The Effect of C–H⋯N Interactions on Crystal Structure and Thermal Properties of Two Novel Diamine Schiff Bases Derived from Terephthaldialdehyde

Vladimir Stilinović, Dominik Cinčić and Branko Kaitner*

Department of Chemistry, Laboratory of General and Inorganic Chemistry, Faculty of Science,
Horvatovac 102a, University of Zagreb, 10000 Zagreb, Croatia

* Corresponding author: E-mail: kaitner @chem.pmf.hr
Phone: +385 1 4606 361; Fax: +385 1 4606 341

Dedicated to the memory of Professor Ljubo Golič

Abstract

Two novel potential bridging ligands derived from terephtaldialdehyde, namely 1,4-bis((pyridine-3-ylimino)methyl)benzene (**1**) and 1,4-bis-((1-benzylpiperidin-4-ylimino)methyl)benzene (**2**), were prepared by the Schiff base condensation. They were characterised by means of IR spectroscopy, thermal analysis and also by powder and single-crystal X-ray diffraction. The molecules of **1** form 1D chains by intermolecular C–H⋯N interactions. The molecular conformation of **2**, governed by intramolecular C–H⋯N interactions, does not permit formation of intermolecular interactions analogous to those in **1**. As a consequence, **2** has a markedly lower melting point and fusion enthalpy than **1**, although its molecular weight is almost double that of **1**.

Keywords: Schiff base, terephthaldialdehyde, C–H⋯N interaction, X-ray structure analysis, thermal analysis

1. Introduction

N-substituted imines, also known as Schiff bases, have been widely studied as ligands for coordinating transition and inner transition metal ions for over a century, and in that time they became some of the most typical ligands in coordination chemistry.[1,2] More recently, however, Schiff bases also started drawing attention due to their interesting physical properties in the crystalline state. These properties are greatly influenced by the topochemistry of the Schiff base molecules which in turn is highly affected by the crystal structure.[3] 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.
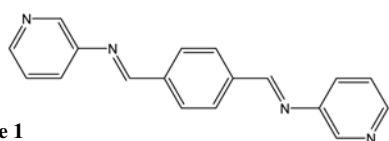
During the past decades it became well-recognised that C–H groups can act as weak hydrogen bond donors and particularly the hydrogen-bond nature of the C–H⋯O and C–H⋯N contacts.[4–6] The nature of C–H⋯N, however, remained a subject of controversy for a longer period, although its similarity to C–H⋯O was established as early as

1982.[7] Today there are numerous examples of crystal structures in which C–H⋯N hydrogen bonds play an important role. The usual hydrogen acceptors in such structures are nitrogen atoms in aromatic systems, such as pyridine and the cyano group, but also aliphatic tertiary amines, imines and other nitrogen species.
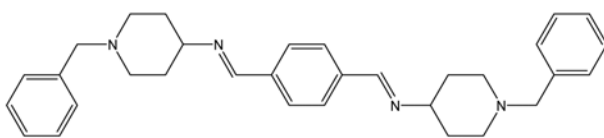
Schiff bases are potentially good models for study of C–H⋯N interactions, particularly if they are further functionalized with nitrogen containing groups. Symmetrical bis(pyridine) functionalised Schiff bases have been widely employed in the synthesis of metaloorganic frameworks (MOF) as rigid bipyridyl-based ligands of high structural stability and special topologies.[8–12] Although most Schiff base ligands used in MOF and metalocycle design are of the 4,4'-bipyridine type, others, such as 3,3'-bipyridine[10,11] and 2,2'-bipyridine[12] have recently been employed. Ligands derived from non-aromatic amines such as tertiary amines have received little or no attention to date.

