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Racemate resolution via diastereomeric helicates in hydrogen-bonded co-crystals: the case of BINOL–diamine complexes

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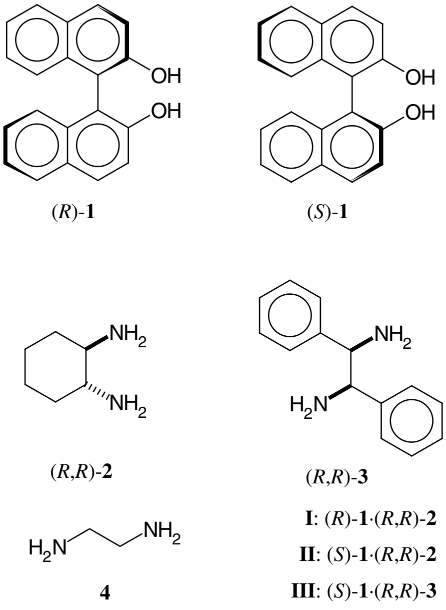
Abstract—The structures of a series of co-crystals formed by enantiomers of BINOL (2,2′-dihydroxy-1,1′-binaphthalene) with (*R*,*R*)-1,2-diaminocyclohexane (DACH) and (*R*,*R*)-1,2-diamino-1,2-diphenylethane have been determined by X-ray diffraction to investigate the factors responsible for diastereoselective co-crystallization, the process responsible for the highly effective resolution of *rac*-BINOL by DACH. The absolute configurations of the molecules and directional preferences of the hydrogen bonds in the supramolecular aggregates have been analyzed. The supramolecular aggregation of hydrogen-bonded BINOL and diamines shows considerable distortions from the helical shape, which indicates that cohesion forces other than hydrogen bonds play a significant role in the diastereoselective resolution.

1. Introduction

Derivatives of 2,2′-dihydroxy-1,1′-binaphthalene **1** (BINOL: Scheme 1) are among the best and the most useful chiral inducers in stoichiometric and catalytic asymmetric reactions.[1] Specific applications of BINOL and its derivatives as chiral ligands and chiral auxiliaries for enantioselective reactions are too numerous to be listed exhaustively. Some examples mentioned here are asymmetric hydrogenation,[2] asymmetric reduction with BINAL,[3] asymmetric Diels–Alder[4] and aza Diels–Alder reactions,[5] asymmetric ene reactions,[6] asymmetric allylic substitutions,[7] asymmetric conjugate additions,[8,9] asymmetric hydroformylations,[10] asymmetric alkylations,[11] asymmetric oxidations,[12] asymmetric epoxidations,[13] asymmetric aldol[14] and nitroaldol reactions,[15] asymmetric protonation of enols,[16] and asymmetric cyclization of polyprenoids.[17] Other uses of BINOL include the preparation of BINAP,[18] a very useful chiral diphosphine ligand developed by Noyori, chiral 1,1′-binaphthyls,[19] chiral crown ethers,[20] chiral poly(1,1′-bi-2-naphthols),[21] chiral stationary phases for HPLC,[22] chiral chromogenic receptors[23] and chiral materials for nonlinear optics.[24] BINOL has also been used as a chiral solvating agent for the determination of the enantiomeric excess of scalemic compounds.[25]



Scheme 1.

Enantiomerically pure BINOL has been prepared by a number of methods,[26] which can be grouped into three categories. Firstly, covalent diastereoisomeric derivatives of racemic BINOL have been resolved enzymatically,[27] or by crystallization of the borate complex with proline,[28]

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its cyclic borate ester with an alkaloid[29] or α-methylbenzylamine,[30] salts of its cyclic phosphoric diester with cinchonine,[31] or α-methylbenzylamine[32] or 2-aminobutanol,[33] its mixed phosphate ester with menthol[34] and by crystallization of diastereomeric camphorsulfonates.[35] These methods often suffer from lengthy procedures due to first making the BINOL derivative and subsequently removing the resolving agent and/or hydrolyzing the derivative.

