

SCHIFF BASES DERIVED FROM HYDROXYARYL ALDEHYDES: MOLECULAR AND CRYSTAL STRUCTURE, TAUTOMERISM, QUINOID EFFECT, COORDINATION COMPOUNDS

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During the last 50 years a vast number of structural studies on Schiff bases derived from hydroxyaryl aldehydes and their coordination compounds have been undertaken. In this review we present a systematic and brief overview of the most important discoveries and achievements accomplished in this field. The occurrence of Schiff bases (and their complexes) derived from nine most commonly used hydroxyaryl aldehydes in the Cambridge Structural Database (CSD) has been investigated. Keto-enol tautomerism and intramolecular hydrogen bonding in salicylaldimines and naphthaldimines is discussed, with a comment of the most common errors in determining the correct tautomeric form. Also, the interrelationship of crystal packing and the substituents on the Schiff base is studied. Finally, we give a short overview of conformational differences between free Schiff bases and Schiff bases bonded to metal ions as well as some structural characteristics of Schiff base metal complexes.

Key words: Schiff bases; Schiff base complexes; tautomerism; quinoid effect; supramolecular interaction

ШИФОВИ БАЗИ ДОБИЕНИ ОД ХИДРОКСИАРИЛ АЛДЕХИДИ: МОЛЕКУЛСКА И КРИСТАЛНА СТРУКТУРА, ТАВТОМЕРИЈА, ХИНОНСКИ ЕФЕКТ, КООРДИНАЦИОНИ СОЕДИНЕНИЈА

Во последните 50 години се направени голем број структурни истражувања на Шифовите бази добиени од хидроксиарилалдехиди и нивни координациони соединенија. Во овој прегледен труд е презентирано систематско и кратко согледување на најзначајните откритија и достигнувања направени на ова поле. Прочувано е добивањето на Шифовите бази (и нивните комплекси) од девет најчесто користени хидроксиарилалдехиди според структурната база на податоци во Кембриџ. Кето-енолната тавтомерија и интрамолекуларното водородно сврзување кај салицилалдимините и нафталдимините е дискутирано со давање посебен коментар на најчестите грешки при одредувањето на правилната тавтомерна форма. Освен тоа, прочувана е поврзаноста на кристалното пакување со супституентите на Шифовата база. Презентиран е и краток осврт на конформациските разлики помеѓу слободните Шифови бази и Шифовите бази сврзани со метални јони, како и на некои структурни карактеристики на металните комплекси со Шифовите бази.

Клучни зборови: Шифови бази; комплекси со Шифови бази; тавтомерија; хинонски ефект; супрамолекуларна интеракција

INTRODUCTION

N-substituted imines, also known as Schiff bases represent one of the most widely used families of organic compounds and their chemistry is essential material in many organic chemistry textbooks [1–3]. In general, they are easily prepared by the condensation reaction of primary amines with carbonyl compounds. The first reports of this kind of reaction have been published by Hugo Schiff in the 1860s [4–6]. Thereafter Schiff bases have been intensively used as synthetic intermediates and as ligands for coordinating transition and inner transition metal ions, and recently also for coordinating anions [7–9]. During the past two decades they have become some of the most typical ligands in the field of coordination chemistry [10–16]. Particularly, a large number of transition metal complexes of Schiff base ligands derived from the condensation of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with various primary amines became the topic of contemporary research [10, 17–21]. These Schiff base ligands may act as bidentate *N,O*-, tridentate *N,O,O*-, *N,O,N*-, *N,O,S*-, tetradentate *N,N,O,O*-, hexadentate *N,N,O,O,S,S*-donor ligands [22–28], *etc.*, which can be designed to yield mononuclear or binuclear complexes or one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) metal-organic frameworks [29–36].

The synthesis and structural research of Schiff bases derived from the above mentioned aldehydes and amines bearing various alkyl and aryl *N*-substituents, as well as their metal complexes have been of interest in our research group for over two decades [37–48].

Schiff base ligands may contain a variety of substituents with different electron-donating or electron-withdrawing groups, and therefore may have interesting chemical properties. They have attracted particular interest due to their biological activities [49–50], *e.g.* acting as radiopharmaceuticals for cancer targeting [51, 52]. They have also been used as model systems for biological macromolecules [53, 54]. Besides the biological activity, solid-state thermochromism and photochromism are another characteristic of these compounds leading to their application in various areas of materials science such as the control and measurement of radiation intensity, display systems and optical memory devices [55–58]. Schiff bases derived from *o*-hydroxyaromatic aldehydes and ketones are excellent models for the study of keto-enol tautomerism both in solution and in the solid state [59–66]. During the past decade such Schiff bases started drawing attention due to their physical properties in the crystalline state [67–78]. These properties are greatly influenced by the topochemistry of the Schiff base molecules which in turn is highly affected by the crystal structure. Therefore the study of crystal packing and the intermolecular interactions in the crystal structures of various Schiff bases can lead to valuable data for the design and synthesis of new materials (Figure 1) [79–85].

SCHIFF BASES IN THE CAMBRIDGE STRUCTURAL DATABASE (CSD)

Searches to determine the number of CSD [10] entries for Schiff bases derived from hydroxyaryl aldehydes as well as for their complexes

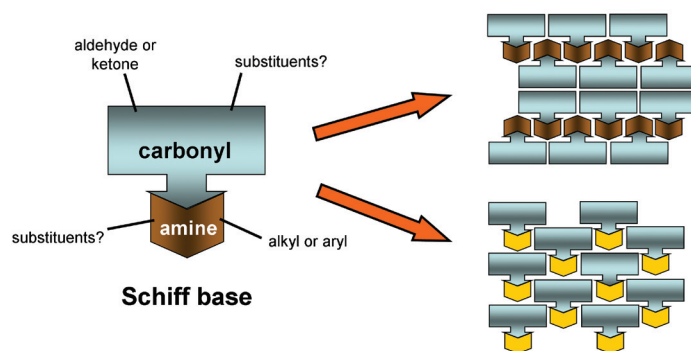
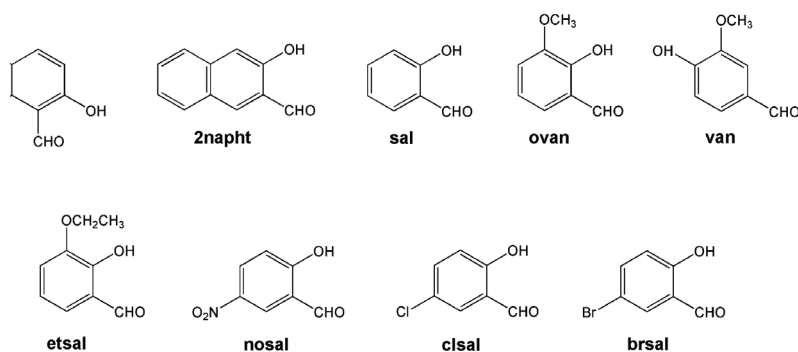


Fig. 1. Varying the type of amine (aliphatic or aromatic) and carbonyl (aldehyde or ketone) subunits, as well as substituents on them, a great number of Schiff bases with different supramolecular bonding capabilities can be prepared, which in turn enables great diversity of crystal packings



Scheme 1. Molecular diagrams of 2-hydroxy-1-naphthaldehyde (naphth), 3-hydroxy-2-naphthaldehyde (2naphth), salicylaldehyde (sal), *o*-vanillin (ovan), vanillin (van), 3-ethoxysalicylaldehyde (etsal), 5-nitrosalicylaldehyde (nosal), 5-chlorosalicylaldehyde (clsal), 5-bromosalicylaldehyde (brsal)

were performed using ConQuest [86] version 5.31 with three updates (November 2009, February and May 2010). The data analysis was performed using the program Vista version 2.1 [87]. For free ligand the search criteria used were drawings of

Table 1

Number of unique structures in CSD for the selection of Schiff bases derived from nine different hydroxy aryl aldehydes

Aldehyde	Number of free Schiff bases
2-hydroxy-1-naphthaldehyde	68
3-hydroxy-2-naphthaldehyde	4
salicylaldehyde	199
<i>o</i> -vanillin	78
vanillin	10
3-ethoxysalicylaldehyde	12
5-nitrosalicylaldehyde	23
5-chlorosalicylaldehyde	37
5-bromosalicylaldehyde	42

the respective motifs of Schiff bases derived from nine different aldehydes: 2-hydroxy-1-naphthaldehyde (**naphth**), 3-hydroxy-2-naphthaldehyde (**2naphth**), salicylaldehyde (**sal**), *o*-vanillin (**ovan**), vanillin (**van**), 3-ethoxysalicylaldehyde (**etsal**), 5-nitrosalicylaldehyde (**nosal**), 5-chlorosalicylaldehyde (**clsal**), 5-bromosalicylaldehyde (**brsal**) (Scheme 1). Also, three filtering criteria were imposed upon the search: entries must have their 3-D coordinates determined, exhibit no errors and should have no transition metals present. Repeat determinations of the same structure, polymorphs and salts were removed from the count manually.

For Schiff base complexes the search criteria used were based on molecular diagrams involving any transition metal bonded to deprotonated hydroxyl oxygen and imine nitrogen of the respective deprotonated Schiff base. Also, searches to determine the number of entries for a particular metal (Cu, Ni, Co, V, Fe, Zn, Mn) were performed. The analyses of entries for Schiff bases and their complexes are summarized in Table 1 and Table 2, respectively.

