8.64	126.2
C-7	8.45	151.6	7.74	139.8	8.50	155.2	7.8 br.		8.56	152.0	7.82	139.1	8.58	155.6
OH	-	-	-	-	-	-	-		-		-	-	-	-
N	-	-101.4	-	-88.9		-113.2				-105.1		-89.3		-102.1
C-1’		101.4		93.2		106.6				101.6 br.		92.8		106.0
C-2’		127.3		129.3		123.4				133.3		123.4		124.2
1’-CN		116.1*		116.6*		116.0*				117.2*		117.9*		115.0*
2’-CN		117.5*		117.0*		115.2*				116.9*		116.7*		115.7*
NH_2	-	-	-	-	-	-			-	-	-	-	-	-
CH_3	2.13	20.56	2.16	20.59										

***- assignment can be reversed**
br.- broad signal

Table 5. ^{13}C and ^{15}N NMR data for imines derived from DAMN in the solid state.

	5-CH_3salDAMN	benzDAMN	5-NO_2salDAMN	5-BrsalDAMN	naphDAMN	salDAMN
C-1	134.2 ov.	136.5	139.0 ov.	125.7 ov.	106.8	124.8 ov.
C-2	157.4	127.1 ov.	164.6	157.0	159.4	158.1 157.5
C-3	117.7	127.1 ov.	118.5	119.2 ov.	119.0	122.6
C-4	134.2 ov.	132.1	132.3*	137.3 br.		134.0*
C-5	128.8 127.5	-	139.0 ov.	119.2 ov.		115.9
C-6	134.2 ov.	-	127.8 ov.	134.5 br.		135.0*
C-7	161.5 159.7	156.4 br.	158.9	160.3	153.3	161.7 159.2
C-1’	104.4	106.1 br.	104.7	105.2	105.0	105.0 105.9
C-2’		127.1ov.	127.8 ov.	125.7 ov.		124.8 ov.
1’-**C**N	111.8 br.	113.3 br.	116.1*	114.2*	115.3*	117.9 117.2
2’-**C**N		113.3 br.	112.9*	113.3*	114.4*	112.6 113.0
CH_3	20.9	-	-	-	-	-
NH_2	-298.7 -301.2	-302.7 -304.1	-295.9	-294.5	-302.5	-301.2
C**N**	-122.4* -120.0*	-121.8* -119.5*	-117.7*	-119.6*	-128.2*	-119.6
C**N**	-116.3* -113.1*	-111.8* -115.5*	-111.5*	-115.2*	-116.8*	-114.8
-C=**N**-	-105.2*	-86.1 -88.0	-109.1	-107.9	-106.8*	-108.3

*-assignment can be changed

?-different position numbers in naphthalene rings with respect to benzene ring

In naphtyl derivative assignment of other aromatic and C-2'carbon atoms was impossible,
136.2 (CH), 132.1 (q), 130. (CH), 128.6 (CH), 127.1 (q), 123.3 (CH)

Table 6. **ATR-FTIR spectral data assignments of DAMN and its derivatives.**

compound / type of vibrations	DAMN	benzDAMN	salDAMN	5-CH_3salDAMN	5-BrsalDAMN	5-NO_2salDAMN	naphDAMN
ν N-H (-NH_2)	**3436, 3366, 3344, 3299**	**3408, 3300, 3177, 3161**	**3415, 3373, 3303**	**3415, 3393, 3305**	**3396, 3297**	**3402, 3303**	**3466, 3337**
ν C=N*	**-**	**1607**	**1623**	**1629**	**1630**	**1626**	**1603**
ν C≡N	**2210, 2167**	**2239, 2204**	**2234, 2204**	**2240, 2212**	**2245, 2209**	**2238, 2219**	**2239, 2200**
ν C=C* (aliphatic part)	**1644**	**1607**	**1623**	**1629**	**1630**	**1626**	**1607**
δ N-H (-NH_2)	**1616**	**a**	**a**	**a**	**1615**	**a**	**1615**
ν C=C (aromatic ring)	**-**	**1607, 1579, 1556, 1449**	**1600, 1562, 1487**	**1599, 1566, 1489**	**1599, 1547, 1474**	**1599, 1556, 1478**	**1603, 1556, 1468**

a – probably the bands from δ N-H vibrations are overlaped with the other strong bands present in this region.
*** - overlaping of ν C=N and ν C=C (aliphatic part) vibrations should be considered.**

Table 7. Crystal data and structure refinement for compounds 5-CH_3salDAMN[a], 5-CH_3salDAMN[b] and benzDAMN