Alternatively, BINOL can be deracemized by a second-order asymmetric transformation using copper(II) chloride and a chiral amine.[36,37] This process is usually coupled with the oxidative dimerization of 2-naphthol, but its chiral efficiency is not very high. Recent examples have shown that the oxidative coupling of 2-naphthol in the presence of chiral oxovanadium(IV) complexes can provide **1** with up to 91% ee.[38–40]

Enantiomerically pure BINOL cannot be readily obtained by direct crystallization of scalemic samples, as it forms a racemic compound.[37] A solution to this problem is the use of diastereoselective co-crystalization with a number of chiral hosts, including chiral sulfoxides,[41] proline,[42] aminoalcohols,[43] a diamide of tartaric acid,[44] *N*-alkylcinchoninium halides,[45] *N*-benzylcinchonidinium chloride,[46] and *trans*-1,2-diaminocyclohexane **2** (DACH).[47] Co-crystallization of BINOL with enantiomerically pure DACH is of particular significance, since the host is readily available commercially, the procedure is very simple, both enantiomers of BINOL can be obtained using only one enantiomer of DACH and the chiral efficiency of crystallization can be increased up to 160% of one enantiomer of DACH, if the crystallization is combined with thermal epimerization of BINOL in the mother liquor.

In view of the significance of this process, and the process of the diastereoselective co-crystallization in general, we started a study of chiral recognition in the co-crystallization of **1** and **2**. This work is based primarily on the analysis of crystal structures of molecular complexes **1** with **2** and related amines, such as **3** and **4**. The issues addressed in this study are the factors responsible for the process of co-crystallization, in particular the role of the hydrogen bonds as well as the role of van der Waals interactions. In this study we intend to compare the strength of the hydrogen bonds with the solubility of the co-crystals, as well as molecular configurations with the directions of hydrogen bonds and with the structures of the helices. We will show that these factors can help us to understand the diastereoselectivity of co-crystallization at the structural level.

2. Results and discussion

2.1. Association of BINOL and amines in solution

We initially intended to examine the process of chiral discrimination in the complex formation between DACH and BINOL in solution, using ^{1}H NMR measurements. We were able to detect the formation of a complex between **1** and **2** in $CDCl_3$ solution, but unlike in the case of a chiral bis-oxazoline:**1** system studied earlier,[50] no separate signals of OH protons due to (*S*)-**1** and (*R*)-**1** on addition of (*R*,*R*)-**2** were observed. In fact, the signals of OH protons of **1** at δ ca. 5.0 and the signals of NH_2 protons of **2** at ca. 1.3 formed a new signal at δ ca. 2.75 upon mixing equimolar amounts of **1** and **2** in $CDCl_3$ solution at 0.04 M concentration, regardless of the configuration of the constituent. Proton signals of the cyclohexane skeleton of **2** were shifted upfield upon complexation with **1** but the shift was practically insensitive to diastereomer composition of the complex. For example, the CHN proton signal of **2** at δ 2.25 moved upfield to δ 2.01 in all combinations of racemic and enantiomerically pure **1** and **2**. It appears that the lack of configurational sensitivity of proton signals shifts in complexes of **1** and **2** merely reflects the lack of aggregation of these entities in $CDCl_3$ solvent (the use of aromatic hydrocarbon solvent, such as C_6D_6, was seriously limited by a low solubility of the complexes in these solvents).

We anticipated that yet another piece of information on the structure of BINOL–DACH complexes in solution could be provided by the CD spectra. It is well known[51] that BINOL and the related structurally chiral derivatives of 1,1′-binaphthalene are characterized by strong exciton Cotton effects in the 220–240 nm region, due to the coupling of the naphthalene ^1B_b electric dipole allowed transitions. According to both experimental and theoretical results[51] several spectral parameters, such as the amplitude, or the magnitude of the long-wavelength Cotton effect or the wavelength splitting of the exciton Cotton effect are related to the magnitude of the dihedral angle defined by the planes of the two naphthalene chromophores. In the present case these parameters (excluding sign of the exciton Cotton effect) are similar for **I**·PhMe and for **II** (Table 1) and are also similar to those of uncomplexed (*R*)-**1** ($A = -453$). This means that the conformation of **1** does not change upon forming a complex with **2**.

