



Dedicated to Prof. Ion Grosu  
on the occasion of his 70<sup>th</sup> anniversary

## STRUCTURAL CHARACTERIZATION OF SOME SYMMETRIC BIS-IMINES\*\*

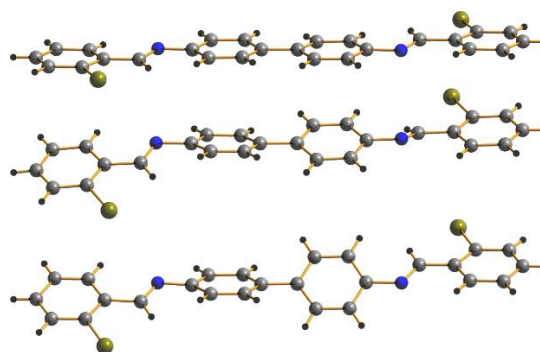
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The symmetric bis-imines [1,1'-{

4,4'-[(2-BrC<sub>6</sub>H<sub>4</sub>)CH=N]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}]<sub>2</sub> (**1**), [1,1'-{3,3'-(CH<sub>3</sub>)<sub>2</sub>-4,4'-[(2-BrC<sub>6</sub>H<sub>4</sub>)CH=N]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}]<sub>2</sub> (**2**) and 1,4-[(2-BrC<sub>6</sub>H<sub>4</sub>)CH=N]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**3**) were prepared by condensation of 2-bromobenzaldehyde with the appropriate diamines. The compounds were characterized in solution by <sup>1</sup>H, <sup>13</sup>C and two-dimensional NMR spectroscopy and mass spectrometry. For all derivatives, the presence of C=N double bonds was confirmed in solid-state by IR spectroscopy. Single-crystal X-ray diffraction analyses revealed the polymorphs for compound **1** and *E* configuration of substituents for all imine bonds.



### INTRODUCTION

The imines (or Schiff bases) are among the most important classes of organic derivatives<sup>1</sup> due to their utility in symmetric synthesis or coordination chemistry<sup>2</sup> ever since their first report by Hugo Schiff.<sup>3</sup> Imines are of interest in a variety of fields for their potential utility in medicinal chemistry,<sup>4–8</sup> material science,<sup>9–11</sup> synthesis of chiral amines,<sup>12</sup> as *C,N*<sub>imine</sub>-chelating ligands,<sup>13–16</sup> or as transient directing group in C–H functionalization.<sup>17</sup> Aromatic C–H bond activation on substituted imines can be achieved

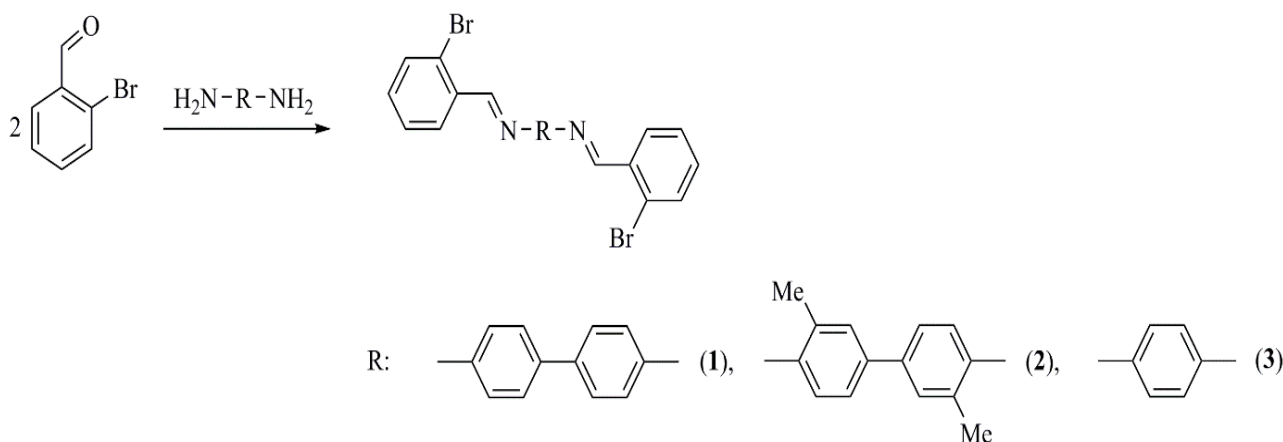
either with transition metal reagents<sup>18,19</sup> or with main group metal containing derivatives.<sup>20</sup> Metals can also be introduced on imine-containing aromatic substrates by oxidative addition of aryl-halogen bonds to metal reagents,<sup>21</sup> by metallation or metathesis pathways.<sup>22</sup> Schiff base containing organometallic derivatives can be prepared by derivatization of a carbonyl group from an organic moiety bonded to a metal<sup>23–26</sup> or by metal exchange reactions between a Grignard or organolithium reagent and a metal salt.<sup>16,27</sup> The imine function in main group metal organometallic compounds can lead to increased