Table 2

Number of CSD hits for hydroxyl aryl Schiff base complexes with transition metals (there are no entries corresponding to complexes of Schiff bases derived from vanillin and 3-hydroxy-2-naphthaldehyde)

Aldehyde	Number of complexes	Cu	Ni	Co	V	Fe	Zn	Mn
2-hydroxy-1-naphthaldehyde	237	83	42	12	24	12	18	17
salicylaldehyde	2616	674	342	215	168	275	162	345
<i>o</i> -vanillin	477	150	77	26	33	46	57	58
3-ethoxysalicylaldehyde	98	38	19	1	11	14	7	7
5-nitrosalicylaldehyde	114	33	15	8	3	11	17	16
5-chlorosalicylaldehyde	130	34	15	9	3	10	10	32
5-bromosalicylaldehyde	198	66	34	10	4	10	34	42

The search of the CSD revealed that during the last 50 years the Schiff bases of the salicylaldehyde type, as well as their transition and inner transition metal complexes, have been studied more intensely than any other Schiff base derivative (Figure 2). It is remarkable that Schiff bases derived from salicylaldehyde make up 42 % of the entire sample of studied Schiff bases and their complexes make up 68 % of the entire sample of studied Schiff base complexes. As many as 199 entries for salicylaldehyde-based Schiff bases were found in the CSD [10]. Of these, 49 have been derived by condensation with aliphatic amines and 150 have been derived from aromatic amines. There are substantially less structural data on the Schiff bases derived from 2-hydroxy-1-naphthaldehyde with only 68 entries found for compounds of this type. Of these, 17 have been derived by

condensation with aliphatic amines and 51 have been derived by using aromatic amines as condensation partners.

The distribution of the particular aldehyde type across the nine searched groups of Schiff bases (and complexes) in the CSD is shown graphically in Figure 3, as a percentage of the total number of entries obtained in this overview.

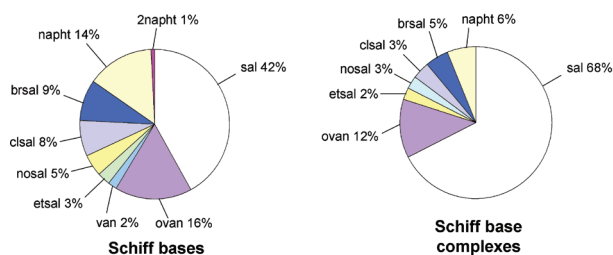


Fig. 3. The occurrence of Schiff bases derived from different aldehydes and their complexes in the CSD

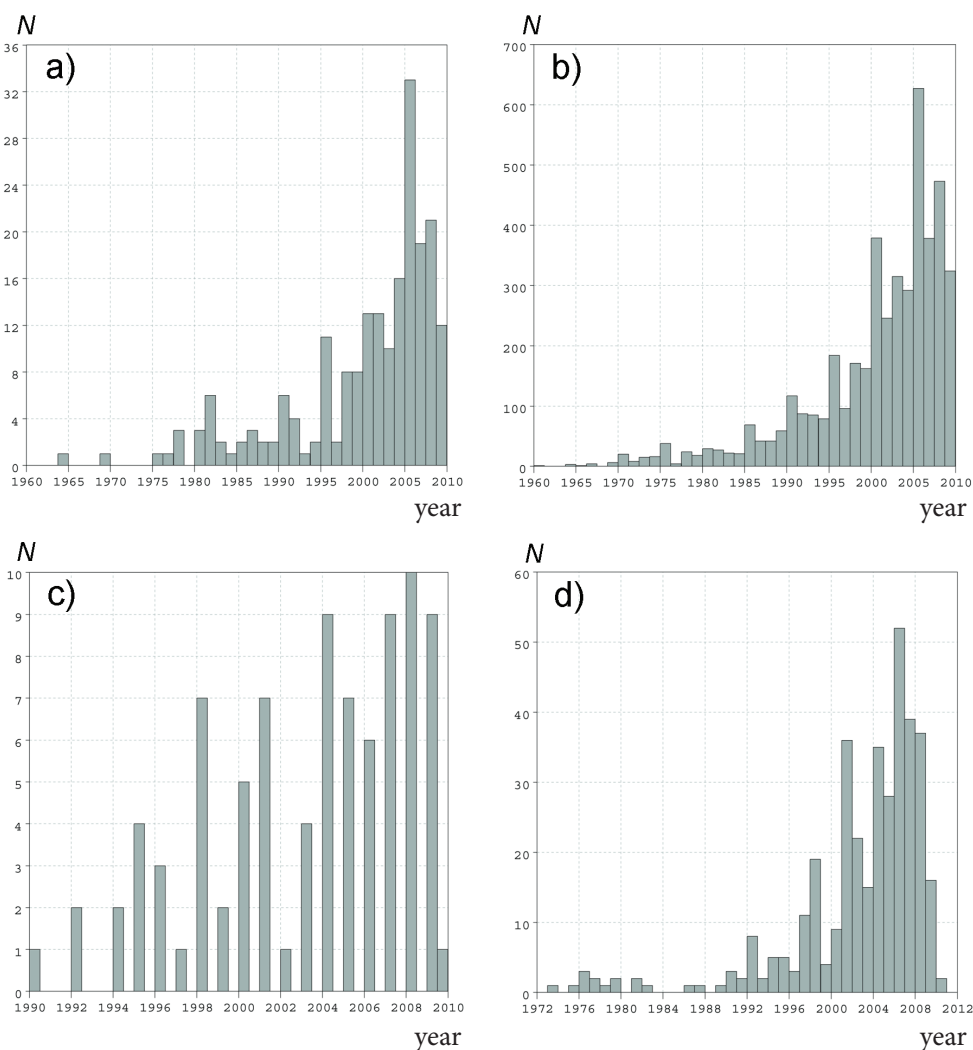


Fig. 2. Number of CSD entries per year for: a) Schiff bases derived from salicylaldehyde, b) coordination compounds with salicylaldehyde Schiff bases, c) Schiff bases derived 2-hydroxy-1-naphthaldehyde and d) coordination compounds with naphthaldehyde Schiff bases

MOLECULAR STRUCTURE,
INTRAMOLECULAR HYDROGEN BONDING,
TAUTOMERISM AND QUINOID EFFECT

Aldimine compounds derived from the aromatic aldehydes having a hydroxyl group in the *ortho* position to the aldehyde group are of interest mainly due to the existence of either O–H···N or O···H–N type of intramolecular hydrogen bond and the related tautomerism between such enol-imine and keto-amino forms. The presence of a particular tautomer in the crystal depends mostly on the parent *o*-hydroxyaryl aldehyde and the type of the *N*-substituent (*i.e.* aryl or alkyl). The electron withdrawing or donating ability of the *N*-substituents, their position and stereo chemistry, as well as hydrogen bond donor-acceptor properties, can stabilize one or another tautomer in the crystal. There does not seem to be any common relationship between molecular conformation and the sort of tautomer present in the crystalline state. During previous decades it was generally believed that the keto-amino naphthaldimines and salicylaldimines with the *N*-aryl substituent are planar and the enol-imino tautomers are non-planar. However, this is not supported by currently available structural data which indicates the existence of non-planar keto-amino salicylaldimines as well as perfectly planar enol-imino naphthaldimines with *N*-aryl substituents (Figure 4) [10, 88–91].

The existence of the enol-imino tautomer has been established in most crystal structures of *N*-substituted salicylaldimines listed in the CSD.

This is clearly represented by the distribution of C_{ar}–O bond lengths (Figure 5a), which makes it evident that 180 out of 199 entries (90 %) belong to the enol-imino and only 19 to the keto-amino tautomer. Unlike salicylaldimines, in naphthaldimines the keto-amino tautomer [46] appears somewhat prevalent over the enol-imino tautomer [31] (Figure 5b). The stabilization of the keto-amino tautomer in naphthaldimines is usually connected with the quinoid effect [92] since the structure of this tautomer is similar to that of *o*-naphthoquinone (Scheme 2). The presence of a fused aromatic ring stabilizes the quinoid ring and renders the geometry of the naphthalene moiety virtually independent on the position of the hydrogen atom along the O···H···N bond. Thus, the process of proton transfer from hydroxyl group to the imino nitrogen atom does not alter the approximate *D*_{2h} symmetry of the naphthalene moiety [45, 59].

Because of the ability of naphthaldimines to exist in both tautomeric forms, particular care must be taken when determining the molecular structures of such compounds in the crystalline state. It has been noted [31, 45, 80, 93] that, together with locating the hydrogen atom from an electron density difference map, the authors must also take molecular geometry (*i.e.* bond lengths, Figure 6) into account. Unfortunately, very often this does not seem to be the case. In the literature one can notice two main types of reported structures, in which misinterpretation of structural data is likely. The first group (for example: [94, 95]), Figure 7a), consists of reports where the hydrogen atom is simply generated on the oxygen atom

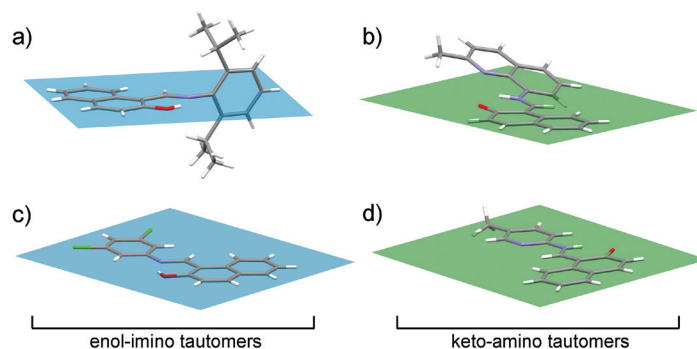


Fig. 4. Examples of planar and non-planar naphthaldimine Schiff bases with the *N*-aryl substituent: a) *N*-(2,6-diisopropylphenyl)-2-hydroxy-1-naphthalideneamine [88], b) *N*-(2-methylquinon-8-yl)-1-aminomethylene-1*H*-naphthalen-2-one [89] c) *N*-(3,5-dichlorophenyl)-2-hydroxy-1-naphthalideneamine [90] d) *N*-(5-pyridin-2-yl)-1-aminomethylene-1*H*-naphthalen-2-one [91]