Racemic BINOL **1** forms a racemic compound on crystallization (racemate—mp 217–220 °C, enantiomer—mp 208–210 °C); this precludes the resolution of BINOL by preferential crystallization. However, when crystallized from toluene in the presence of an equimolar amount of (*R*,*R*)-**2**, *rac*-**1** gave crystalline complex (*R*)-**1**·(*R*,*R*)-**2**, that is, **I**·PhMe, in high yield.[47] It should be noted that for the crystallization, toluene could be successfully replaced by either benzene or cumene. We have found that complex **I**·PhMe shows properties of a conglomerate, although the two diastereomeric complexes, that is, (*R*)-**1**·(*R*,*R*)-**2** (**I**) and (*S*)-**1**·(*R*,*R*)-**2** (**II**) do not constitute a conglomerate in the usual sense.[52] However a conglomerate-like behavior was evident on inspection of the melting points and solubility data (Table 1).

Both diastereomeric complexes, **I**·PhMe or **II** have higher melting points than the racemate (*rac*-**1**·*rac*-**2**). In addition, the solubility data of the distereomeric complexes obey the Meyerhoffer rule for conglomerates.[52] The rule has been established for diastereomeric salts but the present case shows that it can also be applied to characterize conglomerates of molecular complexes, such as **1**·**2**. In the present case, racemate **1**·**2** is twice as soluble as the more readily crystallizing diastereoisomer **I**·PhMe, in accordance with

Table 1. Melting points, solubility in toluene, and circular dichroism data for complexes of **1** and **2**

Complex	Mp (°C)	Solubility in toluene at 22 °C (mmol l^{-1})	CD (cyclohexane–CH_2Cl_2, 9:1) Δε (nm)	Amplitude (A)
I·PhMe	143–155	0.73	−242 (233 nm); +214 (221 nm)	−456
II	133–135	25.2	+240 (233 nm); −202 (221 nm)	+442
Rac-**1**·*rac*-**2**	90–125	1.44	—	

Meyerhoffer's rule. It is noteworthy that the solubility of **II** is more than 30 times higher compared to that of **I**; this assures high diastereoselectivity of the process of resolution by crystallization. A further evidence of conglomerate crystal structure of **I** is the identity of the solid state IR spectra (KBr pellet) of (*R*)-**1**·(*R*,*R*)-**2**(**I**). and racemate **1**·**2**.[52]

In contrast, whereas **1** forms a crystalline complex with ethylenediamine **4** on crystallization from toluene, the crystals belong to the domain of racemic compounds; melting point of (*S*)-**1**·**4** is much lower (95–104 °C) compared to the melting point of *rac*-**1**·**4** (215–216 °C).

3. Crystal structures of complexes of BINOL and diamines

3.1. Molecular geometry

Crystal structures of four complexes of BINOL with diamines: **I**, **I**·PhMe, **II** and **III** were investigated and their supramolecular structures analyzed. As expected, in all these complexes, the substrate molecules have formed OH–N hydrogen bonds between the hydroxyl and the amino groups, leading to well defined one-dimensional aggregates in a form of left- or right-handed helices. In the case of nonsolvated **I**, there are two symmetry-independent helical aggregates in the crystal, hereafter denoted **Ia** and **Ib**.