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\*\* Supplementary information on <https://www.icf.ro/rrch/> or <https://revroum.lew.ro>

coordination number at the metal center<sup>24</sup> and stabilization of unusual species.<sup>28,29</sup>

Our interest in organometallic compounds containing ligands with imine functions impelled the synthesis and structural characterization of three symmetric bis-imines, *i.e.* [1,1'-{4,4'-(2-BrC<sub>6</sub>H<sub>4</sub>)CH=N]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}]<sub>2</sub> (**1**), [1,1'-{3,3'-(CH<sub>3</sub>)<sub>2</sub>-4,4'-(2-BrC<sub>6</sub>H<sub>4</sub>)CH=N]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}]<sub>2</sub> (**2**) and 1,4-[(2-BrC<sub>6</sub>H<sub>4</sub>)CH=N]<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**3**) to be used as proligands in obtaining new organometallic derivatives. Compounds **1** and **3** were previously mentioned in an scientific article without any analytical data, just as obtained intermediates for Schiff base cyclopalladated complexes.<sup>21</sup>



Scheme 1 – Synthesis of compounds **1–3**.

Compounds **1–3** were isolated as yellow, air- and moisture-stable solids, with good solubility in organic solvents. They were characterized by multinuclear NMR spectroscopy, and mass spectrometry, and satisfactory analytical results were obtained. For all species **1–3** the base peaks in the HRMS-APCI+ mass spectra are assigned to [M + H<sup>+</sup>] fragments. The IR stretching vibration of the carbon–nitrogen double bond in derivatives **1–3** appears in the region 1617–1609 cm<sup>-1</sup> as typical for compounds containing Schiff-base ligands.<sup>30</sup>

For compound **1**, three polymorph structures were determined from single-crystals suitable for X-ray diffraction obtained from toluene at room temperature over several days (**1a**), methanol (**1b**), and hot toluene (**1c**), respectively. Single-crystals suitable for X-ray diffraction for compounds **2** and **3** were obtained by slow diffusion of n-hexane into CH<sub>2</sub>Cl<sub>2</sub>. The molecular structures of these compounds are depicted in Figs. 1–3.

## RESULTS

The condensation reactions between 2-bromobenzaldehyde and 1,4-diamminobenzene, benzidine and 3,3'-dimethyl-4,4'-diammino-1,1'-biphenyl, respectively, which afforded (1*E*,1'*E*)-*N,N'*-([1,1'-biphenyl]-4,4'-diyl)bis(1-(2-bromophenyl) methanimine), (E,E')-biPh (**1**), (1*E*,1'*E*)-*N,N'*-(3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(1-(2-bromophenyl) methanimine), (E,E')-Me<sub>2</sub>biPh (**2**) and (1*E*,1'*E*)-*N,N'*-(1,4-phenylene)bis(1-(2-bromophenyl) methanimine), (E,E')-Ph (**3**), were carried out in toluene at boiling temperature using a Dean-Stark system for water elimination (Scheme 1).

## DISCUSSION

### Solid state structure

The structures of the three bis-imines share several similar features: (i) an aromatic center motif, a biphenyl fragment for **1** and **2** and a phenyl group for **3**, (ii) two *N*-(2-bromobenzylidene)imine fragments bonded in 4,4'-positions of the biphenyl core and *para*-positions of the phenyl ring, respectively, (iii) an *E* configuration of the substituents around each imine double bond, and (iv) a *trans* configuration of the organic fragments in regard to the central aromatic motif of the compounds.