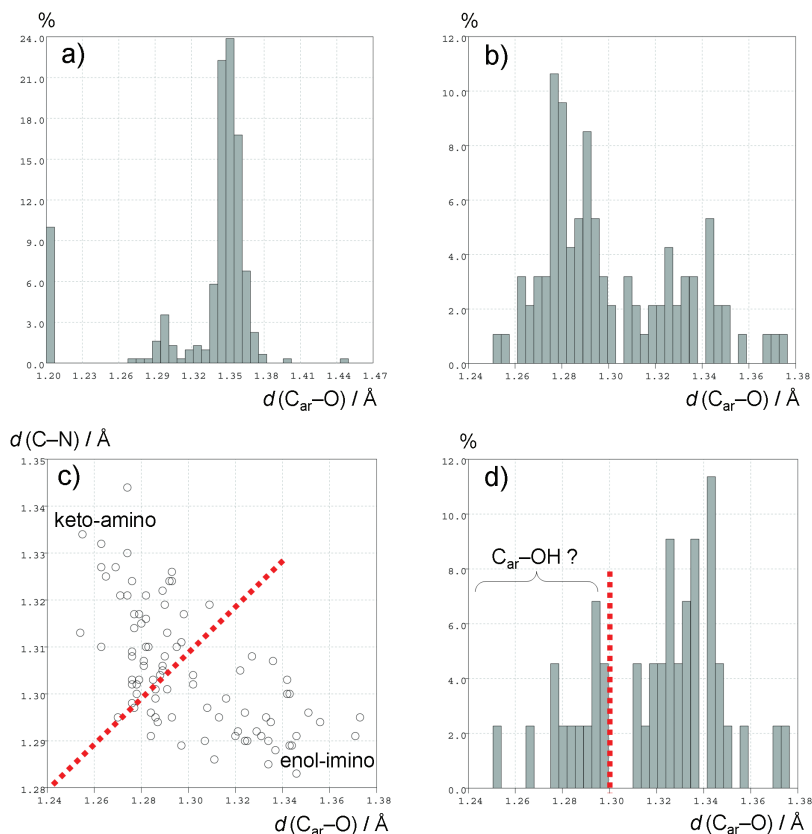
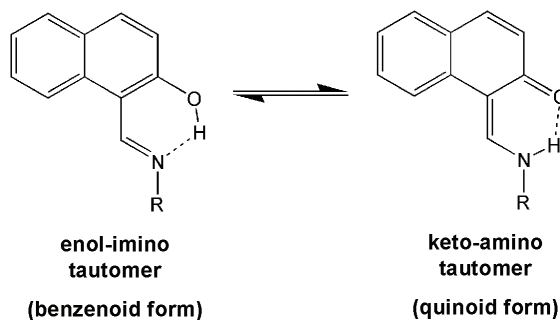


Fig. 5. a) The distribution of $C_{ar}-O$ bond lengths of Schiff bases derived from salicylaldehyde, b) the distribution of $C_{ar}-O$ bond lengths of Schiff bases derived from 2-hydroxy-1-naphthaldehyde, c) scattergram of $C-N$ and $C_{ar}-O$ bond lengths of Schiff bases derived from 2-hydroxy-1-naphthaldehyde, and d) the distribution of $C_{ar}-O$ bond lengths of Schiff bases derived from 2-hydroxy-1-naphthaldehyde deposited in the CSD as enol-imino tautomers (bond lengths shown left from dotted line clearly belong to $C=O$ double bonds indicating that they belong to keto-amino rather than enol-imino tautomers)

(probably because a hydroxyaldehyde was a starting compound) instead of being located from the electron difference map. This can, if the molecule is actually a keto-amine tautomer, lead to a structural model with a misplaced hydrogen atom and thus to a misinterpretation of the structure as an enol-imino tautomer. In the second group (for example: [91, 96, 97]), Figure 7b), the hydro-

gen atom was located from the difference map on the nitrogen atom, but the bond lengths were not taken into account when assigning the bond type (single or double) and thus in some cases of keto-amine tautomers instead of the quinoid form the benzenoid form was used. Because of this, the nitrogen atom seems to be positively and the oxygen atom negatively charged, and the struc-



Scheme 2. Keto-amino tautomerisation in naphthaldimines

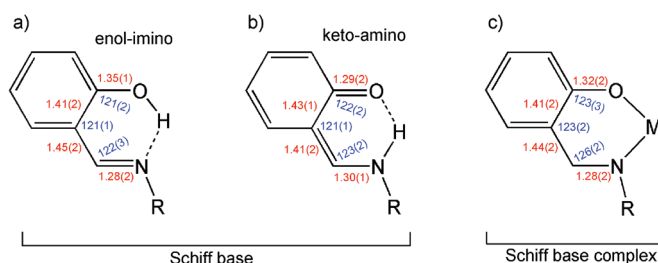


Fig. 6. Characteristic bond lengths (red) and angles (blue) for free Schiff bases derived from *o*-hydroxyaryl aldehydes and their complexes represented as average values for corresponding entries in the CSD: a) for enol-imino tautomer, b) for keto-amino tautomer, c) for a Schiff base coordinated to a metal ion.

All bond lengths are given in Å and angles in °

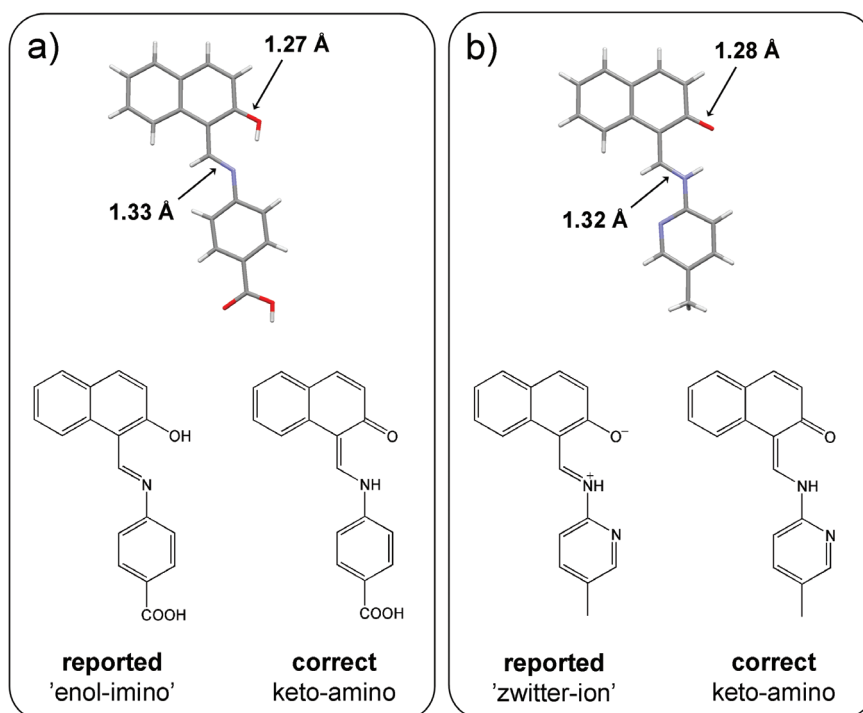


Fig. 7. Examples of two most common types of errors ensuing from the failure to detect the quinoid effect in naphthaldimines: a) 'enol-imino' [94] and b) 'zwitter-ion' [91]. In both cases the C–O bond lengths clearly indicate that C=O is in fact a double bond, while the C–N bond lengths show that C–N bonds are single

tures are then reported as zwitter-ions instead of as keto-amine tautomers with no charge separation, which is a much more likely case.

The transfer of proton from hydroxyl oxygen atom of the parent aldehyde to the imino nitrogen atom in crystal state causes remarkable changes in the distribution of π -electrons and such changes are closely connected with physical properties in the crystalline Schiff bases, namely thermochromism and photochromism [56–58, 92, 98]. On the basis of structural studies of salicylaldehydes, which are a well-known class of predominantly thermochromic compounds, it was established that these two effects are conformation-dependent. Non-planar molecules can exhibit photochromism, while planar molecules of this type Schiff bases exhibit thermochromism [12, 99].

SUPRAMOLECULAR INTERACTIONS AND CRYSTAL PACKING

Crystal packing in Schiff bases is determined by interactions between molecules which in turn are determined by functional groups available for forming interactions with neighbouring molecules (Figure 8). Although all the Schiff

bases with aromatic *N*-substituent discussed in this review have the ability of forming intramolecular hydrogen bond, the central keto-amino moiety can interact with neighbouring molecules only if one of the subunits is not sterically demanding (as is the case in some Schiff bases with aliphatic *N*-substituent) [59, 94, 100].

Unless additional hydrogen bond donors and acceptors are present on the subunits themselves, the packing of the Schiff base will often be governed by weak interactions (dispersion forces, C–H \cdots π hydrogen bonding, $\pi\cdots\pi$ stacking *etc.* [101–103]) alone. The presence of strong hydrogen bond donors and acceptors on the molecular periphery leads almost without exception to cross-linking of molecules *via* strong hydrogen bonds into dimers, oligomers, chains and other supramolecular assemblies. On the other hand if only additional hydrogen acceptors (usually O and N atoms), then C–H \cdots O and C–H \cdots N weak hydrogen bonds are usually the most important interactions between molecules.