	5-CH_3salDAMN[a]	**5-CH_3salDAMN[b]**	**benzDAMN**
Chemical formula	$C_{12}H_{10}N_4O$	$C_{12}H_{10}N_4O$	$C_{11}H_8N_4$
Formula weight	226.23	226.23	196.21
Crystal appearance	Yellow needle	Yellow plate	Brown needle
Crystal size [mm]	0.03 x 0.18 x 0.33	0.23 x 0.25 x 0.53	0.11 x 0.19 x 0.40
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell parameters			
a [Å]	7.1040(4)	6.9836(11)	6.9481(2)
b [Å]	14.7515(7)	24.727(4)	22.7995(5)
c [Å]	11.0890(5)	13.700(2)	13.5132(3)
α [°]	90	90	90
β [°]	101.038(3)	102.593(9)	100.938(2)
γ [°]	90	90	90
V [Å^3]	1140.57(10)	2308.9(6)	2101.78(9)
Z	4	8	8
$D_{calc.}$ [g/cm^3]	1.318	1.302	1.240
F(000)	472	944	816
θ range [°]	5.05 to 68.26	3.76 to 66.58	3.86 to 68.63
Absorption coefficient μ [mm^{-1}]	0.730	0.721	0.642
Absorption correction	numerical, SADABS[3]	numerical, SADABS[3]	multi-scan, SADABS[3]
Max. and min. transmission	0.9790 and 0.7960	0.8530 and 0.7010	0.9330 and 0.7810
Index ranges	$-8 \le h \le 7$ $-17 \le k \le 17$ $-12 \le l \le 13$	$-8 \le h \le 8$ $-29 \le k \le 29$ $-12 \le l \le 16$	$-8 \le h \le 7$ $-27 \le k \le 27$ $-16 \le l \le 16$
No. of measured reflections	32921	29652	41348
No. of independent reflections	2069 (R_{int} = 0.0745)	3873 (R_{int} = 0.0673)	3856 (R_{int} = 0.0573)
Completeness	98.3 %	94.9 %	99.1 %
Refinement method	*Full-matrix least-squares on F^2*		
Final R indices: R_1, wR_2	0.0428, 0.1006	0.0640, 0.1428	0.0423, 0.1045
Goodness-of-fit on F^2	1.062	1.064	0.984
Data/restraints/parameters	2069/0/175	3873/0/357	3856/0/336
R indices (all data):	0.0715, 0.1162	0.1126, 0.1670	0.0601, 0.1172

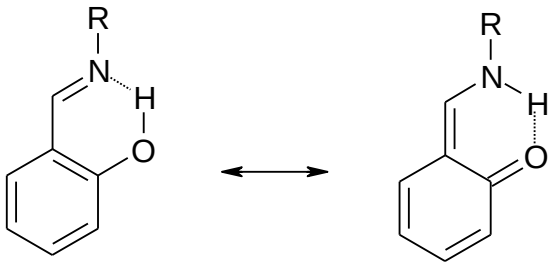
R_1, wR_2			
Excitation coefficient	None	None	0.0021(2)
Δ/σ_{max}	0.002	0.028	0.001
Absolute structure parameter	-	-	0.0(3)
Largest diff peak and hole [eÅ^{-3}]	0.199 and -0.147	0.228 and -0.224	0.194 and -0.193

Table 8. Selected bond lengths (Å) and angles (°) for 5-CH_3salDAMN[a], 5-CH_3salDAMN[b] and benzDAMN.

	5-CH_3salDAMN[a]	**5-CH_3salDAMN[b] _I**	**5-CH_3salDAMN[b] _II**	**benzDAMN _I**	**benzDAMN _II**
O1–C2	1.363(2)	1.356(4)	1.355(4)	-	-
N1–C7	1.286(2)	1.292(4)	1.289(4)	1.2738(17)	1.2763(18)
N1–C8	1.388(2)	1.398(3)	1.400(3)	1.3894(17)	1.3878(17)
N2–C9	1.140(2)	1.138(4)	1.142(4)	1.144(2)	1.142(2)
C8–C10	1.363(2)	1.361(4)	1.365(4)	1.3587(19)	1.3617(19)
N3–C10	1.341(2)	1.337(4)	1.338(4)	1.345(2)	1.348(2)
N4–C11	1.138(2)	1.138(4)	1.136(4)	1.1360(19)	1.136(2)
C1–C7–N1	121.36(17)	123.0(3)	123.1(3)	121.70(14)	121.04(15)
C7–N1–C8	122.95(15)	119.2(3)	119.2(3)	121.06(13)	121.37(13)
N1–C8–C9	120.64(15)	120.3(3)	120.9(3)	122.04(12)	122.67(13)
N1–C8–C10	118.37(16)	120.6(3)	119.9(3)	117.88(12)	117.43(13)
C8–C10–N3	127.71(17)	126.3(3)	125.7(3)	124.09(13)	124.13(13)
C8–C10–C11	116.28(16)	118.6(3)	118.5(3)	119.79(13)	119.37(14)
N3–C10–C11	115.99(16)	115.1(3)	115.7(3)	116.12(13)	116.45(14)
C7–C1–C2–O1	0.9(3)	4.5(5)	-1.5(5)	-	-
C2–C1–C7–N1	2.6(3)	-1.8(5)	-1.2(5)	0.9(2)	2.5(2)
C7–N1–C8–C9	2.2(3)	0.7(5)	-0.4(4)	5.6(2)	-2.9(2)
N1–C8–C10–N3	-176.45(17)	-1.7(5)	-2.9(5)	-1.9(2)	0.8(2)
C9–C8–C10–N3	1.6(3)	179.2(3)	177.0(3)	177.12(15)	-178.83(15)
N1–C8–C10–C11	1.8(3)	175.0(3)	179.0(3)	178.73(13)	178.38(14)
C9–C8–C10–C11	179.84(17)	-4.1(5)	-1.1(5)	-2.2(2)	-1.3(2)