Compound **1** crystallizes in three different forms dependent on the crystallization conditions. One polymorph is completely planar (**1a**, Table 1, Fig. 1d) and the other two forms are twisted. A moderate torsion of the phenyl rings from the biphenyl fragment is present in **1b** [20.09(14)°], while in **1c** the torsion in the central fragment is more pronounced [43.67(31)°]. This trend is also

preserved in the dihedral angles between the phenyl rings from the central biphenyl fragment and the

aromatic rings from the (2-bromobenzylidene)amine moieties (Table 1, Fig. 1d).

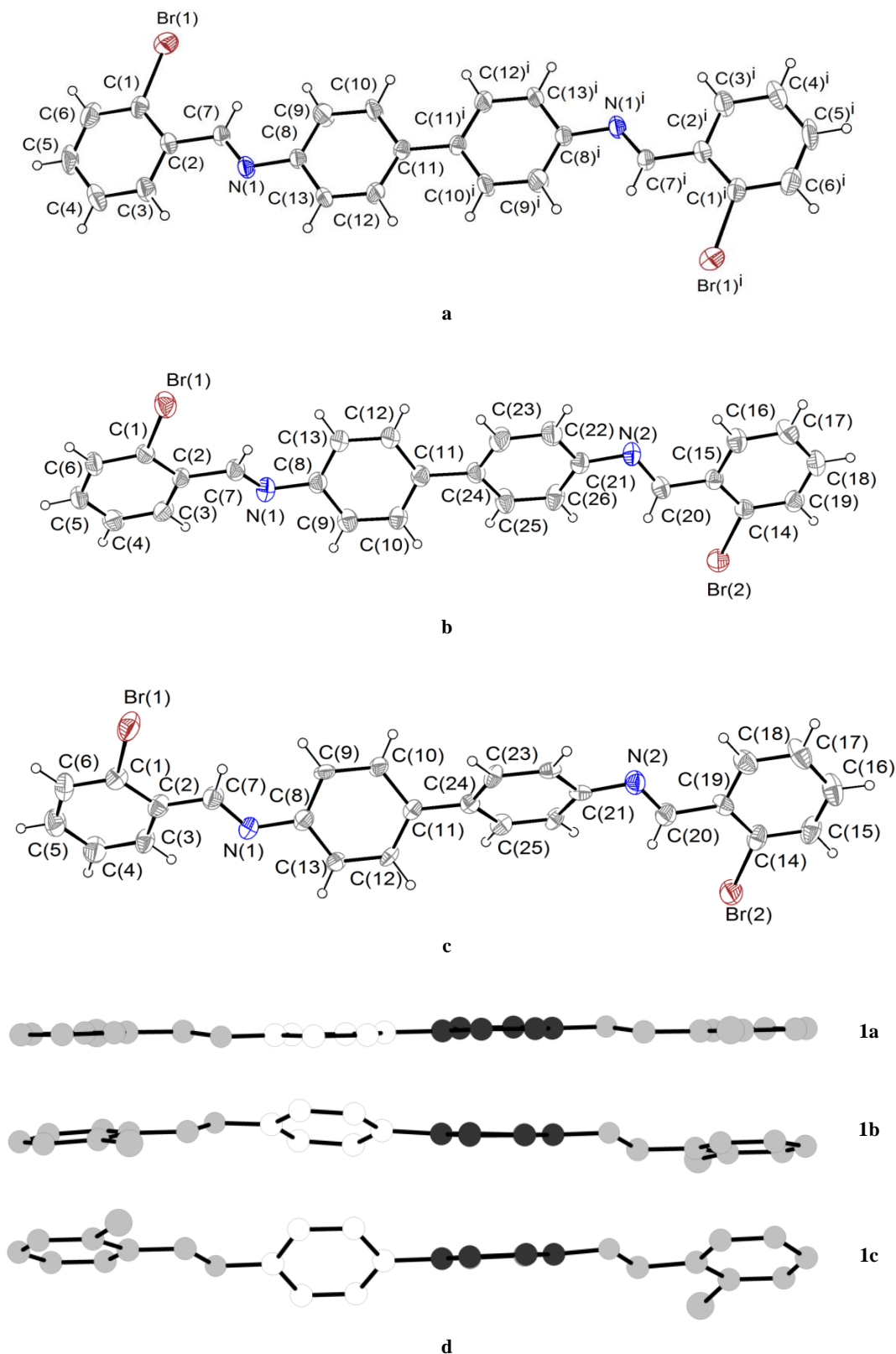


Fig. 1 – General view (ORTEP) of the molecular structure of: (a) **1a**, (b) **1b**, (c) **1c** showing 30% probability displacement ellipsoids and the atom numbering scheme and (d) side view of the three polymorphs of **1** showing the torsion in the molecules.