The hydrogen-bonded aggregates of the BINOL and the diamine molecules in the investigated co-crystals are shown in Figure 2. The properties of the co-crystals strongly depend on the formation of the aggregates and their interactions in the crystal lattice. The main components of the co-crystals, BINOL and 1,2-diamine molecules, have specific dimensions, which are unlikely to change, and adjust only in a narrow range in different co-crystal structures. The absolute configurations and conformations of these molecules can be conveniently described by torsion angles. Torsion angle C2–C1–C1′–C2′ in binaphthalene derivatives, assuming positive values for the (*S*)-configuration and negative values for (*R*)-configuration, can vary between 60° and over 100°. In the nonsolvated enantiomer (*R*)-**1** the C2–C1–C1′–C2′ angle is 101.65(5)°, and in the racemate ±90.58(4)°.[53] These angles in the enantiomer and racemate of 1,1′-binaphthyl are 103.1° and 68.6°, respectively.[54] The torsion angles describing the conformation of hydrogen-bonded aggregates in BINOL–diamine co-crystals are given in Table 3. Angles **a**, **b**, and **b**′ describe the conformation of BINOL, and angle **f**, the conformation of diamine, while angles **c**, **d**, **e**, and **c**′, **d**′, **e**′ the mutual arrangement of the hydrogen-bonded molecules (for the symbols of the torsion angles, see Fig. 1). Where the values of the nonprimed and primed parameters are identical (**I**·PhMe), the diamine in the helix is located on a twofold axis. The symmetry codes at the bottom of Table 2 relate the neighboring links of the aggregates. The values shown in bold are the softest torsion angles of the aggregates describing either the conformation of the hydroxyl hydrogen in BINOL (**c**, **c**′) or the arrangement of the molecules across the H-bond (**d**, **e**, **d**′, **e**′). The handedness of the BINOL and diamine turns, as well as the lengths of the N–HO hydrogen bonds are also listed. The superscripts indicate the atoms related by the symmetry codes.

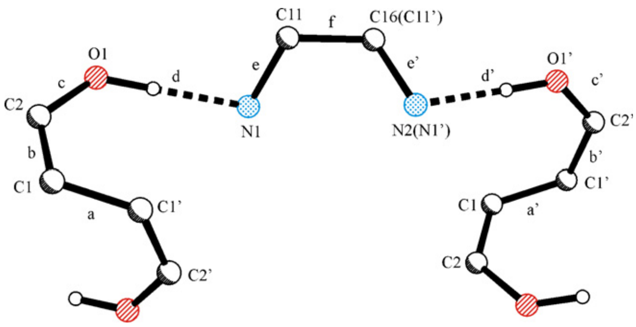

Figure 1. Covalent and hydrogen bonds of the helical backbone in the co-crystal of BINOL and diamines. The torsion angles describing the helix conformation have been labelled by lower-case letters **a**–**f** and **a**′–**e**′ (cf. Table 2). Hydrogen atoms have been ignored when defining the torsion angles along molecular and hydrogen bonds.

Similarly, the molecules of **2** can be characterized by the torsion angle N1–C1–C2–N2, which in the (*R*,*R*)-enantiomer assumes a negative value of about −60°. In **3** this angle is not constrained by a ring and can change due to a rotation about the C1–C2 bond. These torsion angles have also been included in Table 2. It can be concluded that the substrate molecules exhibit a considerable flexibility for adjusting their conformation to the requirements of their aggregation: of over 35° for **1**, and of over 10° for **2** (angles **a** and **f** in Table 2).

3.2. Hydrogen bonds

Donor–acceptor distances in the NH–O bonds are listed in Table 3. Except for one of the four symmetry-independent H-bonds in **I**, the O···N distances fall within the 2.74–2.81 Å range. The exceptionally short N1···O1 bond in **Ia** (Table 2) is by over 0.1 Å shorter than the four longest ones. This testifies that the packing forces can significantly influence the hydrogen-bonds geometry in these co-crystals. The H-bond geometry can be described, apart from such parameters as the bond lengths and bond angles involving the H-atom, also by rotations about the line drawn through H-donor and acceptor atoms (O and N). These rotations, controlling the mutual arrangement of

Table 2. Selected torsion angles (°) and hydrogen bond lengths (Å)