N-(propyl)-1-aminomethylene-1*H*-naphthalen-2-one [59] (Figure 9), is an example of a Schiff base where the substituent on the imino nitrogen atom is the sterically non-demanding propyl group. The only noteworthy interaction

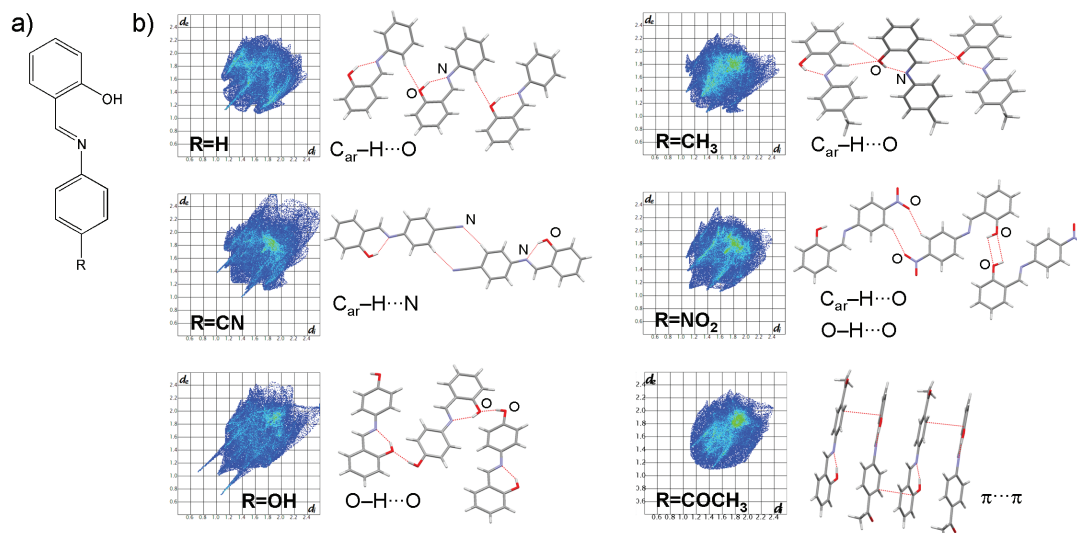


Fig. 8. a) Molecular diagram of a Schiff base derived from salicylaldehyde, b) two-dimensional fingerprint plots and fragments of packing for six Schiff bases with different substituent on *N*-substituted benzene ring: *N*-phenylsalicylideneamine [104], *N*-(4-cyanophenyl)salicylideneamine [105], *N*-(4-hydroxyphenyl)salicylideneamine [106], *N*-(4-methylphenyl)salicylideneamine [107], *N*-(4-nitroxyphenyl)salicylideneamine [108], *N*-(4-acetylphenyl)salicylideneamine [109]

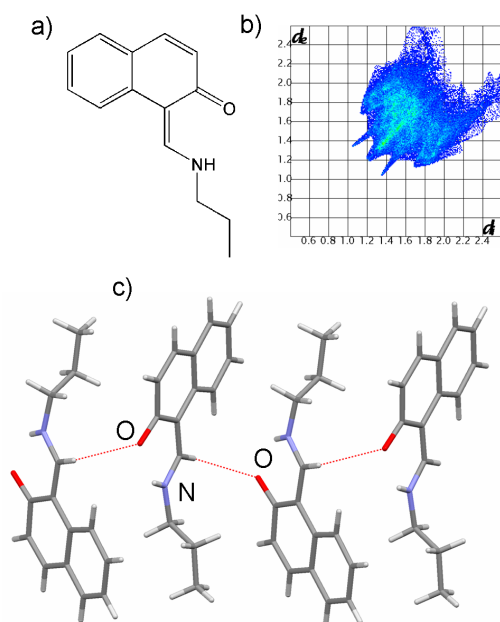


Fig. 9. a) Molecular diagram, b) two-dimensional fingerprint plot, and c) fragment of the chain in the crystal of *N*-(propyl)-1-aminomethylene-1*H*-naphthalen-2-one

between molecules in the crystal structure is a weak C–H...O interaction of 3.23 Å between the imino methine and the oxygen atom of the central keto-amino group. The described interaction can be observed by close analysis of the two-dimensional fingerprint plot derived from the Hirshfeld surface [110] of the molecule. Similarly, in the crystal structure of *N,N'*-hexylene-bis(1-aminomethylene-1*H*-naphthalen-2-one) [99], a bis Schiff base derived from naphthaldehyde and an aliphatic diamine, the keto oxygen atom is the hydrogen acceptor in a C_{ar}–H...O interaction of 3.46 Å leading to the formation of chains (Figure 10).

In the crystal structure of *N,N'*-butylene-bis(1-aminomethylene-1*H*-naphthalen-2-one) [100] the central keto-imino groups of neighbouring molecules are sufficiently close to one another that an intermolecular N–H...O hy-

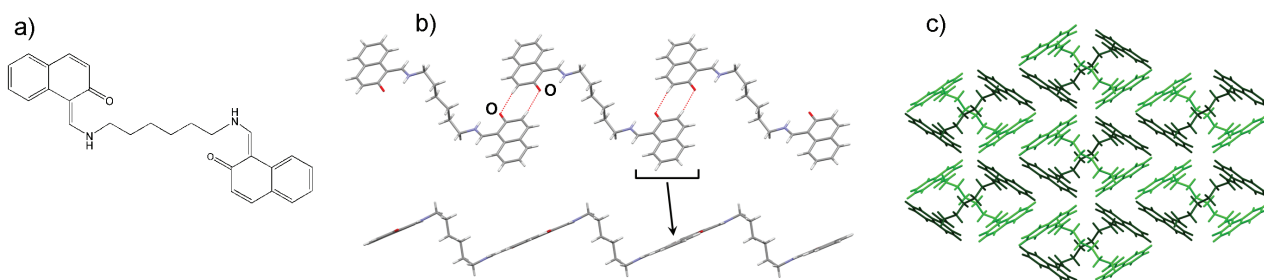


Fig. 10. a) Molecular diagram, b) fragment of the chain in the crystal, and c) view of the packing of molecules for *N,N'*-hexylene-bis(1-aminomethylene-1*H*-naphthalen-2-one) [100]

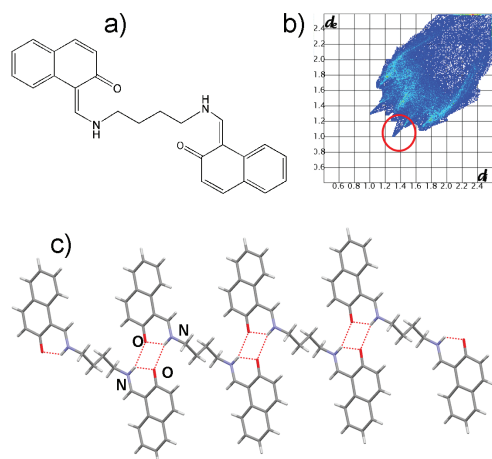


Fig. 11. a) Molecular diagram, b) two-dimensional fingerprint plot (marked corresponding region for N-H...O hydrogen bond), and c) a fragment of the hydrogen-bonded chain in the crystal of *N,N'*-butylene-bis(1-aminomethylene-1*H*-naphthalen-2-one) [100]

drogen bond is formed. Each amino hydrogen atom participates in an intramolecular (2.59 Å) and a somewhat longer intermolecular hydrogen bond (2.98 Å). This bonding results in the formation of chains in the crystal structure (Figure 11) and is reflected in a considerably higher melting point.

If an additional hydrogen donor is present, providing the *N*-substituent is sufficiently small, it can form a hydrogen bond with the keto-amino oxygen atom. This occurs in the crystal structure of *N*-(2-hydroxyethyl)-1-aminomethylene-1*H*-naphthalen-2-one [43] where the *N*-substituent is a primary alcohol which acts as a hydrogen donor forming a O-H...O intermolecular hydrogen bond of 2.71 Å with the keto-amino oxygen atom forming dimers. The dimers in the crystal structure are further linked *via* weak C_{ar}-H...O contacts generating a 3D-network (Figure 12).

Unlike Schiff bases derived from *o*-hydroxyaromatic aldehydes, those derived from *m*- and *p*-hydroxyaromatic aldehydes will not be able to form an intramolecular hydrogen bond as described above. Instead, a free hydrogen bond donor (hydroxyl group) and an acceptor (imino group) are available for intermolecular hydrogen bonding. This can be observed in the structure of *N*-(4-methylphenyl)-hydroxy-3-methoxybenzilideneamine [111] where intermolecular O-H...N hydrogen bonds of 2.84 Å connect the molecules into chains (Figure 13).

Increasing the size of the *N*-substituent

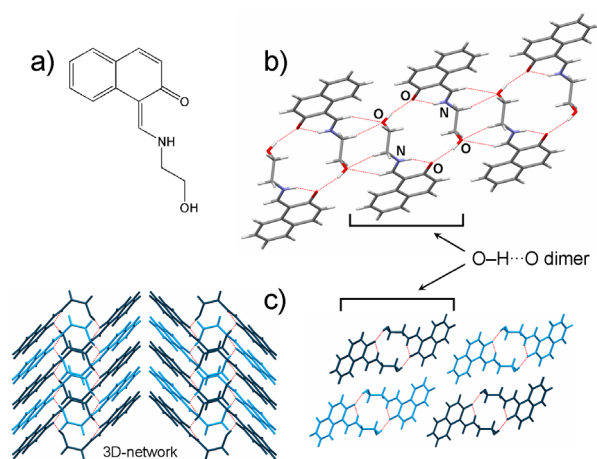


Fig. 12. a) Molecular diagram, b) fragment of the chain in the crystal, and c) view of the packing of molecules for *N*-(2-hydroxyethyl)-1-aminomethylene-1*H*-naphthalen-2-one [43]

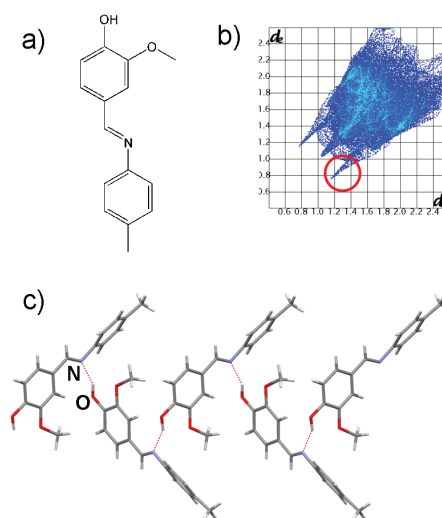


Fig. 13. a) Molecular diagram, b) two-dimensional fingerprint plot (marked corresponding region for O-H...N hydrogen bond), and c) a fragment of the hydrogen-bonded chain in the crystal of *N*-(4-methylphenyl)-hydroxy-3-methoxybenzilideneamine [111]

renders the participation of hydrogen donors and acceptors of the central keto-amino group in intermolecular bonding less probable. In such cases, and if additional hydrogen donors and acceptors are absent, the packing is governed by weak interactions. Two Schiff bases, namely *N*-(α -naphthyl)-1-aminomethylene-1*H*-naphthalen-2-one and *N*-(β -naphthyl)-1-aminomethylene-1*H*-naphthalen-2-one, differ only in the spatial orientation of *N*-naphthyl group with regard to the 2-oxy-1-naphthaldeimine [59]. Both molecules show a high degree of planarity with essentially identical interplanar twist angles between the *N*-substituents and the rest of the molecule. Because