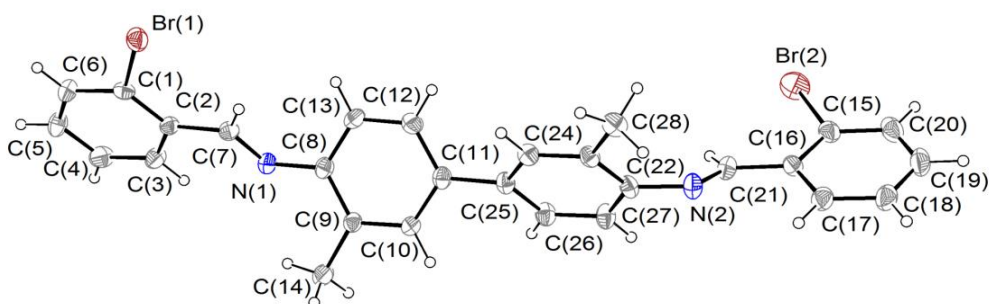


Fig. 2 – General view (ORTEP) of the molecular structure of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme.

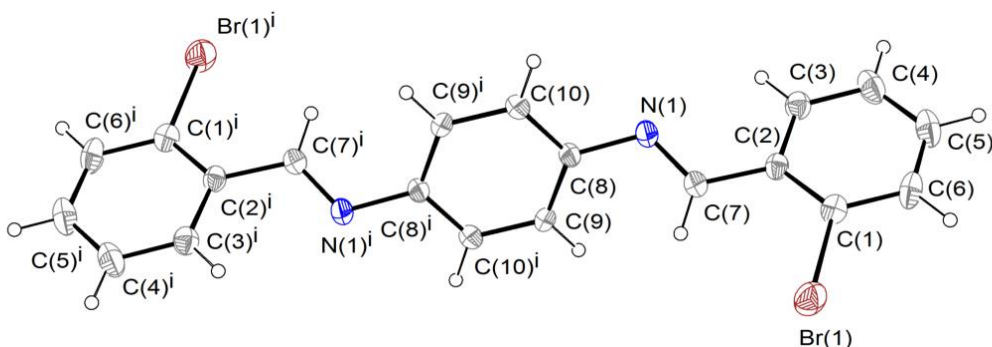


Fig. 3 – General view (ORTEP) of the molecular structure of **3** showing 30% probability displacement ellipsoids and the atom numbering scheme.

The geometry of **2** resembles the one found in the twisted structure of **1**. The dihedral angles and the angles formed by the planes generated by the phenyl rings have similar values as those observed in **1c** (Table 1).

The molecule of compound **3** is centrosymmetric with an inversion center in the middle of the central phenyl ring. The torsion between the phenyl rings is more pronounced than in the other compounds and is reflected in the dihedral angles (Table 1).

Table 1

Torsion angles (°) in E,E'-biPh (**1**), E,E'-Me<sub>2</sub>biPh (**2**), E,E'-Ph (**3**)

	<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>2</b>	<b>3</b>
plane1-plane2	0	26.04(14)	30.50(31)	38.22(18)	67.04(14)
plane2-plane3	0	20.09(14)	43.67(31)	43.92(17)	67.04(14)
plane3-plane4	0	7.08(14)	24.913(30)	73.07(20)	
C <sub>2</sub> -C <sub>7</sub> -N <sub>1</sub> -C <sub>8</sub>	179.47(94)	177.13(40)	178.46(10)	179.09(50)	174.74(41)
C <sub>12</sub> -C <sub>11</sub> -C <sub>24</sub> -C <sub>23</sub>	180.00(60)	19.00(70)	43.60(13)		
C <sub>15</sub> -C <sub>20</sub> -N <sub>2</sub> -C <sub>21</sub>	179.47(94)	179.43(39)	179.76(98)		
C <sub>16</sub> -C <sub>21</sub> -N <sub>2</sub> -C <sub>22</sub>				179.91(50)	
C <sub>10</sub> -C <sub>11</sub> -C <sub>25</sub> -C <sub>26</sub>				43.34(80)	

For **1b**, **1c**: plane 1: C(1)-C(6), plane 2: C(8)-C(13), plane 3: C(21)-C(26), plane 4: C(14)-C(19).