In this paper we describe the combined use of diffraction and thermal methods in the study of intermolecu-

lar interactions in the solid state. Two novel Schiff bases derived from terephtaldialdehyde, namely 1,4-bis((pyridine-3-ylimino)methyl)benzene (**1**) (Scheme 1) and 1,4-bis-((1-benzylpiperidin-4-ylimino)methyl)benzene (**2**) (Scheme 2) were synthesised and characterised by FT-IR spectroscopy, and their molecular and crystal structures were determined. Compound **1** is an analogue of a previously described ligand,[10] from which it differs by opposite orientation of the imine groups and thus a different potential for the formation of C–H···N interactions. Compound **2** is derived from an aminopiperidine with a sterically hindering benzoyl substituent on the nitrogen atom. To the best of our knowledge, this is the first structurally characterised Schiff base with an imino group bound directly to a piperidine ring. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study solid state thermal properties as well as the non-isothermal melt crystallisation of the compounds **1** and **2**. Data thus obtained were correlated with the crystal structures in order to examine the structure – properties relationships.

fraction data were collected at 292 K for both crystals. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated MoK_α (λ = 0.71073Å) radiation.[13] The data sets were collected using the ω scan mode over the 2θ range up to 54°. The structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively.[14,15] The structural refinement was performed on F^2 using all data. The hydrogen atoms were placed in calculated positions and treated as riding on their parent atoms [C–H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C); C–H = 0.97 Å and U_{iso}(H) = 1.2 U_{eq}(C)]. All calculations were performed using the WINGX crystallographic suite of programs.[16] The crystal data are listed in Table 1. Further details are available from the Cambridge Crystallographic Centre with quotation numbers[17] CCDC 682911 for **1** and CCDC 682912 for **2**.

The crystal of **1** was twinned by non-merohedry and only one twin component was used for structure solution and refinement. The unresolvable overlap in several ref-

Scheme 1

Scheme 2

2. Experimental

2. 1. Synthesis

All chemicals and solvents used in this work were commercially available and used without further purification. For preparation of **1**, 3-aminopyridine (3.8 g, 0,040 mol) and terephtaldialdehyde (3.2 g, 0,020 mol) were dissolved at room temperature in ethanol (30 mL and 10 mL, respectively). The solutions were mixed; to the resulting solution 3 drops of acetic acid were added and the mixture left at room temperature. Yellow crystals of **1** appeared after a period of 3 days. **2** was prepared analogously using 4-amino-*N*-benzylpiperidine (7.6 g, 0,040 mol). Pale yellow, almost colourless crystals of **2** appeared after 2 days.

2. 2. X-ray Structure Determination

The crystal and molecular structures of **1** and **2** were determined by single crystal X-ray diffraction. The dif-

Table 1. Crystal data and summary of experimental details for compounds **1** and **2**.

	1	**2**
Molecular formula	$C_{18}H_{14}N_4$	$C_{32}H_{38}N_4$
M_r	286.33	478.64
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal data:		
a / Å	3.8852(2)	5.901(3)
b / Å	9.8802(6)	9.911(6)
c / Å	10.3048(7)	12.965(8)
α / °	112.672(6)	106.47(5)
β / °	96.776(5)	96.75(5)
γ / °	92.135(4)	103.87(5)
V / Å^3	*360.97(4)*	*691.3(8)*
Z	1	1
ρ_{calc} / g cm^{-3}	1.317	1.150
λ(MoK_α) / Å, graphite monochromator	0.71073	0.71073
T / K	292(2)	292(2)
Crystal dimension / mm^3	0.49 × 0.23 × 0.17	0.38 × 0.21 × 0.18
μ / mm^{-1}	0.081	0.068
$F(000)$	150	258
θ range/°	4–27	4–27
hkl range	–4, 4; –12, 12; –13, 13	–7, 7; –12, 12; –16, 16
Number of measured reflections	7309	5416
Number of independent reflections	1544	2972
Number of reflections with $I > 4\sigma(I)$	1163	1242
Number of parameters	100	163
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.602 –0.244	0.166 –0.173
$R[F^2>4\sigma(F^2)]$	0.0846	0.0945
$wR(F^2)$	0.2167	0.2214
Goodnees-of-fit, S	1.022	1.054

lections caused somewhat large maxima in the final electron difference map.