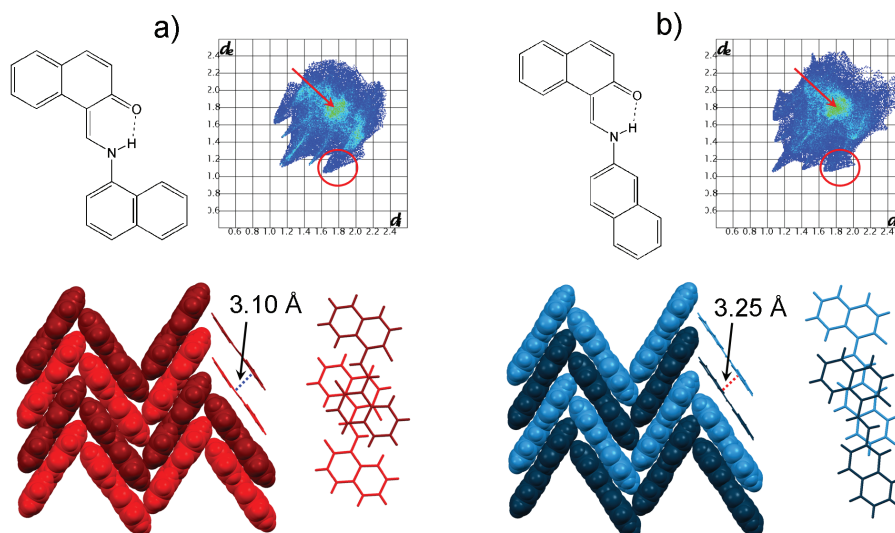


Fig. 14. Molecular diagram, two-dimensional fingerprint plot (marked corresponding regions: red arrow for $\pi\cdots\pi$ contacts and red circle for $C-H\cdots\pi$ contacts) and view of the packing and $\pi\cdots\pi$ stacking for compounds: a) *N*-(α -naphthyl)-1-aminomethylene-1*H*-naphthalen-2-one, b) *N*-(β -naphthyl)-1-aminomethylene-1*H*-naphthalen-2-one [59]

of the lack of hydrogen-bonding functionalities on the *N*-substituents, all interactions between neighbouring molecules in both compounds are on the basis of the weak intermolecular contacts. The discrete molecules are stacked to give a π -stacked chains. The adjacent chains are further linked *via* weak $C-H\cdots\pi$ contacts and generate a herringbone motif (Figure 14).

Crystal structures of Schiff bases derived from aldehydes and amines which have additional groups containing non-bonding electron pairs (alkoxy, acyl, nitro, cyano, pyridine etc.) which may act as hydrogen bond acceptors are often directed by weak hydrogen bonds formed between such groups and aromatic hydrogen donors. An example of such intermolecular bonding can be seen in the crystal structure of *N*-(2-pyridyl)-3-methoxysalicylideneamine [112] (Figure 15a), where methoxy oxygen and pyridine nitrogen atoms participate as acceptors of intermolecular hydrogen bonds. The crystal

structure comprises of $C_{ar}-H\cdots O$ hydrogen-bonded dimers (Figure 15b), which are linked *via* another set of weak $C-H\cdots O$ interactions into a 2D-network. The layers are further interconnected by $C-H\cdots N$ interactions between imino methine group and pyridine nitrogen with $C\cdots N$ distances of 3.62 Å, which is comparable with $C-H\cdots N$ intermolecular bonding in other Schiff bases derived from pyridylamines [113].

$C-H\cdots N$ intermolecular bonding frequently occurs in crystal structures of Schiff bases derived from aminonitriles. Figure 16 depicts hydrogen bonding motifs in Schiff bases derived from naphthaldehyde and 2-, 3- and 4-aminobenzonitrile demonstrating the effect of the position of the cyano group on the crystal packing [114–116]. In the case of the 3-aminobenzonitrile derivative, a combination of $C_{ar}-H\cdots N$ and $C_{ar}-H\cdots O$ interactions results in the formation of molecular chains (Figure 16b). In 2-aminobenzonitrile derivative, due to different directionality

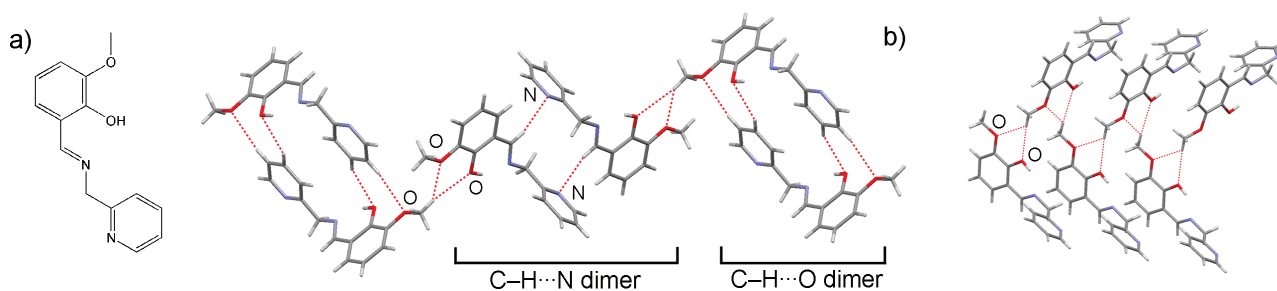


Fig. 15. a) Molecular diagram, b) fragments of packing in the crystal of *N*-(2-pyridyl)-3-methoxysalicylideneamine [112]

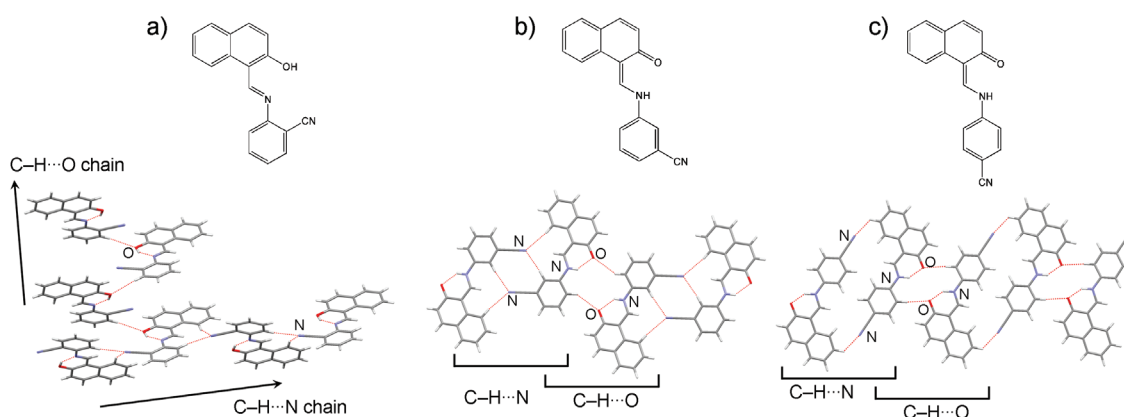


Fig. 16. Molecular diagram and fragment of the chain in the crystal for compounds: a) *N*-(2-cyanophenyl)-2-hydroxy-1-naphthalideneamine [114], b) *N*-(3-cyanophenyl)-1-aminomethylene-1*H*-naphthalen-2-one [115], c) *N*-(4-cyanophenyl)-1-aminomethylene-1*H*-naphthalen-2-one [116]

of the cyano group, the hydrogen bond involving the same donor/acceptor set results in a different supramolecular topology. The molecules are connected into chains via $C_{ar}-H\cdots N$ interactions and the chains are further connected by $C_{ar}-H\cdots O$ interactions into layers (Figure 16a). A different type of supramolecular topology is observed in the crystal structure of the 4-aminobenzonitrile derivative, where $C_{ar}-H\cdots N$ and $C_{ar}-H\cdots O$ interactions leads to a 3D-network (Figure 16c).

In the crystal structures of Schiff bases with carboxyl substituents the formation of strong hydrogen bonds is expected, with the carboxyl group acting as the hydrogen donor and

either carboxyl group or the central keto-amino group acts as hydrogen acceptors. Both cases are illustrated by Schiff bases derived from 2-hydroxy-1-naphthaldehyde and different aminobenzoic acids (Figure 17). In the crystal structure of *N*-(3-carboxyphenyl)-1-aminomethylene-1*H*-naphthalen-2-one [94] (Figure 17a) the hydrogen bond acceptor is the keto-amino oxygen atom and hydrogen bonding leads to chains, while in the structure of *N*-(4-carboxyphenyl)-1-aminomethylene-1*H*-naphthalen-2-one [117] (Figure 17b) the hydrogen bond acceptor is the carboxyl group which results in the formation of characteristic carboxyl dimers.