Torsion angle	**Ia**	**Ib**	**I**·PhMe	**II**	**III**
a	−77.7(5)	−103.7(4)	−101.6(6)	79.4(3)	67.7(9)
b	−2.1(6)	−0.2(6)	1.7(5)	0.2(4)	1.3(1.0)
c	**−178.7(3)**	**18.5(6)**	**7.2(5)**	**27.0(4)**	**18.3(1.0)**
d	**72.3(5)**	**−135.8(4)**	**−121.6(4)**	**133.8(3)**	**−151.6(6)**
e	**42.3(5)**	**−170.8(3)**	**−179.0(4)**	**−53.8(3)**	**−177.3(4)**
f	−65.7(4)	−54.7(5)	−52.5(7)	−64.0(3)	68.3(8)
e′	**−45.8(4)**	**−177.5(3)**	**−179.0(4)**	**−44.6(3)**	**−168.4(4)**
d′	**−104.4(4)**	**−117.8(4)**	**−121.6(4)**	**−141.2(4)**	**124.8(6)**
c′	**−21.8(6)**	**2.2(6)**	**7.2(5)**	**9.1(5)**	**25.5(9)**
b′	0.6(6)	−0.6(6)	1.7(5)	1.1(5)	2.2(1.0)
BINOL turn	Right	Left	Left	Right	Right
Diamine turn	Left	Left	Left	Left	Left
N1···O1	2.691(4)	2.741(4)	2.756(5)	2.745(3)	2.800(9)
N2···O1′	2.795(5)	2.807(4)	2.756(5)	2.809(4)	2.780(8)
Symmetry codes	$1.5 - x, 1 - y, 0.5 + z$	$0.5 + x, 1.5 - y, 1 - z$	$-x, -y, 0.5 + z$	$x + 1, y, z$	$x + 1, y, z$

Table 3. Crystal data and structure refinement for (**I**), (**I**·PhMe), (**II**), and (**III**) co-crystals

	I	**I**·PhMe	**II**	**III**
Empirical formula	$C_{26}H_{28}N_2O_2$	$C_{33}H_{36}N_2O_2$	$C_{26}H_{28}N_2O_2$	$C_{34}H_{30}N_2O_2$
Formula weight	400.50	492.64	400.50	498.60
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	1.54178	1.54178	1.54178	1.54178
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$C222_1$	$P2_1$	$P2_12_12_1$
Unit cell dimensions (Å, °)				
a	15.397(2)	12.380(2)	8.052(2)	8.910(4)
b	28.663(3)	14.296(3)	13.549(3)	12.350(3)
c	9.962(6)	15.277(3)	10.821(2)	24.196(6)
β			111.55(3)	
Volume (Å^3)	4397(3)	2703.8(9)	1098.0(4)	2663(2)
Z	8	4	2	4
Calculated density (g cm^{-3})	1.210	1.210	1.211	1.244
Absorption coefficient (mm^{-1})	0.602	0.584	0.603	0.605
F(000)	1712	1056	428	1056
Crystal size (mm)	0.3 × 0.2 × 0.1	0.5 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.6 × 0.3 × 0.2
θ range for data collection (°)	3.08–65.10	4.72–60.02	4.39–65.06	3.65–60.08
Index ranges	$0 \leqslant h \leqslant 18$, $-33 \leqslant k \leqslant 33$, $0 \leqslant l \leqslant 11$	$0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 17$	$0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 15$, $-12 \leqslant l \leqslant 11$	$0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 27$
Reflections collected	5776	1016	1803	2199
Independent reflections	5213 [$R_{int} = 0.0175$]	1016 [$R_{int} = 0.0000$]	1659 [$R_{int} = 0.0151$]	2199 [R(int) = 0.0000]
Completeness to θ	=65.10°, 96.5%	=60.02°, 88.6%	=65.06°, 84.2%	=60.08°, 96.9%
Refinement method	Full-matrix least-squares on F^2			
Data/restraints/parameters	5213/1/626	1016/0/204	1659/0/320	2199/0/366
Goodness-of-fit on F^2	1.079	1.092	1.071	0.871
Final R indices [$I > 2\sigma(I)$]				
R_1	0.0438	0.0439	0.0273	0.0510
wR_2	0.1024	0.1124	0.0690	0.0913
R indices (all data)				
R_1	0.0840	0.0722	0.0432	0.0742
wR_2	0.1266	0.1201	0.0714	0.1105
Absolute structure parameter	−0.3(4)	−1.2(8)	0.1(3)	1.4(9)
Extinction coefficient	0.00112(13)	0.0016(3)	0.0223(14)	0.0015(2)
Largest diff. peak/hole (e Å^{-3})	0.204/−0.180	0.186/−0.173	0.111/−0.091	0.243/−0.213

the hydrogen-bonded molecules and the supramolecular structure of the aggregates, are discussed below.