For **2**: plane 1: C(1)-C(6), plane 2: C(8)-C(13), plane 3: C(22)-C(27), plane 4: C(15)-C(20).

For **3**: plane 1: C(1)-C(6), plane 2: C(8)/C(9)/C(10)/C(8')/C(9')/C(10'), plane 3: C(1')-C(6').

A closer check of the crystal packing revealed the presence of intermolecular contacts which involve hydrogen atoms, including  $\pi$  interactions between hydrogen atoms and the aromatic rings present in the molecules.

Thus, molecules from the **1a** polymorph are double connected to the neighboring molecules through Br $\cdots$ H intermolecular interactions [Br(1) $\cdots$ H(10') = 2.966(7) Å,  $\Sigma_{r_{vdW}}(\text{H}, \text{Br}) \approx 3.15$  Å]<sup>31</sup> resulting in a zig-zag chain like arrangement stacked along the bisecting lines of axis *b* and *c* (Fig. 5).

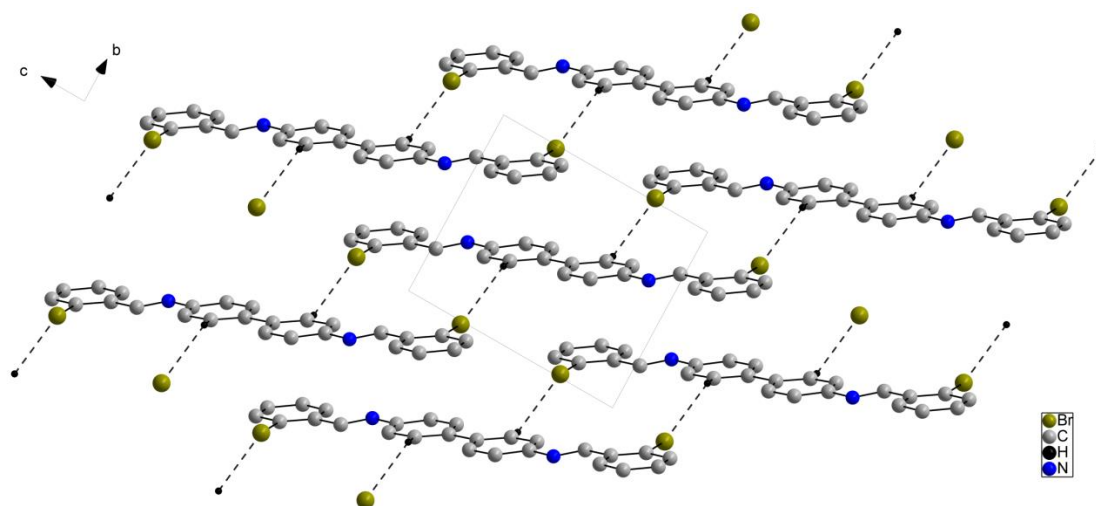


Fig. 5 – View along *a* axis of the crystal packing of **1a** showing the zig-zag chain like arrangement based on intermolecular bromine-hydrogen contacts (only hydrogen atoms involved in the interactions are shown).

In contrast, the structure of **1b** contains two intermolecular C–H $\cdots\pi$  stacking interactions. One stacking interaction is formed between the phenyl ring containing C(14)–C(19) carbon atoms (*Cg1<sub>1b</sub>*) and H(4) hydrogen from another molecule and one stacking interaction between the phenyl ring bonded to the bromide atom, formed by C(21)–C(26) carbon atoms (*Cg2<sub>1b</sub>*) and H(9) proton atom from a neighboring molecule [*Cg1<sub>1b</sub>* $\cdots$ H(4') = 2.694(2) Å, *Cg2<sub>1b</sub>* $\cdots$ H(9') = 2.862(2) Å, respectively], to form a zig-zag ribbon like arrangement (Figure S1), stacked along the *a* axis (See Supplementary material).

