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A. Reyes[a]; J. NÁjera[a]; R. Mendoza[a]; E. Molins[b]; I. Grau[b]; E. Espinosa[b]; H. Salgado[a]; J. Tamariz[a]; M. Soriano[c]; K. Panneerselvam[c]

[a] Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, IPN, México, D.F [b] Institut de Ciència de Materials de Barcelona, Bellaterra, España [c] Instituto de Química, Universidad Nacional Autónoma de México, México, D. F.

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Bisimines in Supramolecular Synthesis

A. REYES[a,*], J. NÁJERA[a], R. MENDOZA[a], E. MOLINS I GRAU[b], E. ESPINOSA[b],
H. SALGADO[a], J. TAMARIZ[a], M. SORIANO[c] and K. PANNEERSELVAM[c]

[a] *Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, IPN. Prolongación de Carpio y Plan de Ayala S/N. Col. Santo Tomás, 11340 México D. F;* [b] *Institut de Ciència de Materials de Barcelona. Campus de la UAB, 08193-Bellaterra, España;* [c] *Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria Coyoacán 04510, México, D. F*

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Aldimines, but not ketimines, are complexed with hydroquinone or *meso*-hydrobenzoin to give a supramolecular structure. A bisimine aromatic ring is an indispensable condition for this type of complexation. When hydroquinone is complexed with a bisimine carrying a central aliphatic chain with more than two methylenes, a complex with a liquid crystal structure resemblance is formed.

Keywords: C—H...π interactions, bisimines, supramolecules, crystal engineering

Interest amongst researchers towards supramolecular synthesis lies on two fundamental reasons. The first is the utility conferred to supramolecular structures by very special physical and chemical properties coupled to a tight relationship with biological systems [1]. The second is the search for new horizons to widen the scope of synthetic chemistry [2].

Various noncovalent bonding interactions have been utilised in the synthesis of supramolecules [3-6]. Hydrogen bonding is the most important of such interactions, hence it is not surprising that it has been most widely used in supramolecular synthesis [6]. Different types of hydrogen bonds are involved in supramolecular building [7], *i.e.*, from functional group pairs such as amines and alcohols [8], amide or amines and carbonylic compounds [9], ammonium salts and crown ethers [4], hydroquinone and quinone [10], *etc.* However the synthons imine-alcohol or imine-phenol have been little studied [8, 11]. Sustmann *et al.*, initiated the study of supramolecular synthesis using bisimines and *meso*-1, 2-diphenyl-1,2-ethanediol (*meso*-hydrobenzoin) [11a]. Ermer and his group have reported the complexation between hydroquinone and 1,4-bisisopropylenediaminobenzene [8].

Bisimines 1-14 were selected in order to investigate the possibility of complex formation with hydroquinone and *meso*-hydrobenzoin. Table I shows the cocrystallization complexes obtained from bisimines and hydroquinone or *meso*-hydrobenzoin [12]. As expected the supramolecular structures obtained with hydroquinone formed stronger hydrogen bonds than the

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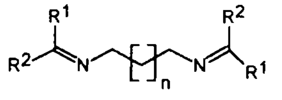
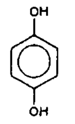
*Corresponding author.

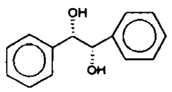
ones obtained with *meso*-hydrobenzoin. The cocrystallisation of hydroquinone with bisimines **1**, **3**, **4** and **9** gave solid crystalline structures with melting points very different from that of the starting material.



R^1	R^2	n	Bisimine
C_6H_5	H	0	1
$4\text{-}CH_3C_6H_4$	H	0	2
$4\text{-}(CH_3)_2CHC_6H_4$	H	0	3
$4\text{-}CH_3OC_6H_4$	H	0	4
$4\text{-}(CH_3)_2NC_6H_4$	H	0	5
$4\text{-}NO_2C_6H_4$	H	0	6
C_6H_5	H	1	7
C_6H_5	H	6	8
$C_6H_5CH{=}CH$	H	0	9
$C_{10}H$-(naphthyl)	H	0	10
n-C_5H_{11}	H	0	11
C_6H_{11}	H	0	12
CH_3	CH_3	0	13
C_6H_5	C_6H_5	0	14