The powder X-ray diffraction (PXRD) experiments of the samples were performed on a PHILIPS PW 1840 X-ray diffractometer with Cu$K_{\alpha1}$ (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range was from 3° to 50° (2θ) with steps of 0.02°, and the measuring time was 1 s per step. The data collection and analysis was performed using the program package *Philips X'Pert*.[18–20]

2. 3. Thermal and Spectroscopic Analysis

Thermal analysis was carried out on a Mettler Toledo TGA/SDTA 851 and DSC823 modules in sealed aluminium pans (40 μL), heated in flowing nitrogen (200 mL min^{-1}) at 10 °C min^{-1}. The data collection and analysis was performed using the program package *STARe Software 9.01*.[21] The non-isothermal crystallisation experiments for **1** and **2** were carried out under a nitrogen atmosphere with a flow rate of 60 mL min^{-1}. The experiments started with heating of the sample from 25 °C at heating rate 50 °C min^{-1} to fusion temperature of compound (165 °C for **1** and 154 °C for **2**). To ensure complete melting, the sample was kept at the respective fusion temperature for a holding period of 4 minutes. After this period, each sample was cooled at cooling rate 2 °C min^{-1}.

Infrared spectra were recorded on an EQUINOX 55 FTIR spectrophotometer using a KBr pellet. The data collection and analysis was performed using the program package *OPUS 4.0*.[22]

3. Results and Discussion

Both compounds **1** and **2** were obtained in relatively high yields, 84% and 91% respectively. The measured PXRD patterns of both compounds are in good agreement with those calculated from single crystal data, thus confirming that both products were obtained as pure single phases.

The strong bands at 1617 cm^{-1} for **1** and 1635 cm^{-1} for **2** in their respective IR spectra are assigned to the C=N stretching vibration. The spectrum of **1** also shows several weak bands corresponding to aromatic C–H stretching (at 3023 cm^{-1}, 3040 cm^{-1} and 3072 cm^{-1}) and aromatic C–C stretching (1571 cm^{-1} and 1509 cm^{-1}). In the spectrum of **2** there are multiple bands corresponding to aliphatic C–H stretching (the strongest at 2759 cm^{-1}, 2806 cm^{-1}, 2835 cm^{-1}, 2851 cm^{-1} and 3004 cm^{-1}), aromatic C–H stretching (the strongest at 3024 cm^{-1} and 3032 cm^{-1}) and aromatic C–C stretching (1606 cm^{-1} and 1492 cm^{-1}).

The molecular structures of compounds **1** and **2** with the atom numbering schemes are given in Figures 1 and 2 respectively. All bond lengths and angles are normal.[23] All C=N bonds in both molecules in both compounds are of the *E* configuration.

The molecule of **1** consists of two 3-pyridyl groups linked by a diimine unit (–N=CH–C$_6$H$_4$–CH=N–) with the overall distance between pyridine nitrogen atoms of *ca* 13.93 Å. The central diimine unit in compound is planar and centrosymmetric at an angle of *ca* 42.6° to the planes of the pyridine rings. The molecules of **1** are non-planar and are connected in the structure by weak C–H⋯N interactions of 3.62 Å (C4–H4⋯N2, [1-x, 1-y, 1-z]) over in-
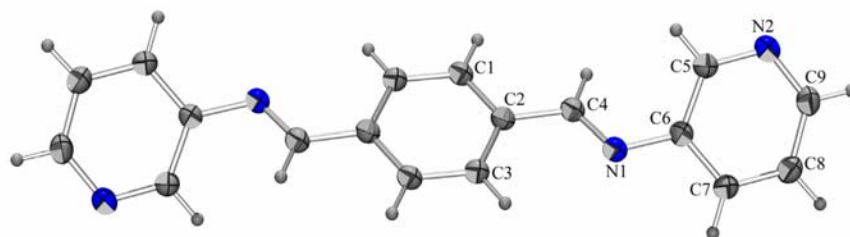