Table 9. Hydrogen bond distances (Å) and angles (°) for compound 5-CH_3salDAMN[a], 5-CH_3salDAMN[b] and benzDAMN

D-H ⋯A	D-H	H⋯A	D⋯A	Angle	Symmetry codes
5-CH_3salDAMN[a]					
O1–H1⋯N1	0.95(2)	1.72(2)	2.597(2)	152(2)	
N3–H3A⋯N2	0.86	2.24	3.094(2)	169.7	[-x + 2, -y, -z + 3]
N3–H3B⋯O1	0.86	2.28	3.126(2)	169.7	[x + ½, -y - ½, z + ½]
C3–H3⋯N4	0.96(2)	2.64(2)	3.532(3)	154.7(18)	[x - ½, -y - ½, z - ½]
5-CH_3salDAMN[b]					
O1–H1⋯N1	1.00(5)	1.82(5)	2.692(3)	144(4)	
O2–H2⋯N5	1.00(5)	1.85(5)	2.719(3)	143(4)	
N3–H3A⋯N2	0.86	2.15	2.910(4)	146.8	[x – 1, y, z]
N3–H3B⋯N8	0.86	2.27	3.119(4)	168.5	[-x + ½, y - ½, -z + ½]
N7–H7A⋯N6	0.89(4)	2.21(4)	2.998(4)	147(3)	[x +1, y, z]
N7–H7B⋯N4	0.87(4)	2.20(4)	3.063(4)	168(3)	[-x + $^3/_2$, y + ½, -z + ½]
benzDAMN					
N3–H3A⋯N2	0.93(2)	2.25(2)	3.099(2)	151.9(16)	[x + 1, y, z]
N7–H7A⋯N6	0.95(2)	2.34(2)	3.226(2)	156.1(15)	[x – 1, y, z]
N3–H3B⋯N8	0.89(2)	2.22(2)	3.095(2)	168.8(18)	[-x + 1, y - ½, -z + ½]
N7–H7B⋯N4	0.89(2)	2.20(2)	3.065(2)	166(2)	[-x, y + ½, -z + ½]



enol-imine form **keto-amine form**

Figure 1. **Tautomeric forms of Schiff bases.**

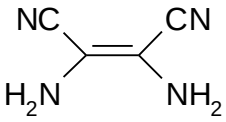
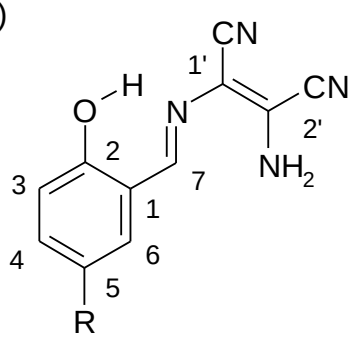
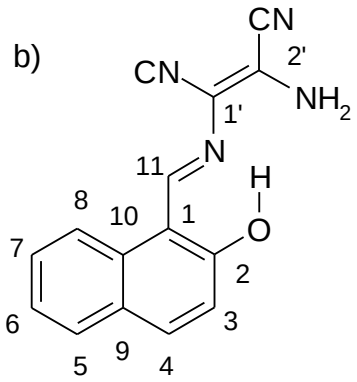


Figure 2. **Structure of diaminomaleonitrile (DAMN).**

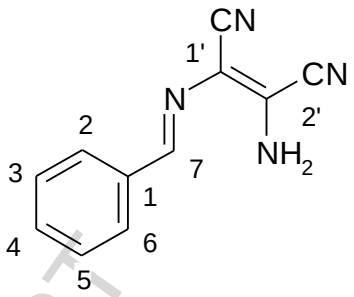
a)



b)



c)