In the structure of polymorph **1c**, both Br $\cdots$ H and C–H $\cdots\pi$  intermolecular interaction are present. Weak hydrogen bond type intermolecular interactions between the bromide atom and hydrogen atoms from neighboring molecules lead to the formation of a head-to-tail dimer unit [Br(2) $\cdots$ H(5') = 3.028(14) Å] (Figure S3). The dimers are linked by C–H $\cdots\pi$  intermolecular interaction [*Cg1<sub>1c</sub>* $\cdots$ H(22') = 3.026(5) Å, *Cg2<sub>1bc</sub>* $\cdots$ H(13') = 3.046 Å, respectively; *Cg1<sub>1c</sub>* being the phenyl ring containing C(8)–C(13), *Cg2<sub>1c</sub>* being the phenyl ring containing C(22)–C(26)] in a ribbon like structure along the *a* axis (See Supplementary material).

Symmetric intermolecular H $\cdots\pi$  stacking interactions between the phenyl ring containing atoms C(22)–C(27) (*Cg1<sub>2</sub>*) and H(28C) proton from the neighboring molecule [*Cg1<sub>2</sub>* $\cdots$ H(28C') = 2.881(1) Å] connect the molecules in **2** in dimeric units (Fig. S5), strengthened by a weak hydrogen bond involving one of the bromine atoms and a hydrogen atom from the other molecule in the unit

[Br(1) $\cdots$ H(19') = 3.015(2) Å]. Dimers are further linked in a ribbon-like structure by weak intermolecular H $\cdots\pi$  stacking interactions between the phenyl ring containing atoms C(15)–C(20) (*Cg2<sub>2</sub>*) and H(4) proton from adjoining dimer units [*Cg2<sub>2</sub>* $\cdots$ H(4') = 2.969(1) Å] (See Supplementary material).

Two intermolecular H $\cdots\pi$  stacking interactions between the central phenyl ring [C(8)/C(9)/C(10)/C(8')/C(9')/C(10') = *Cg1<sub>3</sub>*] and one hydrogen atom from terminal phenyl ring of neighboring molecules [*Cg1<sub>3</sub>* $\cdots$ H(3'') = 2.793(2) Å] (Figure S7) result to the formation of a layer type supramolecular arrangement along the *bc* axis in **3** (See Supplementary material).

### Solution behavior

All compounds were investigated by multinuclear ( $^1\text{H}$  and  $^{13}\text{C}$ ) NMR. The assignment of the resonances in the NMR spectra was based on 2D NMR (HSQC, HMBC and COSY) correlation spectra (for the numbering schemes, see Supplementary material).

For all compounds both the  $^1\text{H}$  and  $^{13}\text{C}$  spectra show one set of resonances corresponding to half of each molecule, a behavior that is consistent with the symmetric nature of the compounds in solution. The chemical shifts of the –CH=N– hydrogen resonances in both  $^1\text{H}$  (8.93 ppm for **1**, 8.85 ppm for **2** and 8.91 ppm for **3**) and  $^{13}\text{C}$  (159.0 ppm for **1**, 158.1 ppm for **2** and 158.7 ppm for **3**) spectra, respectively, are in the region reported for similar compounds.<sup>32</sup>

Analysis of the IR spectra shows the characteristic bands for the imine group (–CH=N–)

stretching at 1617  $\text{cm}^{-1}$  for **1**, 1609  $\text{cm}^{-1}$  for **2** and 1613  $\text{cm}^{-1}$  for **3**, respectively. The absence of N-H stretching bands in the IR spectra of all compounds confirms the complete transformation of the amine in imine as the result of the condensation reactions.