Hydroquinone



meso-Hydrobenzoin

TABLE I Supramolecules obtained from bisimines **1–14** with hydroquinone or *meso*-hydrobenzoin

Bisimines	Hydroquinone	*meso*-Hydrobenzoin
1	(+) **I**[13]	(+) **VII**[11a]
2	(−)	(+) **VIII**
3	(+) **II**	(+) **IX**[21]
4	(+) **III**[14]	(+) **X**
7	(+) **IV**	(−)
8	(+) **V**	(−)
9	(+) **VI**	(+) **XI**[22]

Figure 1 and 2 show the polymeric complexes formed between bisimine **1** and **3** with hydroquinone, respectively. These are cases of molecular recognition [3] which is expressed as a hydrogen bonding arrangement, consequently in complex **I** and **III** equal and unequal molecules stack together in a very orderly fashion but the motif of each structure is different from the other.

Similarly as it occurs in other planar supramolecular complexes [15], a small variation in a structural subunit causes a deep variation in the final complex structure. Thus, introduction of a methoxy group at the 4-position of the bisimine aromatic ring (**4**) led to a supramolecular structure very different from that obtained with bisimine **1** and hydroquinone. Figure 2. A structure with cavities was thus afforded which suggests this can be a strategy for the engineering of porous organic crystals (*cf.* the clathrate formed from hydroquinone, methanol and acetonitrile) [16].

Hydrogen bonding is not the only intermolecular interaction that makes supramolecular formation possible; there is evidence of other participating intermolecular interactions. Thus, $\pi-\pi$ interactions are observed in the X-ray analysis of complex **III**, Figure 2. The presence of the hydroquinone π deficient oxygen linked to a π excessive aromatic ring, the bisimine **1** π deficient aromatic ring due to the $C{=}N$ group, coupled to the attained angle of 43.7(0)° formed between the planes of the hydroquinone and the bisimine aromatic ring strongly suggest the existence of $\pi-\pi$ interactions as well [17]. (Fig. 1).

Other intermolecular forces [C—H…O] and [C—H…N] in these complexes comprise interactions between bisimine C-3 and hydroquinone O1S and between bisimine C-1 and hydroquinone O1S in complex **I**, Figure 1, and between hydroquinone C-3S and the bisimine N and the bisimine C-7 and the methoxy group O1 and the bisimine C-6 and hydroquinone O1S in complex **III**, Figure 2.

Distances and angles values caused by these intermolecular contacts are similar to others reported in the literature [18]. Although the nature of these interactions is controversial [19], they are thought to be electrostatic, the more acidic, *ortho* protons to electronwithdrawing