R = H (**salDAMN**)
R = CH_3 (**5-CH_3salDAMN**)
R = Br (**5-BrsalDAMN**)
R = NO_2 (**5-NO_2salDAMN**)

naphDAMN

benzDAMN

Figure 3. The Schiff bases under investigation, derived from diaminomaleonitrile (DAMN) and chosen aldehydes: **a)** salicylaldehydes: salicylaldehyde (sal), 5-methylsalicylaldehyde (5-CH_3sal), 5-bromosalicylaldehyde (5-Brsal), 5-nitrosalicylaldehyde (5-NO_2sal); **b)** 2-hydroxynaphthaldehyde (naph), and **c)** benzaldehyde (benz).

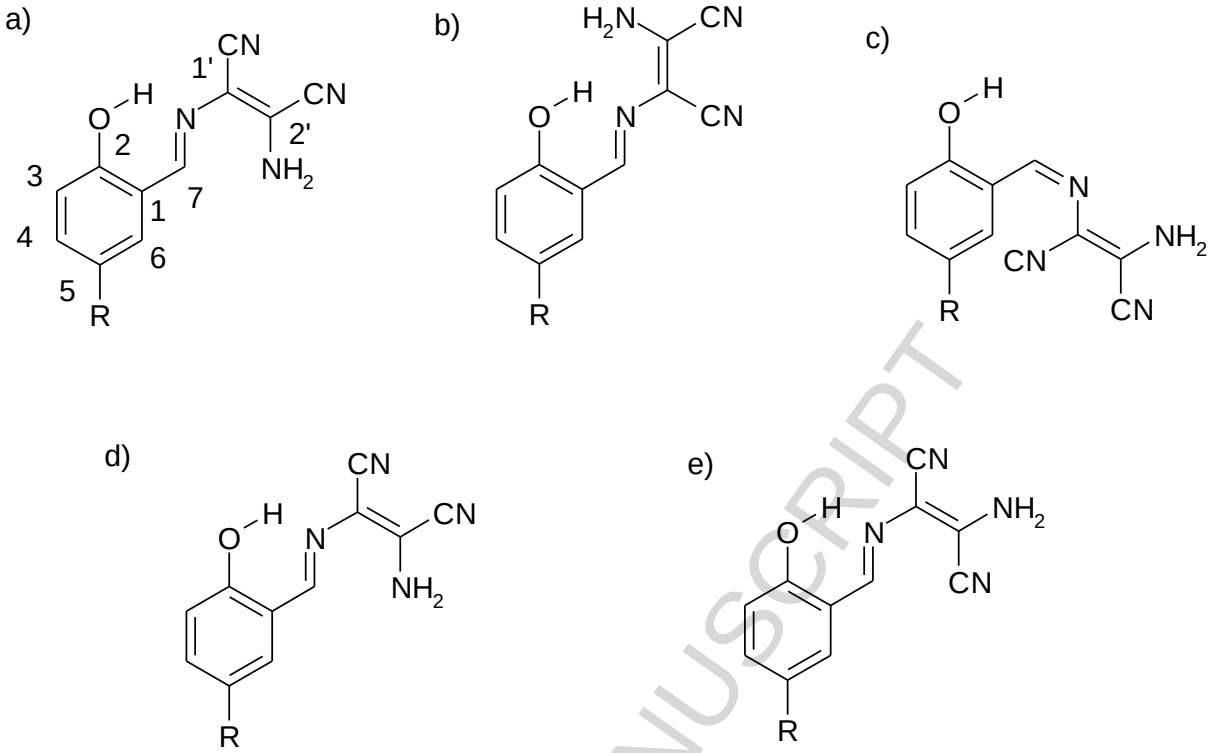
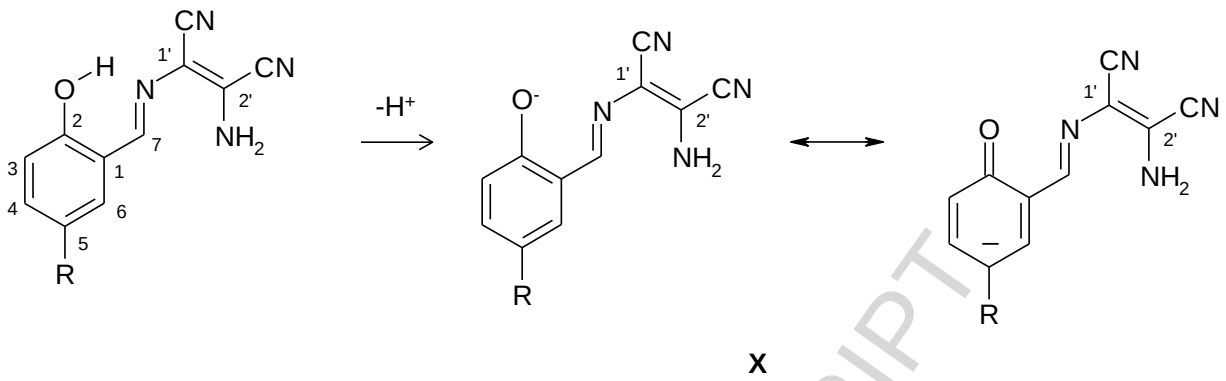