Figure 1. Molecule of **1**, showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.[24,25]
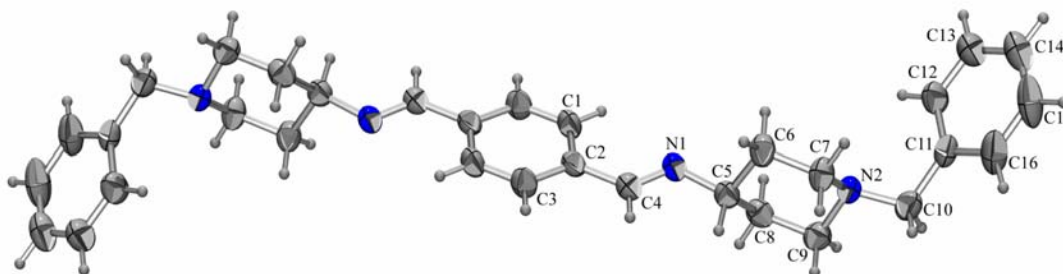

Figure 2. Molecule of **2**, showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.[24,25]

version centres into chains stretching along the [011] direction.

Compound **1** is a "bridge flipped"[27] isomer of previously described Schiff base *N,N'*-bis-(3-pyridylmethylene)phenylene-1,4-diamine[10] *i.e.* it differs from it only by opposite orientation of the imine groups. Although isostructurality is possible among such pairs of compounds, particularly so when strong hydrogen bonds are absent,[27] the crystal structures of *N,N'*-bis-(3-pyridilmethylene)phenylene-1,4-diamine and **1** greatly differ. This is because the formation of a centrosymmetric C–H···N motif analogous to that in **1** in *N,N'*-bis-(3-pyridilmethylene)phenylene-1,4-diamine would lead to an unfavourable geometry for the C–H···N interaction, due to the opposite orientation of the C=N groups (Scheme 3), and thus does not occur. *N,N'*-bis-(3-pyridilmethylene)phenylene-1,4-diamine crystallises with molecules of an almost perfectly planar conformation stacked by π–π interactions into columns. The columns are connected with neighbouring ones by C–H···π contacts into a chiral packing (space group *P* 2₁).
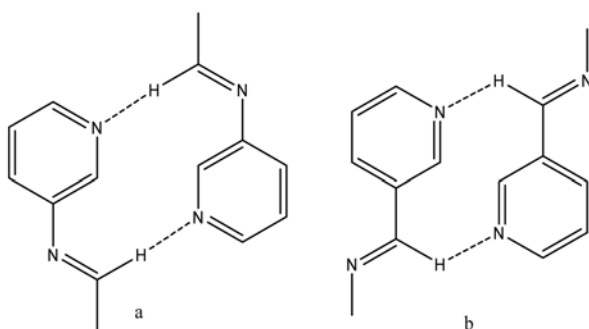
Scheme 3. Representation of the (**a**) C–H···N bonding in **1** showing "linear" C–H···N motif and (**b**) fictitious analogous bonding in its "bridge-flipped" isomer showing unfavourable angular geometry of C–H···N motif.

On further comparison of these two structures we notice that the π-stacked structure of *N,N'*-bis-(3-pyridilmethylene)phenylene-1,4-diamine (density of 1.336 g cm³) leads to closer packing than that of the the centrosymmetric packing in **1** (density of 1.317 g cm³). However, the reported melting point of *N,N'*-bis-(3-pyridilmethylene)phenylene-1,4-diamine (155 °C – 157 °C) is notably lower than that of **1** (165 °C), which is indicative of a higher lattice energy *i.e.* a better connected structure in the C–H···N hydrogen bonded structure of **1**. It is therefore evident that the C–H···N interaction, although not particularly strong, plays a crucial role in the determining of crystal packing of **1**.