## EXPERIMENTAL SECTION

Multinuclear NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$  and 2D) were recorded at room temperature on Bruker Avance 300 NMR spectrometer. The chemical shifts are reported in  $\delta$  units (ppm) relative to the residual resonance signal of the deuterated solvent (ref.  $\text{CDCl}_3$ :  $^1\text{H}$  7.26 ppm and  $^{13}\text{C}$  77.0 ppm).  $^1\text{H}$  and  $^{13}\text{C}$  resonances were assigned using 2D NMR experiments (COSY, HMQC and HMBC). The NMR spectra were processed using *MestReNova* software.<sup>33</sup> Mass spectra were recorded using a Thermo Scientific LTQ Orbitrap XL mass spectrometer equipped with a standard ESI/APCI source. Infrared spectra were recorded using a JASCO FT/IR-615 instrument. Melting points were measured using an Electrothermal 9200 apparatus and are not corrected. Chemicals of commercial grade were used without further purification.

### General procedure:

Two equivalents of 2- $\text{BrC}_6\text{H}_5\text{CHO}$  were added to one equivalent of diamine in 75 mL of toluene. The mixture was refluxed for 2 hours on an oil bath and the resulting water was collected using a Dean-Stark system. The hot solution was filtered, and the solvent was removed in vacuum. Recrystallization of the solid residue gave the desired product as a yellow solid.

**(1E,1'E)-N,N'-(1,1'-biphenyl)-4,4'-diylbis(1-(2-bromophenyl)methanimine)** (**1**): from 2- $\text{BrC}_6\text{H}_5\text{CHO}$  (4.46 ml, 7.14 g, 38.59 mol) and benzidine ( $\text{NH}_2\text{C}_6\text{H}_3\text{C}_6\text{H}_3\text{NH}_2$ ) (3.55 g, 19.29 mmol). Recrystallization from toluene on cooling gave 8.7 g (87%) of the desired product as yellow crystals. M.p. 187–189 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C): 7.33ddd (2H,  $H_5$ ,  $^3J_{\text{HH}}$  7.57 Hz,  $^4J_{\text{HH}}$  1.61 Hz), 7.36d (4H,  $H_9$ ,  $^3J_{\text{HH}}$  8.29 Hz), 7.43dd (2H,  $H_4$ ,  $^3J_{\text{HH}}$  7.58 Hz), 7.64d (2H,  $H_6$ ,  $^3J_{\text{HH}}$  7.90 Hz), 7.68d (4H,  $H_{10}$ ,  $^3J_{\text{HH}}$  8.34 Hz), 8.27dd (2H,  $H_3$ ,  $^3J_{\text{HH}}$  7.73 Hz,  $^4J_{\text{HH}}$  1.58 Hz), 8.93s (2H,  $H_7$ ).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ , 20 °C): 121.69s ( $C_9$ ), 126.09s ( $C_1$ ), 127.67s ( $C_{10}$ ), 127.71s ( $C_4$ ), 129.01s ( $C_3$ ), 132.39s ( $C_5$ ), 133.20s ( $C_6$ ),

134.51s ( $C_2$ ), 138.66s ( $C_{11}$ ), 150.70s ( $C_8$ ), 159.00s ( $C_7$ ). **HRMS-APCI** (m/z):  $[\text{M} + \text{H}^+]$  calcd for  $\text{C}_{26}\text{H}_{18}\text{Br}_2\text{N}_2$ , 518.98890; found, 518.99015. **IR**:  $\nu(\text{CH}=\text{N})$  1617  $\text{cm}^{-1}$ .