Figure 4. **Some possible rotamers of salDAMN (R = H) and 5-BrsalDAMN (R = Br) (upper trace: a, b and c forms) and cis-trans isomers (lower trace: d and e) expected in equilibrium mixture.**



X

Figure 5. Deprotonation of OH group.

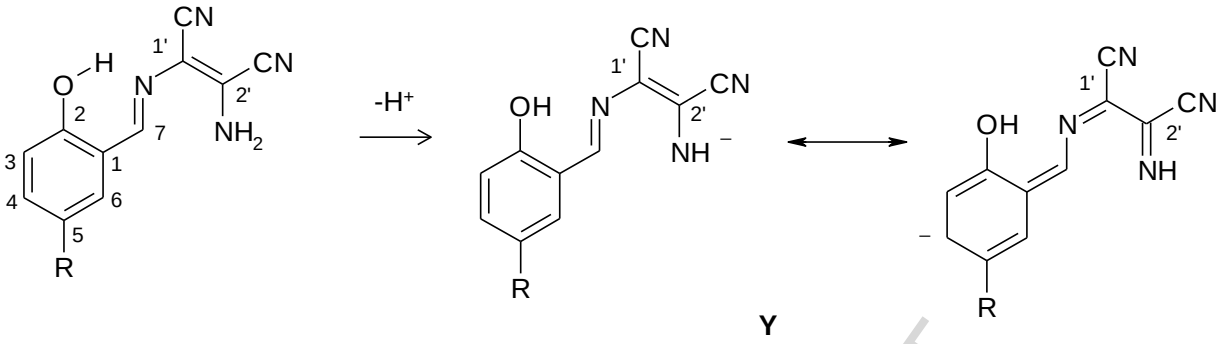
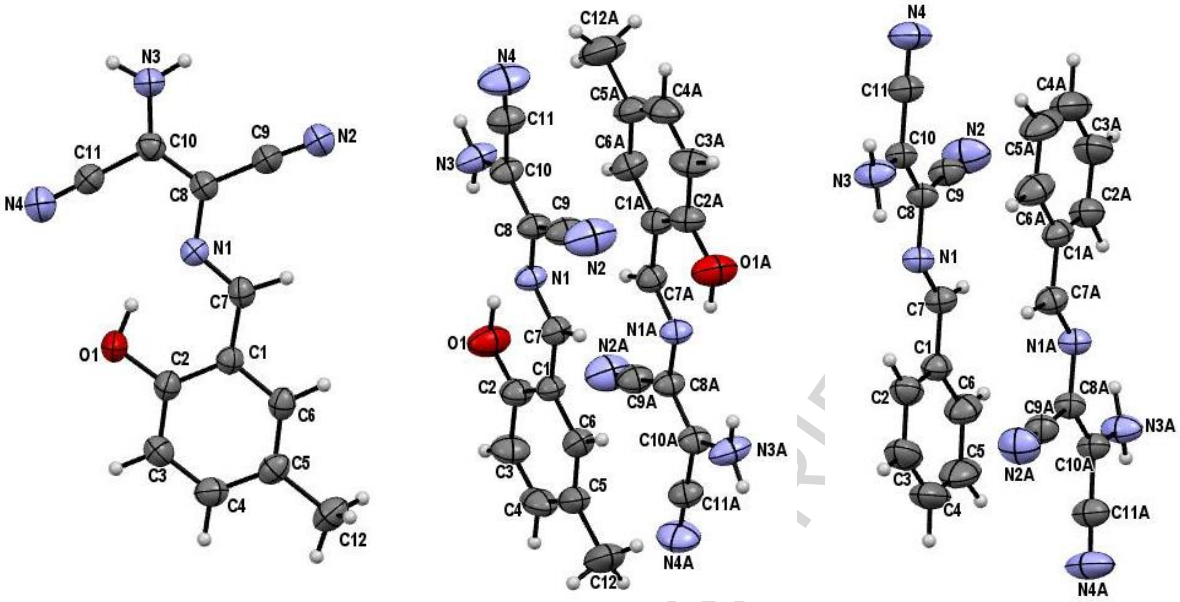
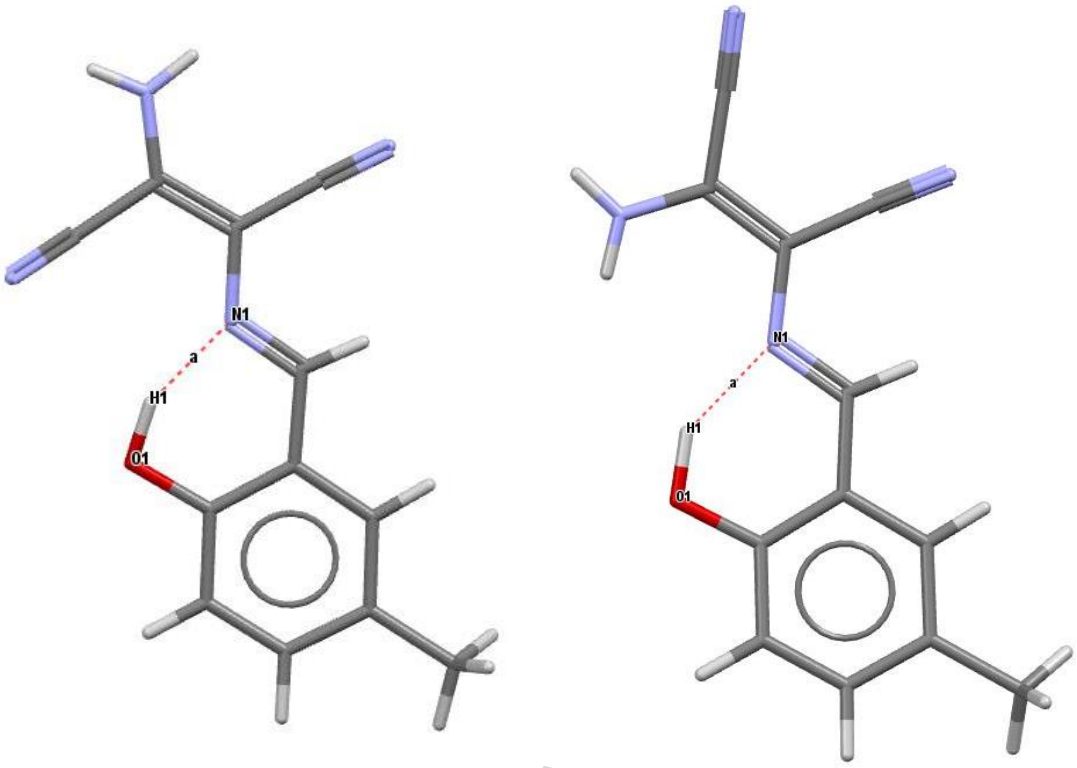