The molecule of **2** consists of two *N*-benzylpiperidine units linked by a diimine unit (–N=CH–C₆H₄–CH=N–) with the overall distance between piperidine nitrogen atoms of *ca* 15.78 Å. Unlike in **1**, the diimine unit is not perfectly planar; the dihedral angle between the plane of
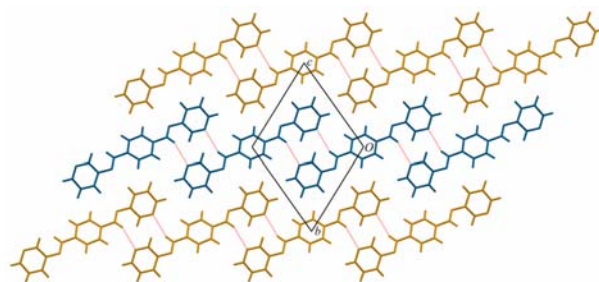
Figure 3. Crystal packing of **1** viewed along the *a* axis showing the one-dimensional hydrogen-bonded chains parallel to the [011] direction. The C–H···N interactions are drawn as dotted lines.[26]

the phenylene ring and the planes of the C–N=C–C bond is *ca* 8.28°. The piperidine ring is in the chair conformation with both the benzyl group and the imine group in equatorial positions. The distance between the imine nitrogen N1 and piperidine carbon C5 is 1.453(4) Å, negligibly shorter than the average for *N*-substituted piperidines. The bond lengths and angles of the piperidine ring are normal.[23]

Compound **2** crystallises in the triclinic system with one molecule per unit cell. (Table 1) The molecules are placed on crystallographic inversion centres. The piperidine nitrogen atom also acts as a hydrogen acceptor. However, instead of forming intermolecular contacts, hydrogen H12 of the phenyl ring is placed ca. 2.57 Å above the piperidine nitrogen thus forming an intramolecular C–H···N contact (C12–N2 distance of *ca* 2.677 Å and C12–H12···N2 angle of *ca* 99,6 °). This interaction causes the conformation of the molecule to take an elongated S-shape and renders the intermolecular C–H···N hydrogen bonding analogous to that in **1** impossible. Because of this the crystal structure comprises discrete molecules without any significant intermolecular interactions and of rather low density (1.150 g cm³). The non-existence of intermolecular C–H···N interactions in the structure of **2** allows for large thermal motion of the molecules in the structure transversal to the axis of the elongation of the molecules,
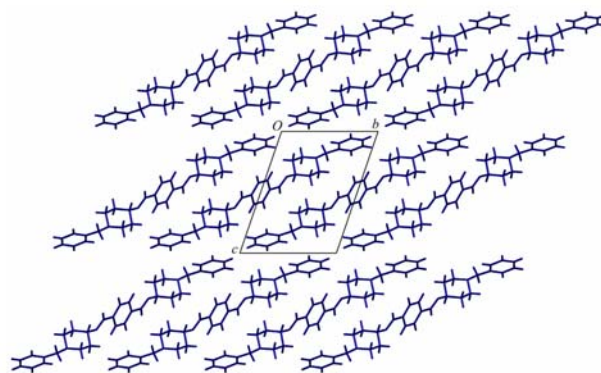
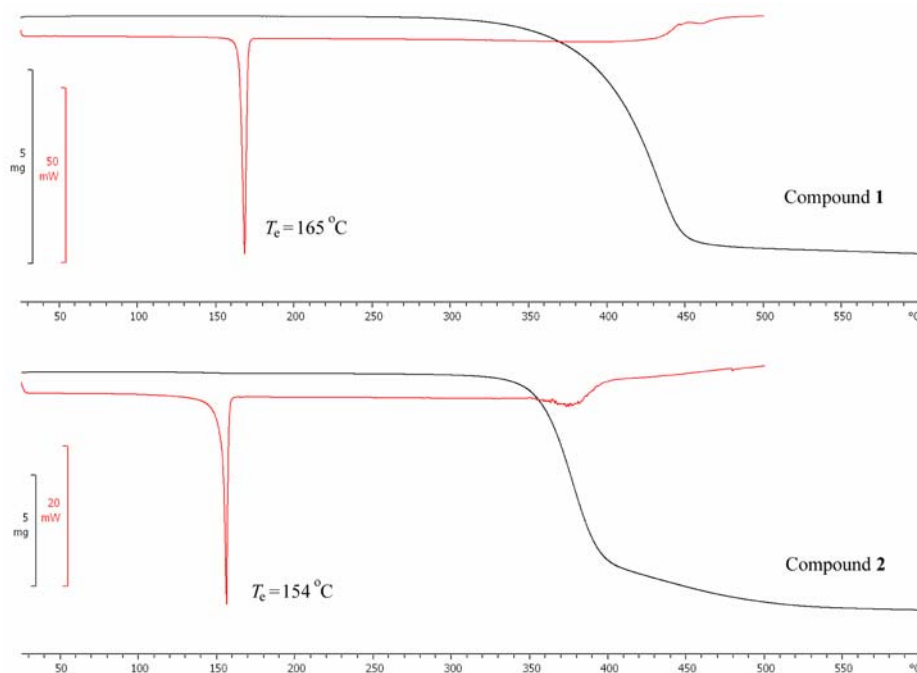**Figure 4.** Crystal packing of **2** viewed along the *a* axis.[26]