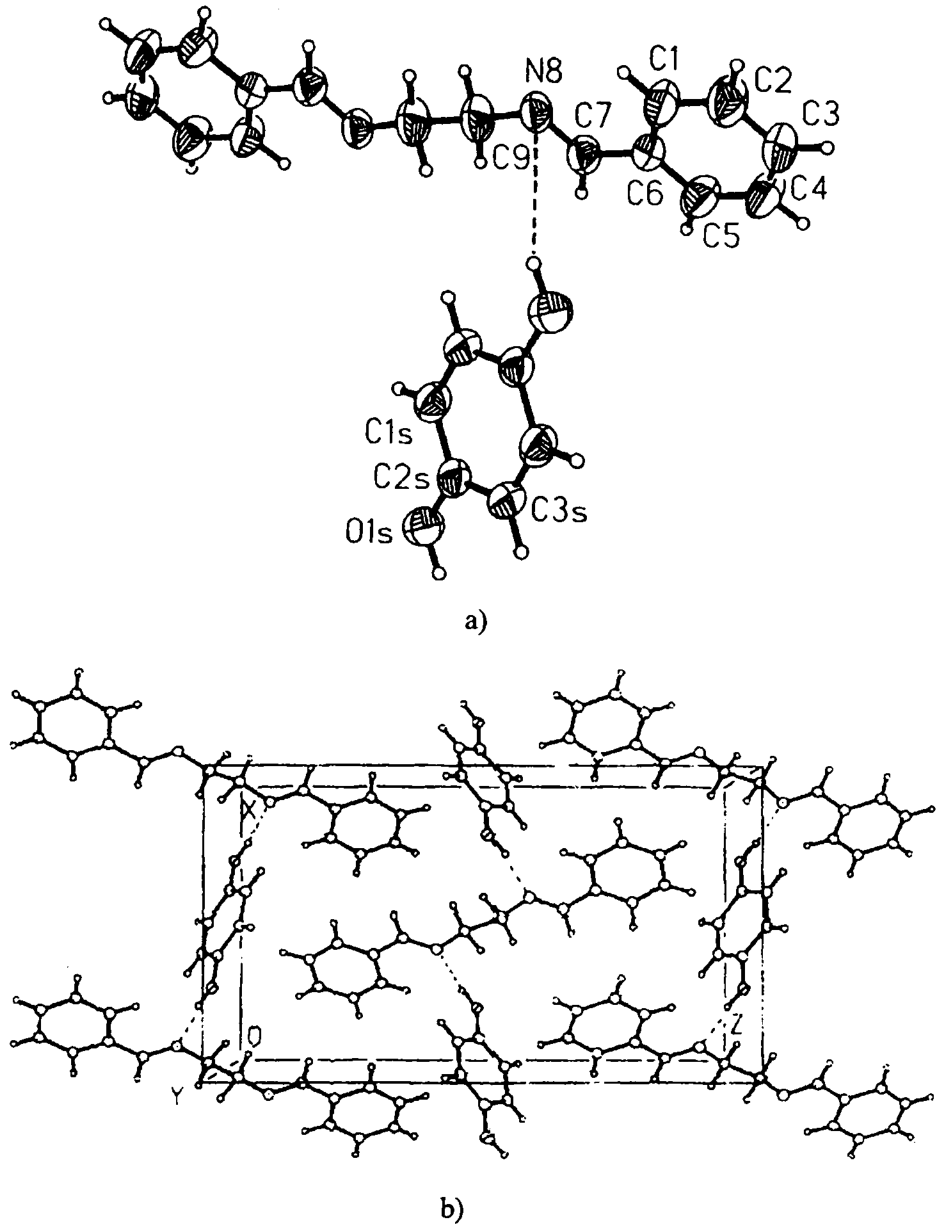


FIGURE 1 Single-crystal structure of *N,N-bis*(benzylidene)ethylenediamine (1) and Hydroquinone. (a) Monomers, (b) Complex I.

groups are the ones participating in them [18]. The latter are observed in complex I. Strikingly interactions amongst protons *ortho* to electron releasing groups are seen in the complex III as well. *i.e.*, interactions between C-7 *ortho* to the methoxy group of bisimine 4 and the methoxy O group of another bisimine and interaction between C-3S *ortho* to the hydroquinone OH and the bisimine N. To our best of knowledge this type of bonding amongst protons *ortho* to electron releasing groups had not been found.