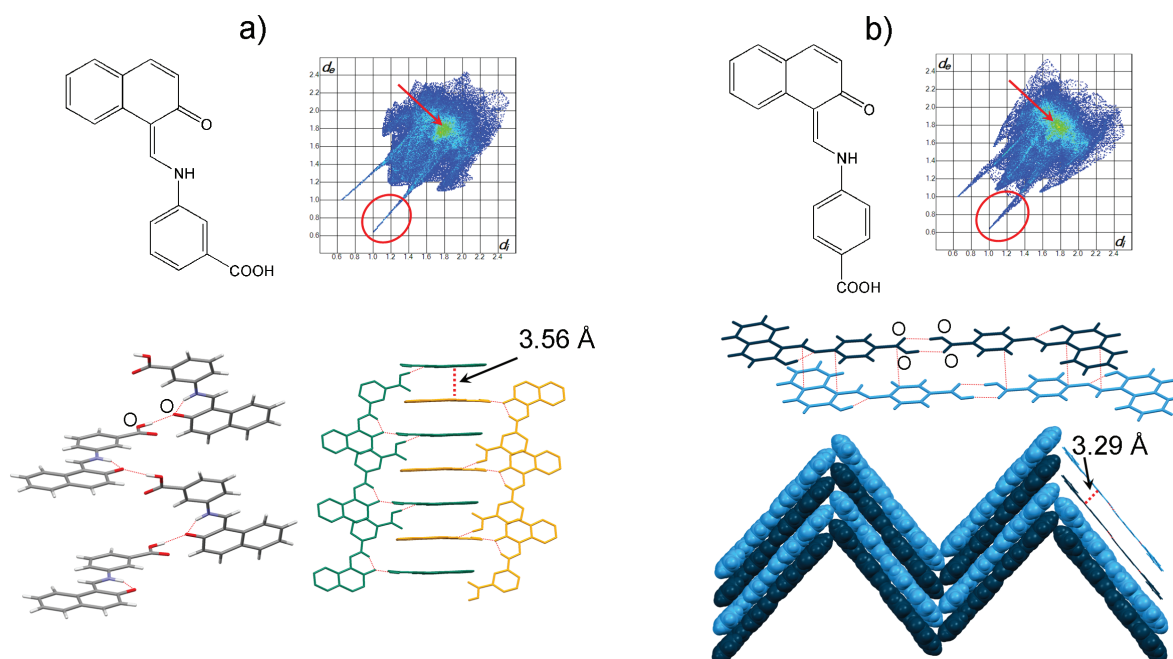


Fig. 17. Molecular diagram, two-dimensional fingerprint plot (marked corresponding regions: red arrow for $\pi\cdots\pi$ contacts and red circle for $O-H\cdots O$ hydrogen bond) and view of the packing and $\pi\cdots\pi$ stacking for compounds: a) *N*-(3-carboxyphenyl)-1-aminomethylene-1*H*-naphthalen-2-one [94], and b) *N*-(4-carboxyphenyl)-1-aminomethylene-1*H*-naphthalen-2-one [113]

METAL COMPLEXES OF SCHIFF BASES

Replacing the hydrogen atom from the intramolecular hydrogen bond in the salicylaldimine and naphthaldimine Schiff bases by a metal ion, can have a significant influence on the geometry of the molecule [31]. The main structural feature distinguishing the free Schiff base from the coordinated ligand appears in: (i) a large difference in the $O\cdots N$ separation, the so called ‘bite’ distance of the chelate ligand; ii) changes in bond distances and angles in what becomes a chelate ring (Figure 6c) which is associated with the re-distribution of π -electrons (pseudoaromaticity), and iii) a significant change in the spatial orientation of the N -substituent (Figure 18).

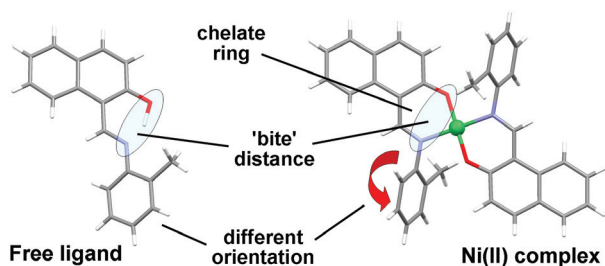


Fig. 18. Representation of conformational differences between free Schiff bases and Schiff bases bonded to metal ions

The distribution of $O\cdots N$ ‘bite’ distances for free Schiff bases and their complexes is shown in Figure 19. The distance increases upon the binding of the metal ion, the average bite distance rising from 2.59(5) Å in free Schiff bases to 2.79(6) Å in complexes. Such behaviour which is to be expected since the metal ion replaces a much smaller hydrogen. Consequently, the bite distance of a Schiff base in a complex is very dependent on the metal atom. The average bite distance in complexes of Cu(II) is 2.80(3) Å, in Co(II) complexes 2.78(6) Å, 2.72(6) Å in V(III) complexes, 2.78(4) Å in Fe(II) complexes, 2.88(5) Å in Zn(II) complexes and 2.77(2) Å in Mn(II) complexes. The bite distance is also noticeably affected by the coordination of the metal ion – the average bite distance in tetracoordinated Ni(II) complexes is 2.72(3) Å and in hexacoordinated 2.87(3) Å.

In the complex chelate ring of bis(N -(2-methylphenyl)-2-hydroxy-1-naphthalidenato)

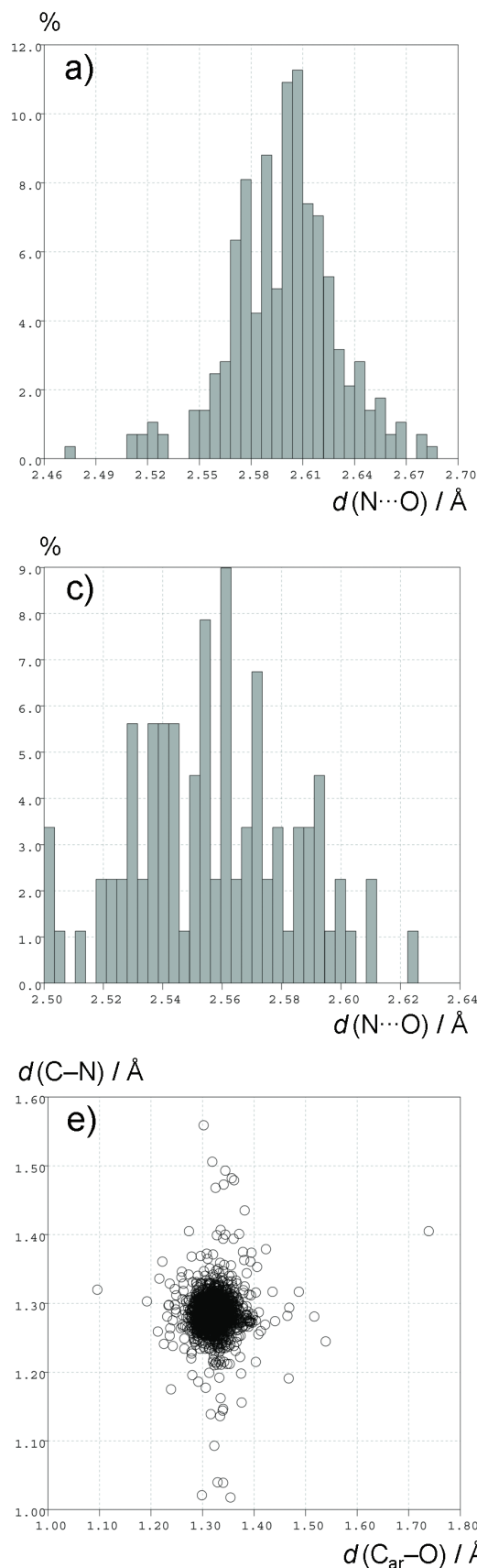
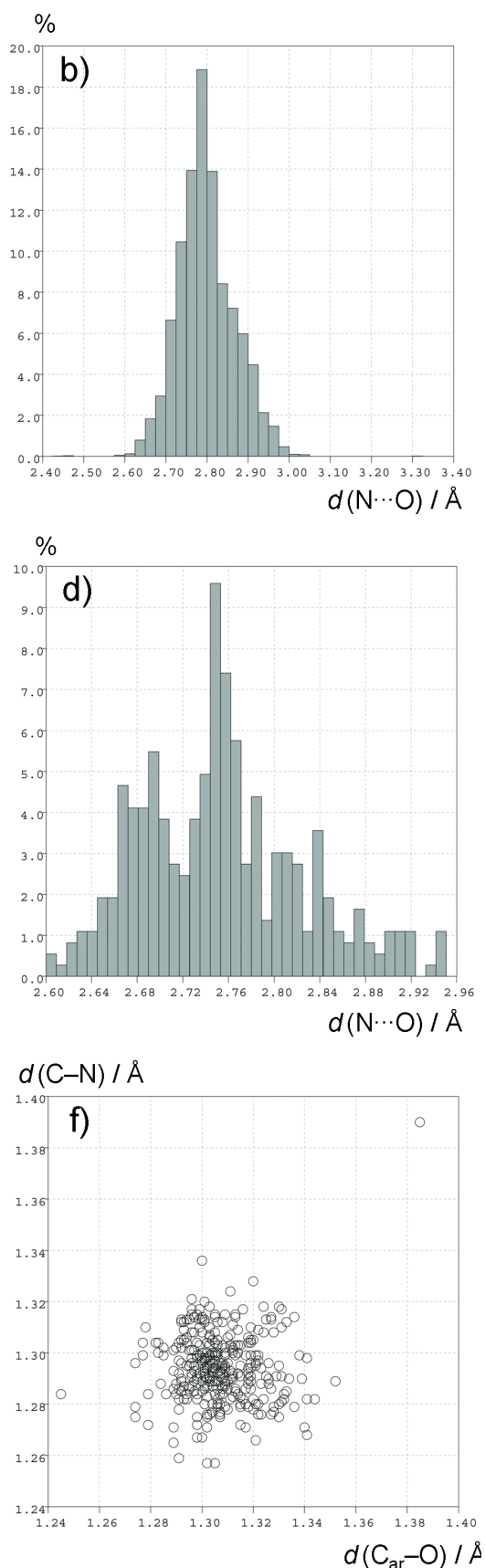


Fig. 19. a) The distribution of $N\cdots O$ bite distance of Schiff bases derived from salicylaldehyde, and b) their complexes c) The distribution of $N\cdots O$ bite distance of Schiff bases derived from 2-hydroxy-1-



naphthaldehyde, d) and their complexes e) The plot of C–N vs. C_{ar}–O bond lengths of Schiff base complexes derived from salicylaldehyde, and f) 2-hydroxy-1-naphthaldehyde

nickel(II) [31] there is a general tendency of shortening the O–C and C–C, and lengthening of the N–C bond distances in comparison to the corresponding bonds in the free Schiff base ligand. The naphthalidimine moiety in the complex exhibits the quinoidal bond lengths assembly. The ligand itself is not planar, due to the twist of the *o*-tolyl ring connected on the amino nitrogen out of the naphthalene moiety plane with the corresponding dihedral angles *ca* 53.0° and 40.2° for free and coordinated molecule, respectively (Figure 20). The twisting of the *o*-tolyl moiety is affected by the molecular environment and packing in the crystal, as a consequence of sterical hindrance due to the approaching of two ligands to each other in the complex and the increase of bond angles in the chelate ring. Similar stereochemical behaviour was observed in the analogous nickel(II) complexes with *N*-(2,6-diisopropylphenyl)- [118] and *N*-(β-naphthyl)-2-hydroxy-1-naphthalidenamine [119].