Figure 5. Thermal analysis (TGA and DSC) curves for **1** (top) and **2** (bottom)**.**

most visible by the thermal ellipsoids of the terminal phenyl rings.

Another consequence of the lack of intermolecular interactions in **2** is the rather low melting point of **2** in comparison to **1**, in spite of the fact that the molar mass of **2** (478.66 g mol^{-1}) is significantly higher that of **1** (286.33 g mol^{-1})·

For both compounds **1** and **2** the TG curve presents no obvious weight loss from 25 °C to 310 °C and 330 °C, respectively (Fig 5). The DSC curve of 1 shows one endothermic peak at 165 °C (40.7 kJ mol^{-1}), which corresponds to the compound melting point. In the range between 310 and 600 °C, a mass loss of 80% can be attributed to evaporation and pyrolytic decomposition. The DSC curve of **2** also shows one endothermic peak, but at lower temperature than that of **1**, 154 °C (38.7 kJ mol^{-1}), which also corresponds to the compound melting point. In the range between 330°C and 400 °C, a mass loss of 75% can be attributed to evaporation and after 400°C up to 600 °C a mass loss of 20% can be attributed to pyrolytic decomposition. The difference in fusion enthalpies of **1** and **2**, which are in direct connection to their respective lattice energies, can also be attributed to the intermolecular C–H···N interactions present in **1** and absent from **2**.

Nonisothermal melt-crystallisation DSC curves for **1** and **2** recorded at a cooling rate of 2 °C min^{-1} show one exothermic peak at 159 °C and 144 °C, respectively, which corresponds to the melt crystallisation. Both compounds were found by PXRD to crystallise from the melt into the same phase as from solution. There was no evidence of formation of another crystal form or amorphous phase, or of decomposition products. The metastable zone

upon melt-crystallisation of **2** (10 °C) is thus approximately double that of **1** (5 °C). This is also indicative of the effect of intermolecular interactions in **1**, leading to easier molecular aggregation and therefore faster nucleation compared to **2**.

4. Conclusions

In summary, we found that the ability to engage in C–H···N interactions greatly influences crystal structures as well as thermal properties of these symmetrical Schiff base diamines. The packing of molecules in the crystal structure of **1** is governed by intermolecular C–H···N interactions leading to one dimensional chains. Comparison of **1** with its "bridge flipped" isomer, which does not form C–H···N interactions in the solid state, shows that although **1** has lower density than its counterpart, its melting point is higher, which indicates that the C–H···N interaction presents an important contribution to the lattice energy. In the structure of **2**, intramolecular C–H···N interactions render the intermolecular C–H···N interactions impossible, which leads to a melting point and fusion enthalpy lower than those of **1**.

5. Acknowledgements

6. References

1. R. H. Holm, G. W. Everett, A. Chakravorty, *Progr. Inorg. Chem.* **1966**, *7,* 83–215 and references therein.

2. M. Calligaris, L. Randaccio, *Comprehensive Coordination Chemistry*, ed. R. L. Reeves, **1985**, *2,* 715–738 and references therein.