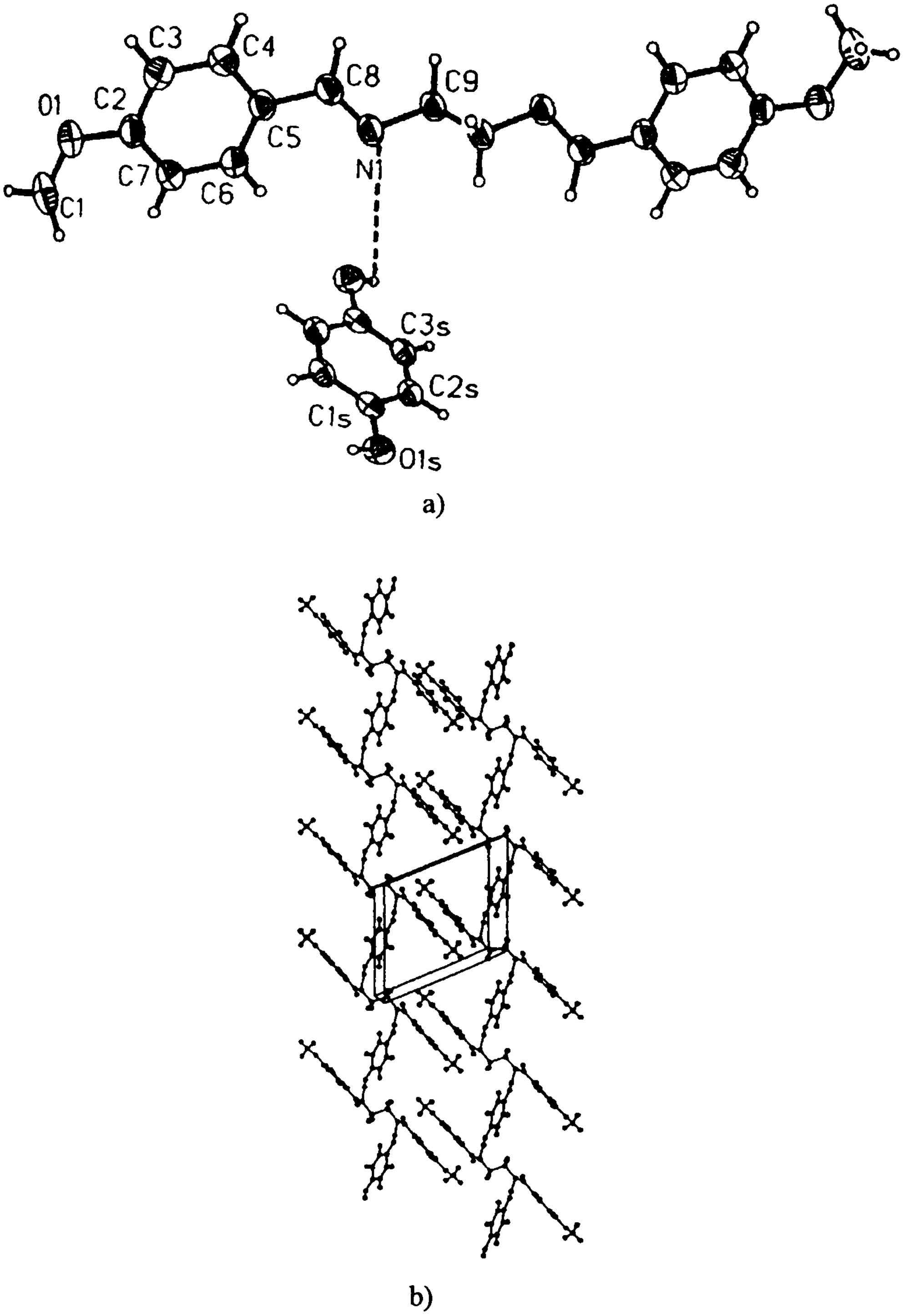


FIGURE 2 Single-crystal structure of *N,N-bis*(4-methoxybenzylidene)ethylenediamine (**4**) and Hydroquinone. (a) Monomers (b) Complex III.

Complexation of hydroquinone with bisimines **7** and **8** did not give solid supramolecular structures, but instead a substance that might have a mesomorphic phase (structures **IV** and **V**). Thus, the obtained substances gave a strong hydrogen bond in the ATR spectrum and preliminary DSC studies showed a phase change in structure **IV**. Besides, it is known that some aldimines yield liquid crystals [20].

Cocrystallization of bisimines **2**, **3** and **4** with *meso*-hydrobenzoin yielded supramolecules **VIII**, **IX** and **X** as crystalline solids. Similarly the conjugated bisimine **9** gave the corresponding supramolecule **XI**. X-ray diffraction structures of supramolecules **IX** and **XI** [21, 22] obtained from bisimine **3** and **9** with *meso*-hydrobenzoin respectively, are shown in Figures 3 and 4. These structures stack in a very orderly fashion forming