Figure 6. **Deprotonation of NH_2 group in diaminomaleonitrile moiety.**



5-CH_3salDAMN[a] **5-CH_3salDAMN[b]** **benzDAMN**

Figure 7. A view of the molecules of 5-CH_3salDAMN[a], 5-CH_3salDAMN[b], and benzDAMN in conformation observed in their crystals with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.



5-CH_3salDAMN[a] **5-CH_3salDAMN[b]**

Figure 8. An intramolecular hydrogen bond in two isomers of 5-CH_3salDAMN.

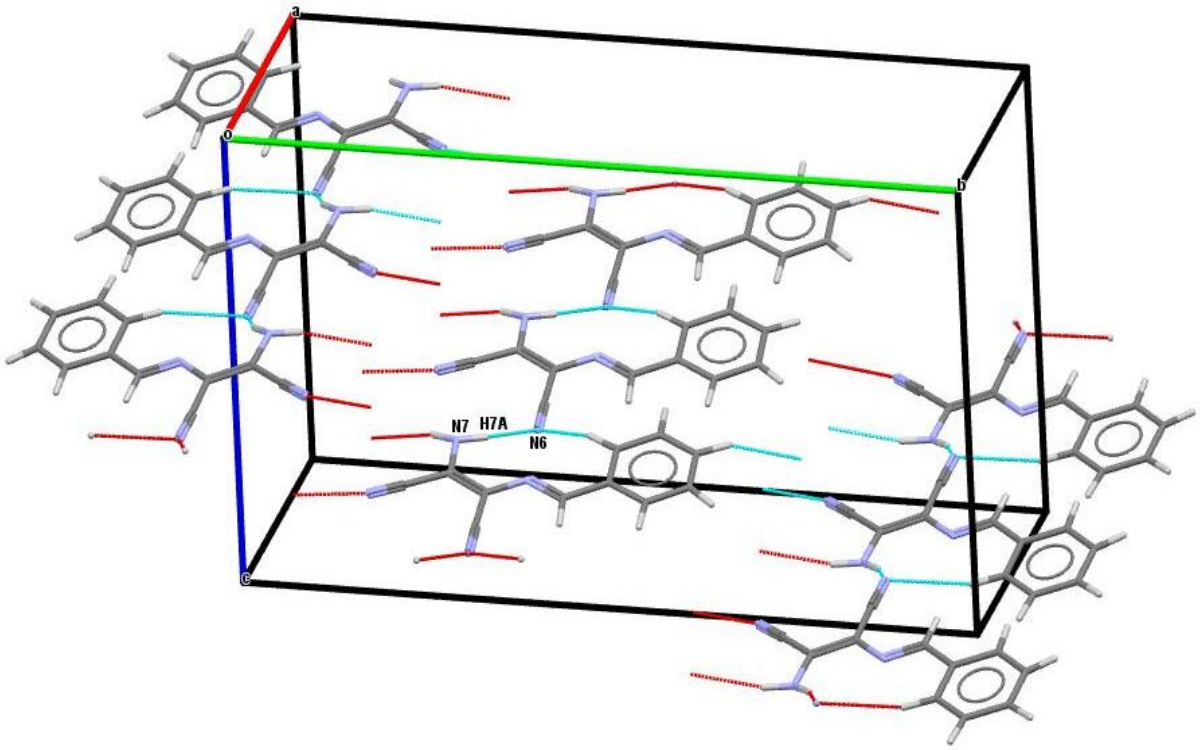


Figure 9. Part of the crystal structure of benzDAMN, showing the formation of ribbons in one direction through hydrogen bonds N—H···N. Hydrogen bonds are indicated by red and blue dashed lines.