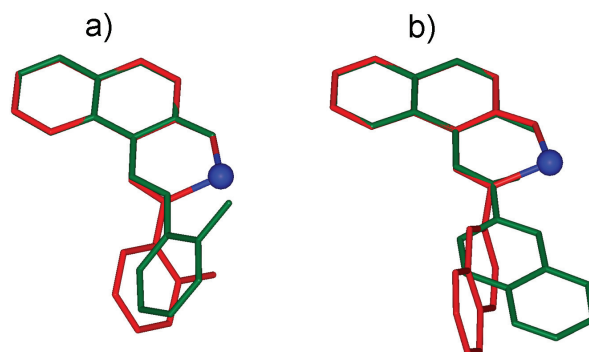


Fig. 20. Overlap of free Schiff base (red) and a Schiff base coordinated to nickel(II) (green), a) *N*-(2-methylphenyl)-2-hydroxy-1-naphthalidenamine [31], b) *N*-(β-naphthyl)-2-oxy-1-naphthalidenamine [119]. The fragments are fitted by best overlap of 10 naphthalene atoms

As noted earlier, there has been continuous interest in the coordination compounds of Cu(II) and Ni(II), and to a somewhat lesser degree of Co(II), with Schiff bases derived from salicyl- and naphthaldehydes. This is mostly due to the variability of the geometric features of the coordination sphere around the metal which can range from square planar to deformed tetrahedral geometry [120–122]. In most complexes both electronic effect [123, 124] and crystal packing [125, 126] have been invoked as the driving forces responsible for the distortion.

However, a significant role in the coordination geometry of the ligands around the metal atom is played by the nature and volume of the *N*-substituent and intermolecular interactions, *i.e.* crystal packing forces.

A simple measure of the coordination polyhedron geometry for bis(bidentate Schiff base) coordination compounds is the $d_{\text{NN}}/d_{\text{NO}}$ ratio *i.e.* the ratio of distances from one donor atom (e.g. N) of one ligand to the equivalent (N) and to the non-equivalent (O) donor atom of the other ligand (Figure 21a). For *trans*-planar expected value of this ratio is $d_{\text{NN}}/d_{\text{NO}} \approx \sqrt{2}$ ($d_{\text{NN}}/d_{\text{NO}} = \sqrt{2}$ for a perfect square and $d_{\text{NN}}/d_{\text{NO}} >$

$\sqrt{2}$ in most real complexes), for tetrahedral $d_{\text{NN}}/d_{\text{NO}} \approx 1$ and for *cis*-planar $d_{\text{NN}}/d_{\text{NO}} \approx \sqrt{2}/2$. $d_{\text{NN}}/d_{\text{NO}}$ plots for mononuclear bis(bidentate Schiff base) complexes of tetracoordinated nickel(II), cobalt(II) and copper(II) are given in Figure 21 and show distribution of data points into regions corresponding to above mentioned coordination geometries.

In the case of nickel complexes there is an extreme tendency towards *trans*-planar coordination with only several examples of tetrahedral complexes (Figure 21b). The *trans*-planar nickel(II) complexes are usually negligibly tet-

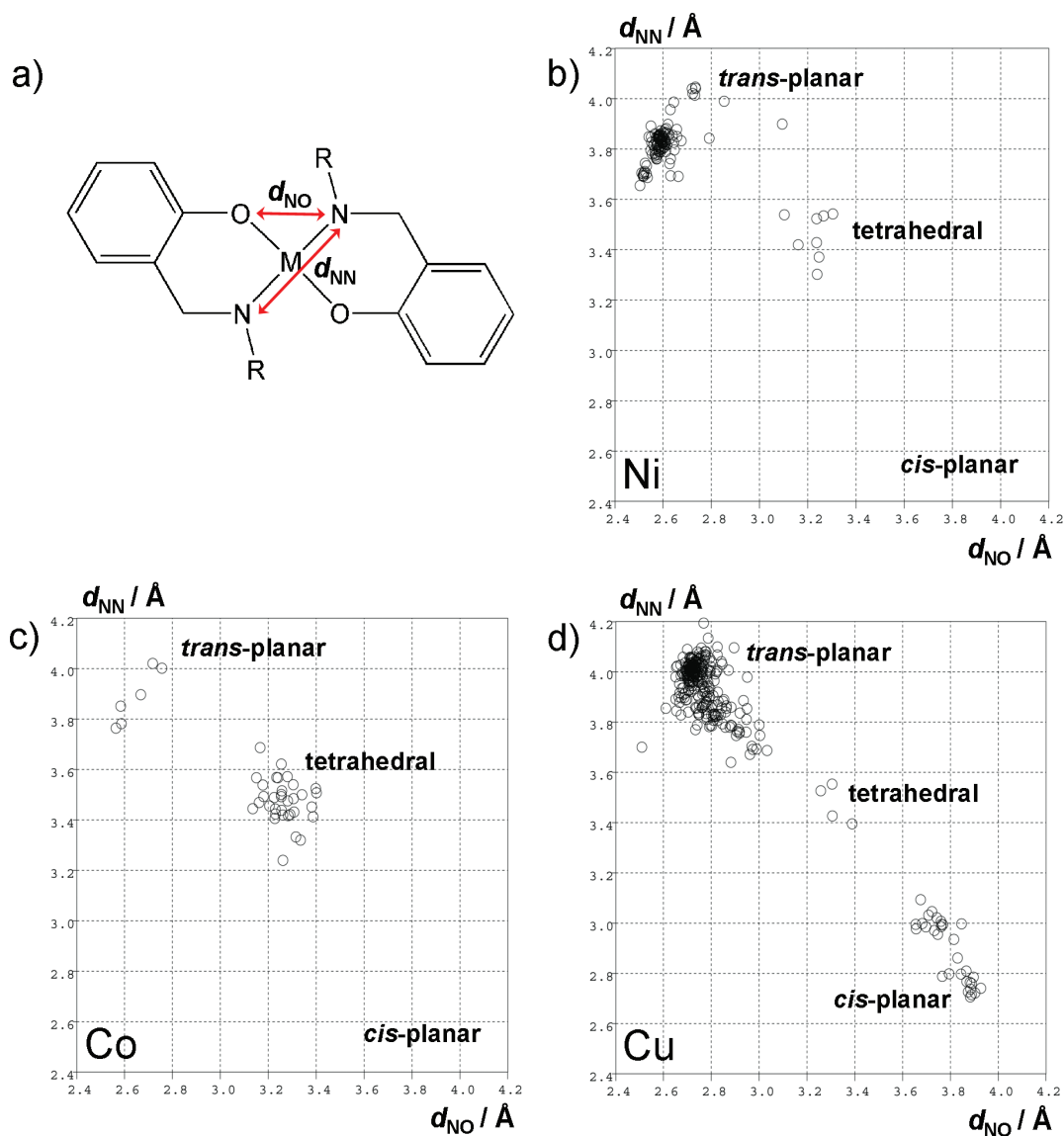


Fig. 21. The distribution of coordination geometries in mononuclear bis(bidentate Schiff base) coordination compounds in the CSD. a) A diagram of the molecular fragment used for the CSD search with the definition of parameters d_{NN} and d_{NO} b) $d_{\text{NN}}/d_{\text{NO}}$ correlation for nickel(II) complexes (116 data points), c) $d_{\text{NN}}/d_{\text{NO}}$ correlation for cobalt(II) complexes (38 data points), d) $d_{\text{NN}}/d_{\text{NO}}$ correlation for copper(II) complexes (277 data points). For detailed discussion see text.

rahedrally deformed, but can show an increase of both d_{NN} and d_{NO} compared to a 'perfect' square due to stepwise bending of complex molecules, as will be discussed below. *Cis*-planar Ni(II) complexes occur only in polynuclear species where the Schiff base ligands bridge between two or more metal ions as well as in complexes with tetradentate Schiff bases usually derived from diamines such as *o*-phenylenediamine [23].

Although it is commonly accepted that the stereochemistry of cobalt(II) is similar to that of nickel(II), there is a marked increase of the occurrence of tetrahedral bis(bidentate Schiff base)cobalt(II) complexes in comparison to those of nickel(II) with tetrahedral coordination seemingly to be preferred to *trans*-planar coordination. *Cis*-planar coordination is entirely absent as is among the nickel compounds.

The coordination to copper(II) is usually less rigid than that to cobalt and nickel. This is demonstrated in the $d_{\text{NN}}/d_{\text{NO}}$ plot by the smearing of the data points along the line connecting top left and bottom right corners of the plot. This corresponds to the rotation of one chelate ring plane in respect to the other and indicates that such rotation is energetically less demanding than in corresponding copper and nickel compounds. In spite of the smearing, the data points are still grouped into three well distin-

guishable regions corresponding to *trans*-planar, tetrahedral and *cis*-planar. The majority of compounds exhibit a *trans*-planar coordination which can be somewhat distorted towards tetrahedral. The second most abundant group corresponds to the *cis*-planar coordinated species, while only four structures can be described as tetrahedrally coordinated (Figure 22). Another feature of copper(II) complexes is their tendency to form dimers [127, 128] and tetramers [129]. Formation of dimers can also be noticed in nickel(II) and cobalt(II) complexes but there it occurs much less frequently.