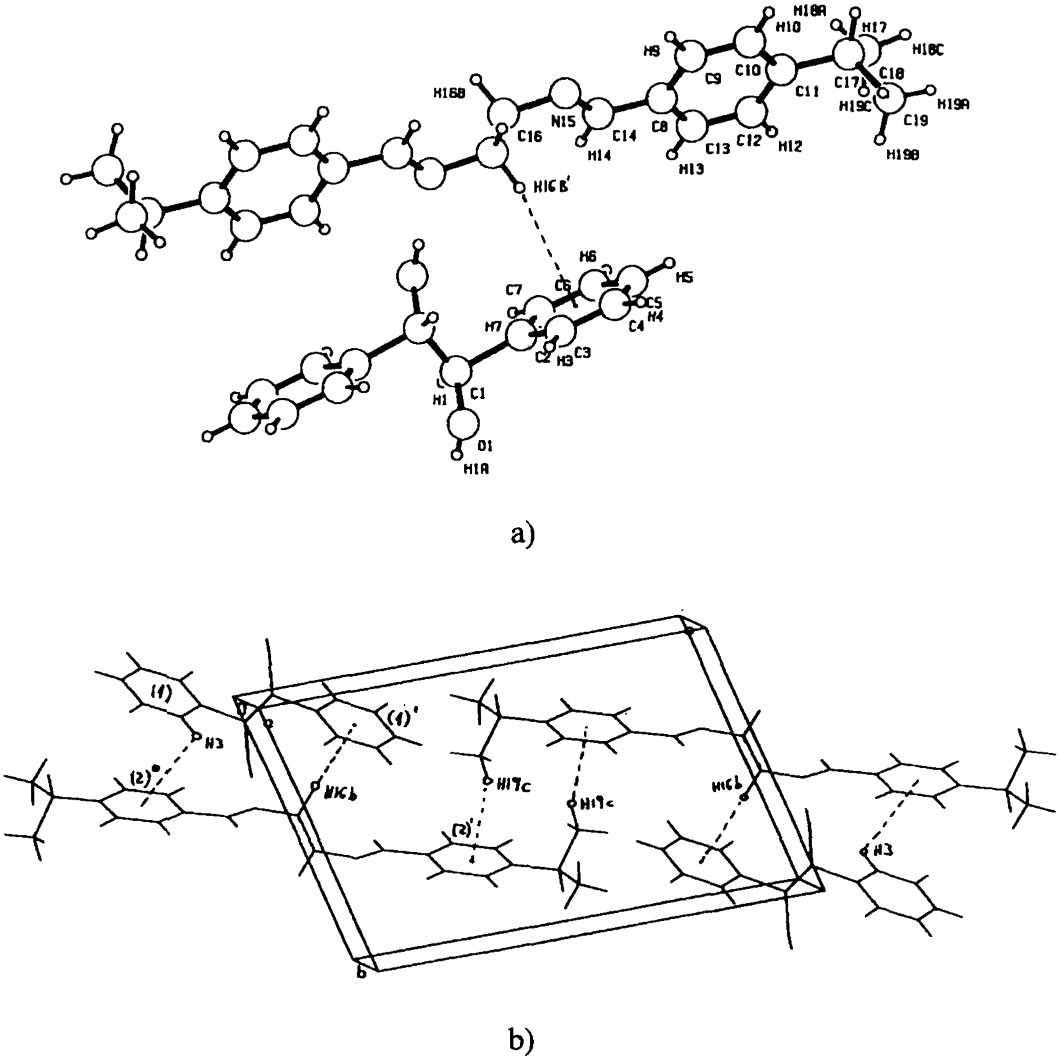


FIGURE 3 Single-crystal structure of *N,N-bis*(4-methylethylbenzylidene)ethylenediamine (3) and *meso*-hydrobenzoin. (a) Monomers (b) Complex XI.