**(1E,1'E)-N,N'-(3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)bis(1-(2-bromophenyl)methanimine)** (**2**): from 2- $\text{BrC}_6\text{H}_5\text{CHO}$  (4.24 ml, 6.78 g, 36.6 mmol) and 3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine [ $\text{NH}_2(\text{CH}_3)\text{C}_6\text{H}_3\text{C}_6\text{H}_3(\text{CH}_3)\text{NH}_2$ ] (3.88 g, 18.3 mmol). Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{n-hexane}$  yielded 8.35 g (83.5%) of the desired product as yellow crystals. M.p. 176–178 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C): 2.47s (6H,  $H_{14}$ ), 7.09d (2H,  $H_{12}$ ,  $^3J_{\text{HH}}$  7.95 Hz), 7.34ddd (2H,  $H_5$ ,  $^3J_{\text{HH}}$  7.62 Hz,  $^4J_{\text{HH}}$  1.61 Hz), 7.44dd (2H,  $H_4$ ,  $^3J_{\text{HH}}$  7.48 Hz), 7.51m (4H,  $H_{13}$ ,  $H_{10}$ ), 7.65d (2H,  $H_6$ ,  $^3J_{\text{HH}}$  7.93 Hz), 8.32dd (2H,  $H_3$ ,  $^3J_{\text{HH}}$  7.74 Hz,  $^4J_{\text{HH}}$  1.6 Hz), 8.85s (2H,  $H_7$ ).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ , 20 °C): 18.5s ( $C_{14}$ ), 118.28s ( $C_{12}$ ), 125.36s ( $C_{13}$ ), 125.95s ( $C_1$ ), 122.77s ( $C_4$ ), 128.77s ( $C_{10}$ ), 129.01s ( $C_3$ ), 132.35s ( $C_5$ ), 132.77s ( $C_{11}$ ), 133.29s ( $C_6$ ), 134.75s ( $C_2$ ), 138.63s ( $C_9$ ), 149.72s ( $C_8$ ), 158.13s ( $C_7$ ). **HRMS-APCI** (m/z):  $[\text{M} + \text{H}^+]$  calcd for  $\text{C}_{28}\text{H}_{22}\text{Br}_2\text{N}_2$ , 547.02020; found, 547.02135. **IR**:  $\nu(\text{CH}=\text{N})$  1609  $\text{cm}^{-1}$ .

**(1E,1'E)-N,N'-(1,4-phenylene)bis(1-(2-bromophenyl)methanimine)** (**3**): from 2- $\text{BrC}_6\text{H}_5\text{CHO}$  (45.23 ml, 8.37 g, 45 mmol) and benzene-1,4-diamine ( $\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2$ ) (2.44 g, 22.5 mmol). Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{n-hexane}$  afforded 8.88 g (88.8%) of the desired product as yellow crystals. M.p. 148–150 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C): 7.32ddd (2H,  $H_5$ ,  $^3J_{\text{HH}}$  7.62 Hz,  $^4J_{\text{HH}}$  1.74 Hz) 7.34s (4H,  $H_9$ ), 7.42dd (2H,  $H_4$ ,  $^3J_{\text{HH}}$  7.53 Hz) 7.63dd (2H,  $H_6$ ,  $^3J_{\text{HH}}$  7.87 Hz) 8.26dd (2H,  $H_3$ ,  $^3J_{\text{HH}}$  7.74 Hz,  $^4J_{\text{HH}}$  1.68 Hz), 8.91s (2H,  $H_7$ ).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ , 20 °C): 122.12s ( $C_9$ ), 126.07s ( $C_1$ ), 127.69s ( $C_4$ ), 128.97s ( $C_3$ ), 132.36s ( $C_5$ ), 133.19s ( $C_6$ ), 134.50s ( $C_2$ ), 149.92s ( $C_8$ ), 158.69s ( $C_7$ ). **HRMS-APCI** (m/z):  $[\text{M} + \text{H}^+]$  calcd for  $\text{C}_{20}\text{H}_{14}\text{Br}_2\text{N}_2$ , 442.95760; found, 442.95896. **IR**:  $\nu(\text{CH}=\text{N})$  1613  $\text{cm}^{-1}$ .

### Crystal structures

The details of the crystal structure determination and refinement are given in Tables S1 (See Supplementary material). The crystals were mounted on cryoloops and data were collected with a Bruker SMART APEX diffractometer using graphite-monochromated Mo-K  $\alpha$  radiation ( $\lambda =$

0.71073 Å) at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.<sup>34</sup> The drawings were created using the Diamond program.<sup>35</sup>

## CONCLUSION

The synthesis of three bis-imines is reported. Solid state single crystal X-ray diffraction studies of the compounds show the presence of *E* configuration of the substituents around each imine double bond. The three polymorphs found for compound **1** show different degrees of torsion in the molecules. In the crystal, all the compounds form intermolecular contacts resulting in different levels of aggregation, *i.e.* chain-like structure for **1a**, ribbon arrangement for **1b**, **1c** and **2**, and a layer supramolecular structure for **3**. The solution NMR spectra confirm the formation of the bis-imines showing the resonance signals for the specific Schiff base fragment in the expected regions. The compounds were envisioned as proligands and will be used to obtain novel organometallic derivatives.

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### Supplementary data.

CCDC 2418174-2418178 contain the supplementary crystallographic data for **1–3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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