3. K. Amimoto, T. Kawato, *J. Photochem. Photobiol. C.* **2005**, *6,* 207–226 and references therein.

4. G. R. Desiraju, T. Steiner, *The weak hydrogen bond in structural chemistry and biology*, Oxford University Press, Oxford, **1999.**

5. M. Mazik, D. Bläser, R. Boese, *Tetrahedron Lett.* **2000**, *41,* 5827–5831.

6. Z. Berkovitch-Yellin, L. Leiserowitz, *Acta Cryst.* **1984**, *B40,* 159–165.

7. R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104,* 5063–5070.

8. Y.-B. Dong, M. D. Smith, H.-C. zur Loye, *Inorg Chem.* **2000**, *39,* 4927–4935.

9. Y.-B. Dong, M. D. Smith, H.-C. zur Loye, *J. Solid State Chem.* **2000**, *155,* 143–153.

10. H. N. Kim, H. K. Lee, S. W. Lee, *Bull. Korean Chem. Soc.* **2005**, *26,* 892–898.

11. D. Min, B.-Y. Cho, S. W. Lee, *Inorg. Chim. Acta* **2006**, *359,* 577–584.

12. C. He, L.-Y. Wang, Z.-M. Wang, Y. Liu, C.-S. Liao, C.-H. Yan, *J. Chem. Soc., Dalton Trans.* **2002**, 134–135.

13. Oxford Diffraction (2003), *CrysAlis CCD and CrysAlis RED*. Version 1.170. Oxford Diffraction Ltd, Wroclaw, Poland.

14. G. M. Sheldrick, SHELXS97, *Programs for Crystal Structure Analysis;* Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

15. G. M. Sheldrick, SHELXL93 – *Program for Crystal Structure Refinement*; Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1993.

16. L. J. Farrugia, WinGX, *J. Appl. Cryst.* **1999**, 32, 837–838.

17. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk). These data can be obtained free of charge from the Director upon request quoting the CCDC deposition number CCDC 682911 and CCDC 682912.

18. *Philips X'Pert Data Collector 1.3e*, Philips Analytical B. V. Netherlands, **2001.**

19. *Philips X'Pert Graphic & Identify 1.3e* Philips Analytical B. V. Netherlands, **2001.**

20. *Philips X'Pert Plus 1.0*, Philips Analytical B. V. Netherlands, **1999.**

21. *STAR^e Software V.9.01.*, MettlerToledo GmbH, 2006.

22. *OPUS 4.0*, Brucker Optik GmbH, 2003.

23. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, *J. Chem. Soc. Perkin Trans II* 1987, S1.

24. L. J. Farrugia, ORTEP-3 for Windows, *J. Appl. Cryst.* **1997**, 30, 565

25. Persistence of Vision Pty (2004). Persistence of Vision Raytracer (*POV-RAY*). Version 3.6. http://www.povray.org/download/.

26. Mercury 1.4, Copyright CCDC 2001 2005, 12 Union Road, Cambridge, UK.

27. W. H. Ojala, J. M. Smieja, J. M. Spude, T. M. Arola, M. K. Kuspa, N. Herrera, C. R. Ojala, *Acta Cryst.* **2007**, *B63,* 485–496.

Povzetek

S Schiffovo bazno kondenzacijo sta bila sintetizirana dva potencialna mostovna liganda, ki sta derivata tereftaldialdehida:1,4-bis((piridin-3-il-imino)metil)benzen (1) in 1,4-bis-((1-benzilpiperidin-4-il-imino)metil)benzen (2). Spojini sta bili karakterizirani z IR spektroskopijo, s termično analizo in z rentgensko praškovno ter strukturno analizo na monokristalih. Molekule (1) tvorijo 1D verige povezane z intermolekularno C–H···N vezjo. Konformacija molekule (2), ki jo določa intramolekularna C–H···N interakcija, preprečuje intermolekularne vezi kot jih opazimo v (1). Spojina (2) ima tako bistveno nižje tališče, četudi je molska masa (2) bistveno večja.