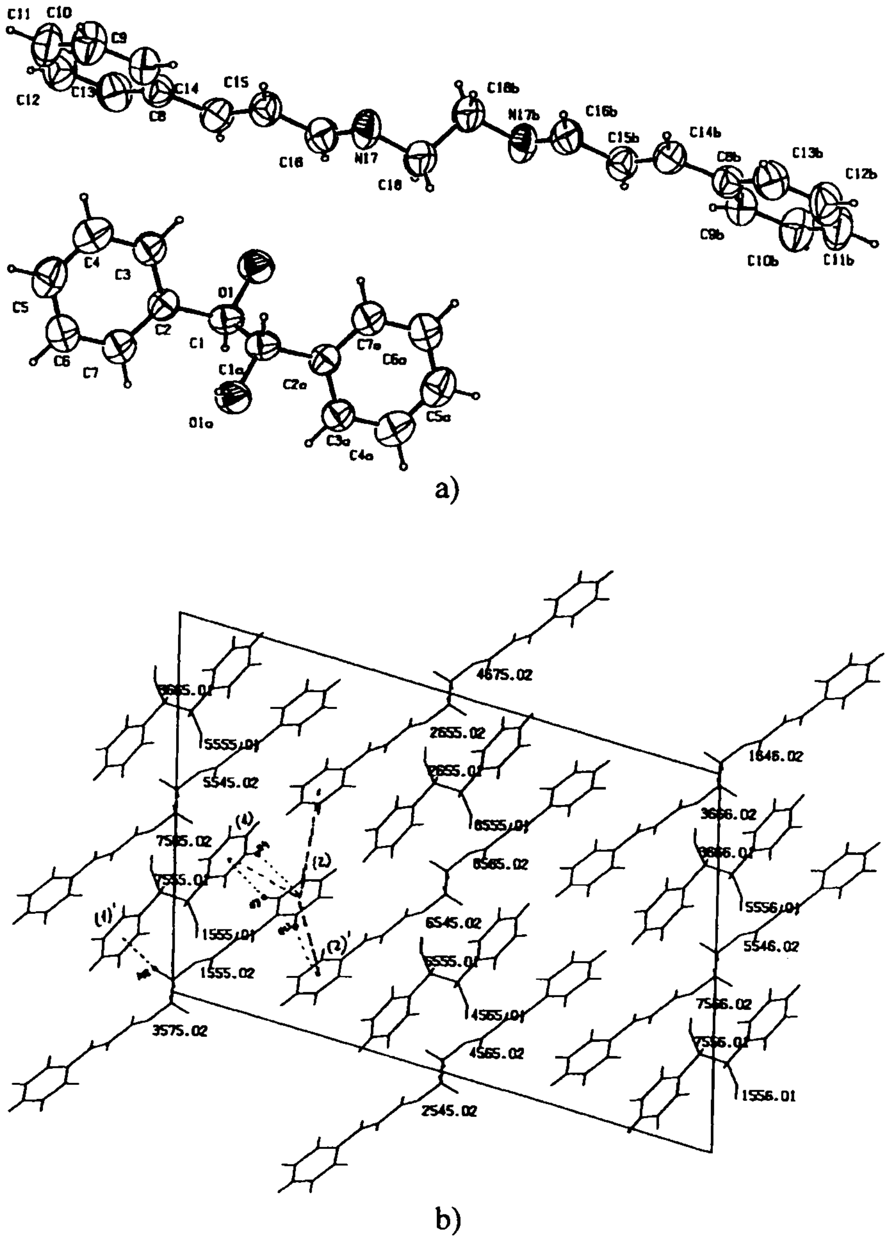


FIGURE 4 Single-crystal structure of *N,N-bis*(cinnamylidene)ethylenediamine (9) and *meso*-hydrobenzoin. (a) Monomers (b) Complex **XI**.

a network, due to C—H-π interactions which are observed in **IX** between H-19C of the bisimine isopropyl and the aromatic ring of another bisimine, between *meso*-hydrobenzoin H-3 and the bisimine phenyl and finally between the bisimine H-16C and the *meso*-hydrobenzoin aromatic ring. On the other hand supramolecule **XI** showed C—H-π interactions between the *meso*-hydrobenzoin H-4 with the bisimine aromatic ring. The bisimine H-9 with other bisimine aromatic ring. The weak interactions (enthalpy for C—H-π interactions is 1 Kcal/mol approximately) should favour the supramolecular structure, because they are numerous and entropycally advantageous [23].

The steric and complementary electronic effects between bisimines and hydroquinone or *meso*-hydrobenzoin are similar amogst them. Then what happens in the case where no complexation exists?