3.3. Helicity of BINOL–diamine supramolecules

A variety of supramolecular one-dimensional aggregates formed in BINOL–diamine co-crystals can be clearly distinguished. The most striking observation is that the aggregates cannot be simply classified as either left- or right-handed helices. For describing the structure of the aggregates, we have analyzed together the conformations of the constituent molecules and the geometry of the hydrogen bonds. Different types of these linear supramolecular structures can be distinguished when comparing the torsion angles (cf. Table 2) along the covalent and hydrogen bonds forming the backbones of the aggregates (excluding the hydroxyl H-atoms in the hydrogen bond) and neglecting the relatively rigid intramolecular torsions **a**, **b**, and **f** (the **f** angle can vary significantly for diamine **3** only), as illustrated in Figure 1.

The conformation of the aggregates can thus be described by the torsion angles involving hydrogen bonds **c**, **d**, **e**, as well as **c**′, **d**′, **e**′ if the molecules are located at general crystallographic sites. In **I**·PhMe the molecules lie at C_2-symmetric special positions and the pairs of angles **c** and **c**′, **d** and **d**′, and **e** and **e**′ are equal. Even these few degrees of freedom combined with the molecular 'soft' torsion angles, lead to considerable variations of the aggregate conformation. As can be seen from Figures 2 and 3, and the torsion angles listed in Table 3, only two of five aggregates are similar (**Ib** and **I**·PhMe), while each of the other aggregates is distinctly different. Moreover, it is difficult to classify the observed supramolecules as simple geometrical individuals. Certainly they cannot be described as regular helices, as can be clearly seen in Figure 4 showing the hydrogen-bonded backbones of the aggregates. These backbones are different and consist of larger and smaller turns, of the same or opposite handedness. The closest resemblance to helices exists in the similar aggregates **Ib** and **I**·PhMe, where two small loops of the diamine fragments are attached to the large and regular turn formed by the H-bonds and BINOL molecules. As specified in Table 1, consistent turns of BINOL and DACH (both left) are introduced into these helical aggregates of **Ib** and **I**·PhMe. In other cases, the turns of BINOL are right-handed, while those of diamines are opposite, which very considerably distorts the structures of the aggregates in **Ia**, **II**, and **III**. Interestingly, two symmetry-independent aggregates in **I**, **Ia**, and **Ib** (Figs. 2–4, and Table 3), have considerably different conformations. This shows that the helical arrangement is only to some extent dependent on the molecular shape and chirality, and that molecular packing and van der Waals forces play equally important roles for the 'secondary structure' of the supramolecules.[55]

3.4. H-Bond structure versus solubility of co-crystals

Solubility and melting point of any substance are complex derivatives of their structures and interactions. It can be noted in the case of the co-crystals investigated that complex **II** has one OH–N hydrogen bond longer than the OH–N bonds in **I**·PhMe. This weaker H-bond can be readily broken, and following this reasoning, the solubility of co-crystal **II** should be higher, and its mp lower than these of co-crystal **I**·PhMe. Indeed, such relations exist between these properties (Tables 1 and 2). On the other hand the molecular weight of **I**·PhMe is higher than that of **II**, which is also consistent with the higher mp of **I**·PhMe. Also the higher molecular and crystal symmetries of **I**·PhMe compared to **II** (Table 3) may be the reason of higher mp and lower solubility of **I**·PhMe, in accordance with Carnelley's rule,[56–58] but to our knowledge no symmetry-solubility relations were so far considered.