It is interesting to note that all the coordination polyhedra achievable in bis(bidentate Schiff base) complexes, other than the perfectly planar ones, are chiral. Although this usually does not affect the properties of the bulk material since the majority of reported structures crystallised as racemates, there are cases where the chirality of the coordination polyhedron dictates the chirality of crystal packing. An example of such behaviour is bis(μ -*N,N'*-hexamethylenedisalicylaldiminato)dicopper(II), where chiral tetrahedrally disordered planar coordination of the copper ions leads to a helicity of binuclear coordination species and in turn to crystallization of enantiomeric compounds in enantiomeric space groups $P4_1$

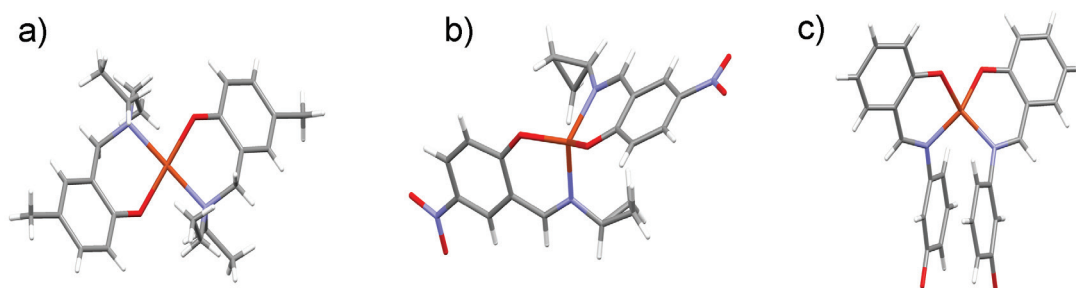


Fig. 22. Examples of limiting coordination geometries of bis(bidentate Schiff base)copper(II) complexes: a) *trans*-planar [131], b) tetrahedral [132], c) *cis*-planar [133]

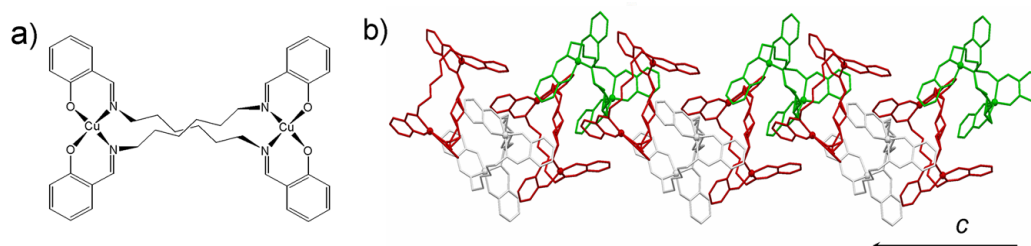


Fig. 23. a) Molecular diagram of bis(μ -*N,N'*-hexamethylenedisalicylaldiminato)dicopper(II)³⁰, b) Helical stacking of molecules along the *c* axis exhibiting a 4_1 symmetry

and $P4_3$ (Figure 23) [30]. By introducing chiral substituents on the Schiff base ligand itself, it is possible to control the chirality of the coordination sphere and thus the entire complex molecule. Many such complexes have been found to be potent chiral catalysts in organic synthesis [130].

A feature of the molecular geometry of many salicylaldimine and naphthaldimine bis-bidentate complexes with divalent copper and nickel is their ‘stepped’ conformation arising from a distinct bend in the otherwise planar molecules along the line joining the two donors within each separate ligand. Such molecules are comprised of two planar regions which lie on parallel planes separated by a distance S referred to as step distance (Figure 24). The step distance S is defined as the perpendicular separation between the planes through the chelate ring and/or through the aromatic ring atoms [38, 121, 134].

The occurrence of ‘stepped’ conformation has been mainly associated with steric fac-

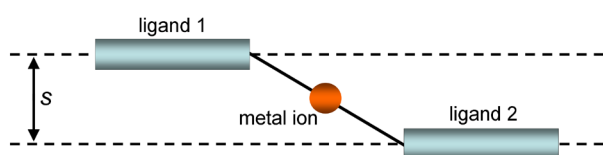


Fig. 24. A schematic representation of a complex molecule in a stepped conformation indicating the step distance (S)

tors [134], and electronic effects [123]. However, steric and packing effects seem to have an important contribution to the formation of stepped conformation. Large N substituents favour larger step distances. This is well demonstrated by comparing molecular conformations of bis(N -methyl-5-chlorosalicylideneiminato)nickel(II) and bis(N -ethyl-5-chlorosalicylideneiminato)nickel(II). The methyl compound is almost planar (step distance $S = 0.121 \text{ \AA}$), while more bulky ethyl substituent renders the molecular conformation markedly stepped (step distance $S = 0.702 \text{ \AA}$) due to the close contact between the methylene hydrogen atoms of one ligand and the coordinated oxygen atom of the other (Figure 25) [38]. Complexes with bulkier N substituents can exhibit even larger values of step distance, so that in bis(N -2-naphthyl-2-hydroxy-1-naphthaldiminato)nickel(II) the step distance is $S = 0.639 \text{ \AA}$ [113] and even larger in complexes of N -*o*-tolyl Schiff bases such as bis(N -(2-methylphenyl)-2-hydroxy-1-naphthaldiminato)nickel(II) ($S = 1.054 \text{ \AA}$) [31].

The conformation of the coordination polyhedron is also largely influenced by the crystal packing, sometimes even to a greater extent than the N -substituent. This is seen in the crystal structure of bis(3-ethoxysalicylideneiminato)nickel(II) (Figure 26) [22], for which a small step distance is expected since there is

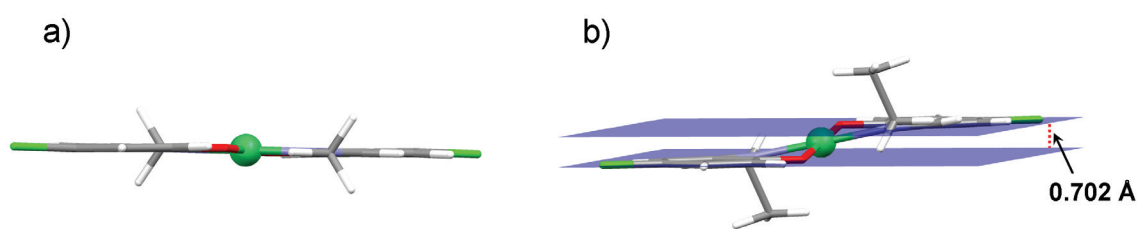


Fig. 25. Molecular structures of bis(N -methyl-5-chlorosalicylideneiminato)nickel(II) and bis(N -ethyl-5-chlorosalicylideneiminato)nickel(II)³⁸ viewed along the edge of the coordination plane. The methyl derivative is almost perfectly planar, while the ethyl derivative adopts a stepped conformation.

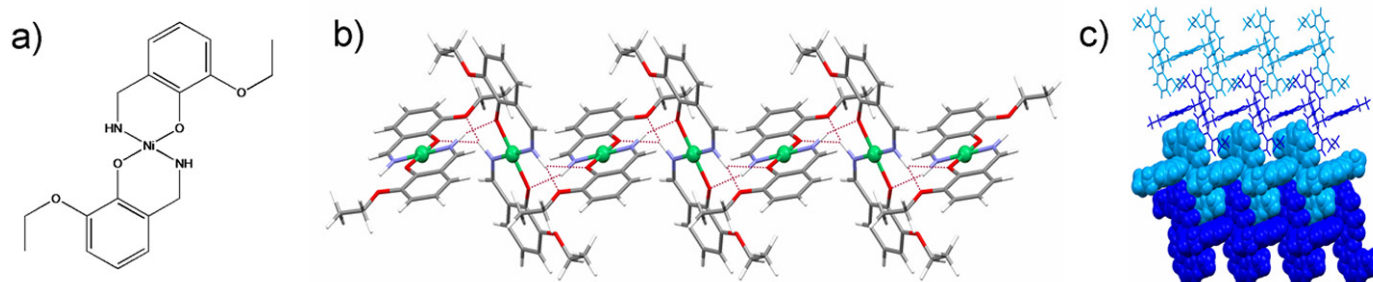


Fig. 26. Crystal packing of bis(3-ethoxysalicylideneiminato)nickel(II): a) molecular diagram, b) hydrogen bonded chains, c) packing of chains [22]

no *N*-substituent. In the crystal structure there are however two symmetrically non-equivalent molecules, which alternate in hydrogen bonded chains along the *b* axis. Of these one is almost planar ($S = 0.144 \text{ \AA}$), while the other molecule has a step distance of $S = 0.696 \text{ \AA}$, which is more than in both *N*-methyl ($S = 0.514 \text{ \AA}$), and *N*-ethyl ($S = 0.616 \text{ \AA}$) derivative [22]. The difference between the two bis(3-ethoxysalicylideneiminato)nickel(II) molecules is in the nature of the interaction between the chelate rings of these molecules and the phenyl rings of molecules from a neighbouring chain – the chelate rings of the planar molecule participates in stacking interaction while the chelate rings of the stepped molecules are acceptors of C–H $\cdots\pi$ hydrogen bonds.

The effect of crystal packing can also be seen comparing the molecular conformations of bis(*N*-methylsalicylideneiminato)nickel(II) in its monoclinic and orthorhombic polymorphs where step distance in the monoclinic polymorph is quite large ($S = 0.891 \text{ \AA}$), while in the orthorhombic one the molecule lies on a crystallographic mirror plane and is thus perfectly planar ($S = 0 \text{ \AA}$) [37, 135, 136].

Acknowledgement: We are indebted to the Ministry of Science, Education and Sport of the Republic of Croatia for the long-lasting financial support in this field of investigation since early 1990's.

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