To answer this question, it is convenient to classify the investigated bisimines as follows:

- The non polar or low polarity aldimines
  - aliphatic (bisimine **11** and **12**)
  - aromatic (bisimines **1**, **2**, **3**, **4**, **7**, **8**, **9** and **10**)
- The polar aldimines (bisimines **5** and **6**)
- The ketimines
  - the aliphatic ketimine (bisimines **13**)
  - the aromatic ketimine (bisimines **14**)

The aliphatic bisimines do not have enough possibilities for intermolecular interactions, they can only form hydrogen bonding between the =N— and O—H groups and have van der Waals attractive forces, but devoid of $\pi-\pi$, C—H...X and another interactions.

Sustmann has reported the complexation of an aliphatic aldimine obtained from glyoxal and 2,4-dimethyl-3-pentylamine with *meso*-hydrobenzoin [11a]. In this case conjugation between two imino groups is present, then, in spite that the aldimine does not posses aromatic ring, the possibility of dipole-dipole and $\pi-\pi$ interactions exists.

Poor solubility of polar **5** and **6** bisimines in usual solvents as compared with hydroquinone was a restrictive factor to obtain supramolecular structures. Furthermore self assembling in bisimine **6** through [C—H...O] intermolecular interactions, between the C-3 and the nitro group O-12 is observed. Most probably the addition of these interactions is greater than those between bisimines and hydroquinone or *meso*-hydrobenzoin.

Ketimines **13** and **14** did not yield supramolecules in contrast with Ermer former results [8], in which, 1,4-bisisopropylenediaminobencene did complex with hydroquinone. In this case complexation was due probably to the presence of an aromatic ring, consequently a high conjugation and the possibility of $\pi-\pi$ interactions, characteristics which are absent in ketimine **13**. However the same reasoning does not apply to ketimine **14**.

In conclusion, aldimines, but not ketimines, are complexed with hydroquinone or *meso*-hydrobenzoin to give a supramolecular structure. It seems that a bisimine aromatic ring is an indispensable condition for this type of complexation. When hydroquinone is complexed with a bisimine carrying a central aliphatic chain with more than two methylenes, a complex with a liquid crystal structure resemblance is probably formed. In the present study a cooperative effect between different types of intermolecular interactions in supramolecular building was observed. Thus weak [C—H...N] bonds can be used in crystal engineering and supramolecular construction Complexation of *N,N*-bis-(4-methoxybenzylidene)ethylenediamine with hydroquinone might be a strategy for the design of porous organic crystals, currently under further investigation.

Acknowledgements

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[12] General procedure for supramolecular synthesis. Equimolecular quantities of bisimine and hydroquinone or *meso*-hydrobenzoin are mixed up to obtain an homogenous mixture, then ethyl acetate is gradually added until the solid is totally dissolved. The solution is protected from light and allowed to crystallize in a hexane atmosphere. After 4 - 6 days the formed crystals are collected by filtration and washed with cold hexane. The crystals are dried 24 hours in a desiccator before being characterized.

[13] Crystallographic data have been published In: Pannerselvam, K., Soriano-Garcia, M., Reyes-Arellano, Tamariz-Mascarúa and Mendoza-Sánchez, R. I. (1996). *Analytical Sciences*, **12**(5), 823.

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[21] Data of a crystal of supramolecule **IX**: Crystal size 0.34 × 0.22 × 0.13 mm; Crystal system = triclinic; Space Group P-1; Cell dimensions; a = 5.878(2) A; b = 9.388(2) A; c = 14.869(3) V = 772.5(3) A^3; α = 75.45(2); β = 87.12(2); γ = 76.58(2) Z = 1; ρcal = 1.149 mg/m^3.

[22] Data of a crystal of supramolecule **XI**: Crystal size 0.45 × 0.17 × 0.10 mm. Crystal system Monoclinic; Space Group C 2/c; Cell dimensions a = 18.619(3) A; b = 5.734 (1) A; c = 27.985(2) A; V = 2875.7(7)A^3; β = 105.74(1) Z = 8; ρcal = 1.161 mg/m^3.

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