4. Conclusions

A series of four co-crystals of BINOL with diamines reveals a considerable variety of association modes of these molecules. It demonstrates that, apart from the chirality of constituent molecules and the directional hydrogen bonds linking them into one-dimensional aggregates, also other intermolecular interactions and in particular the requirements of close molecular packing, play a significant role in the formation of these crystal structures. This is illustrated by the formation of two symmetry-independent and different aggregates of (*R*)-**1**·(*R*,*R*)-**2** in complex **I**, that is, that several types of association are possible for the same compounds. Despite this different association by hydrogen bonds, the diastereoselective co-crystallization is observed. In all the BINOL–diamine complexes the directions of H-bonds are consistent with the turns of the BINOL, and these are the diamine molecules which distort the helical arrangement. It thus appears that a considerable flexibility of the hydroxy H-donor and amine H-acceptor groups to rotate and adjust the H-bonding directions is a very important feature allowing the differences of molecular sizes to be compensated and requirements of close packing to be fulfilled. It has been observed that the crystal packing considerably affects the dimensions of hydrogen bonds, and that in this group of co-crystals, the length of the longest hydrogen bonds in specific structures can be correlated with the lowest melting points and highest solubility of co-crystals. However, these observations for a very limited number of co-crystals studied in this report should be confirmed for a larger number of substances. Therefore, further more systematic studies on the relations between H-bonds dimensions and properties of chiral co-crystals are required. Such systematic studies allowed the relations between H-bond dimensions and physical properties to be resolved for OH–O hydrogen-bonded ferroelectrics[59,60] and H_2O ice I*h* crystals.[61]

5. Experimental

Racemic BINOL **1** was resolved with either (*R*,*R*)-**2** or (*R*,*R*)-**3** according to the reported procedure[47] and the complexes of BINOL with diamines thus obtained were used in X-ray structure determinations. The crystals were glued to a glass fiber and mounted on a KUMA CCD diffractometer. The structures of four complexes (**I**, **I**·PhMe, **II**, **III**) have been solved by direct methods using SHELXS-