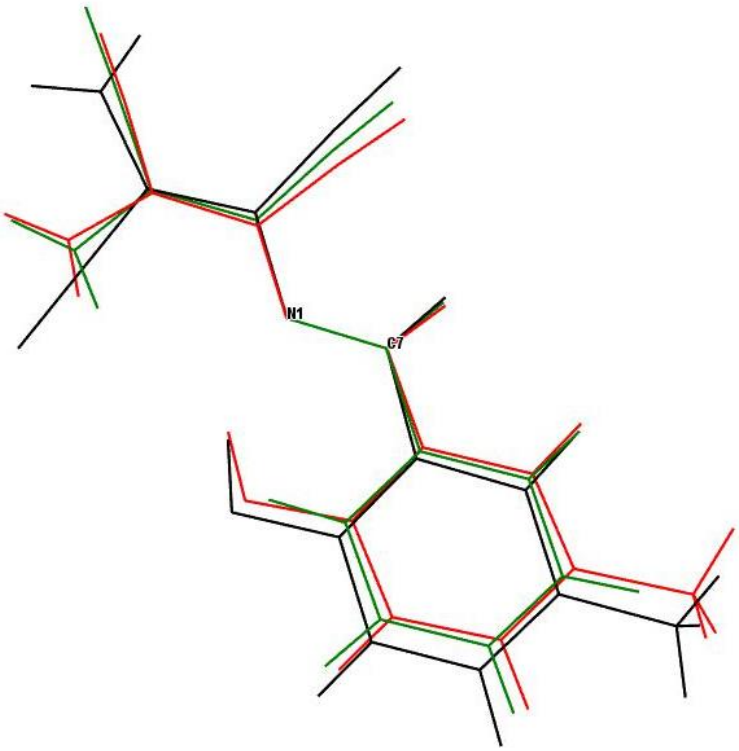
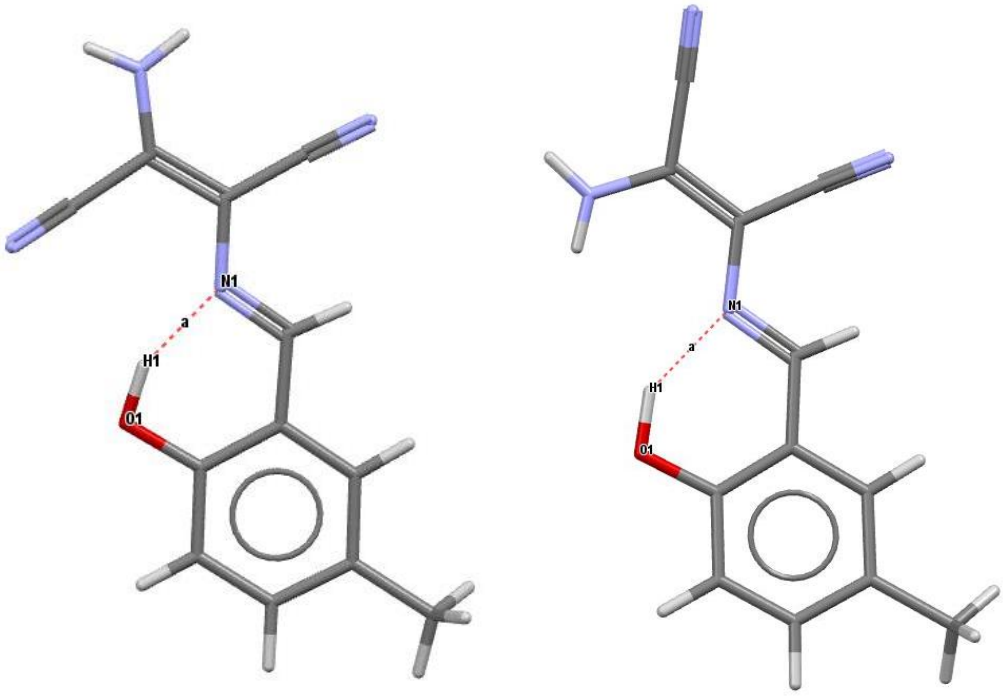
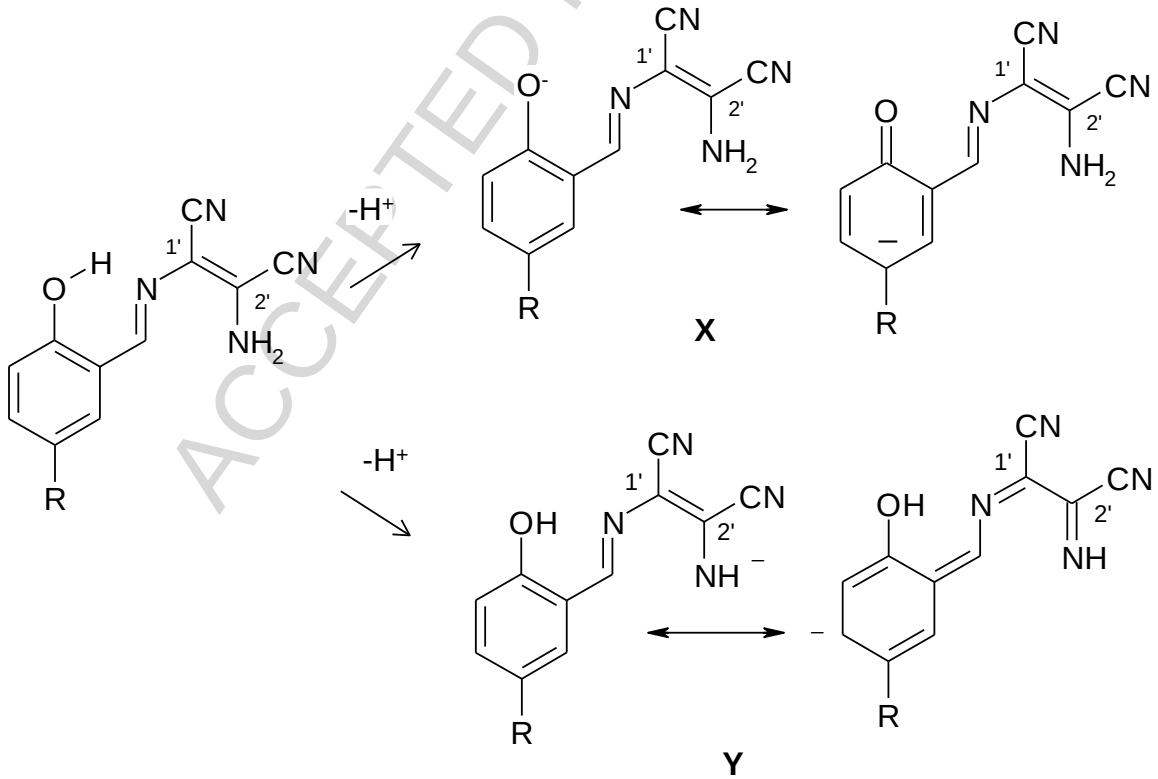


Figure 10. Overlay of X-ray molecules of compounds 5-CH_3salDAMN[a], 5-CH_3salDAMN[b], and benzDAMN by least-squares fitting of the atoms C7=N1 (RMS = 0.00596 Å).

Graphical abstract



5-CH$_3$salDAMN^a **5-CH$_3$salDAMN^b**



Highlights

1. Six imines and their deprotonated products were examined using spectroscopic methods.

2. The lack of affinity of type of aldehyde on proton transfer in studied imines was found.

3. Some of imines occur as two-component equilibrium mixtures.

4. Deprotonation reaction of imine derivatives of DAMN takes place in two different ways.