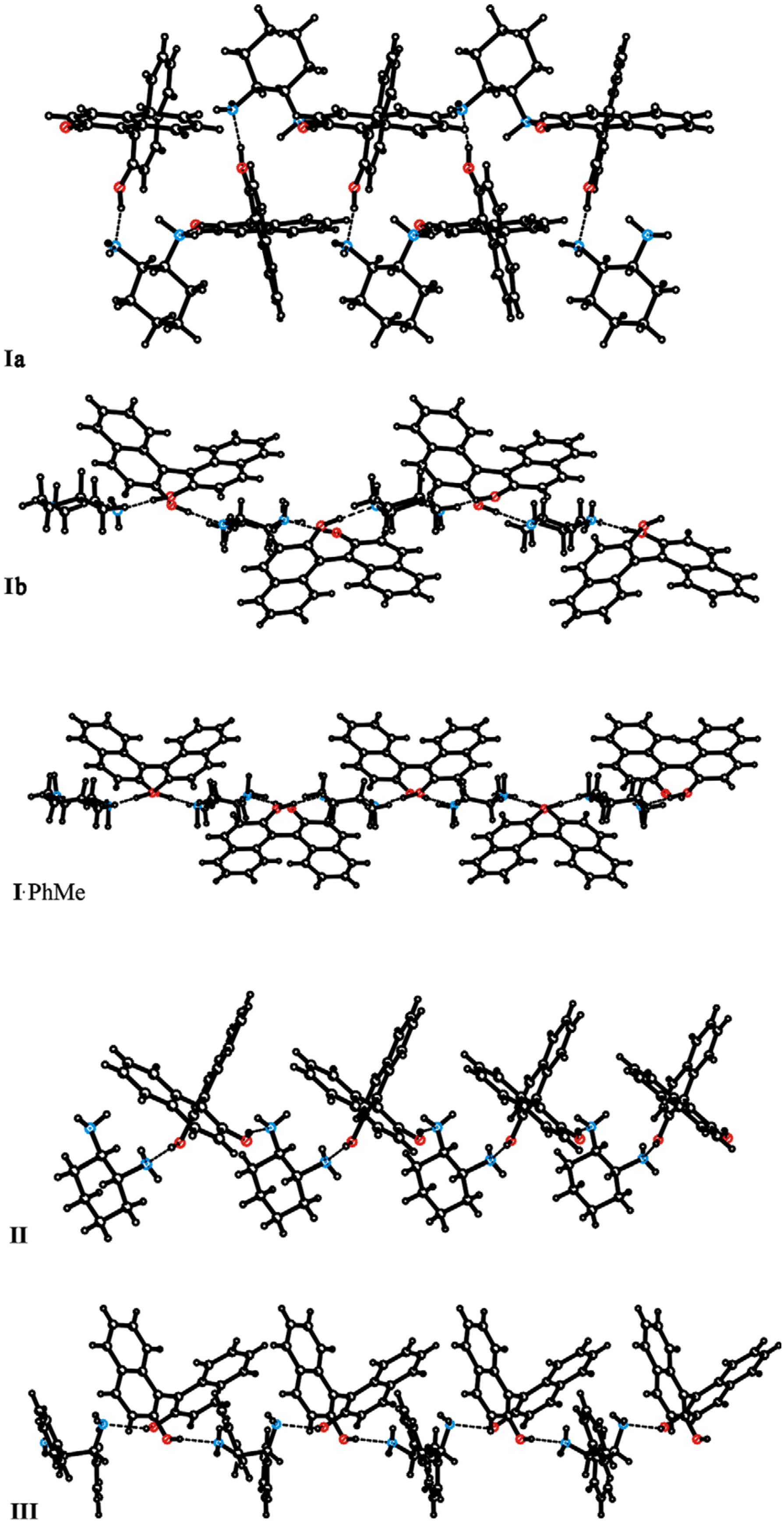

Figure 2. Autostereographic projections[62] of BINOL–diamine aggregates viewed perpendicular to the chains axes: two symmetry independent aggregates **Ia** and **Ib**, **I**·PhMe (toluene molecules omitted for clarity), **II**, and **III**. The hydrogen bonds are represented as dashed lines.

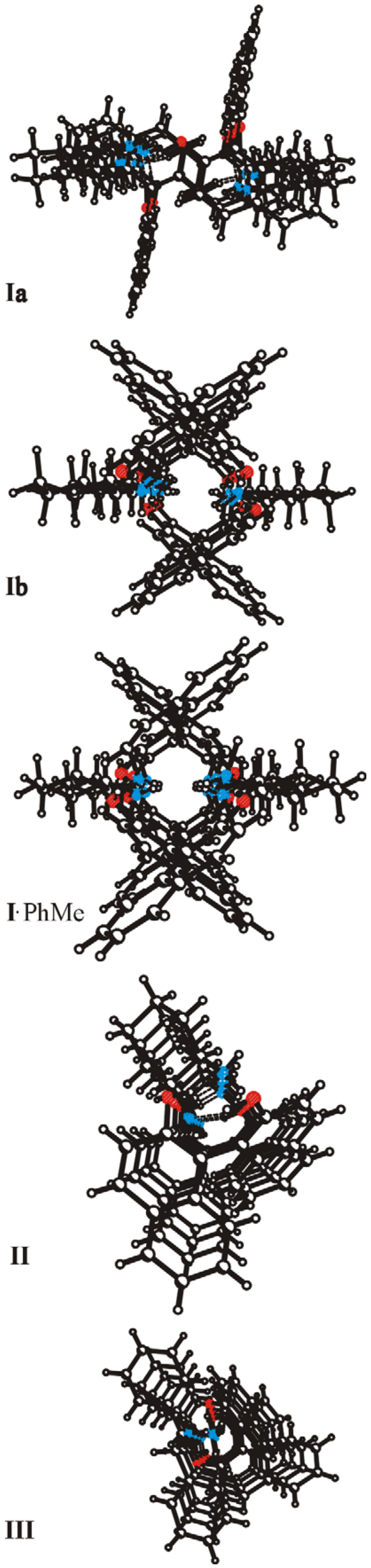

Figure 3. BINOL–diamines aggregates viewed down their axes: two symmetry independent aggregates **Ia** and **Ib**, **I**·PhMe (toluene molecules omitted for clarity), **II**, and **III**.

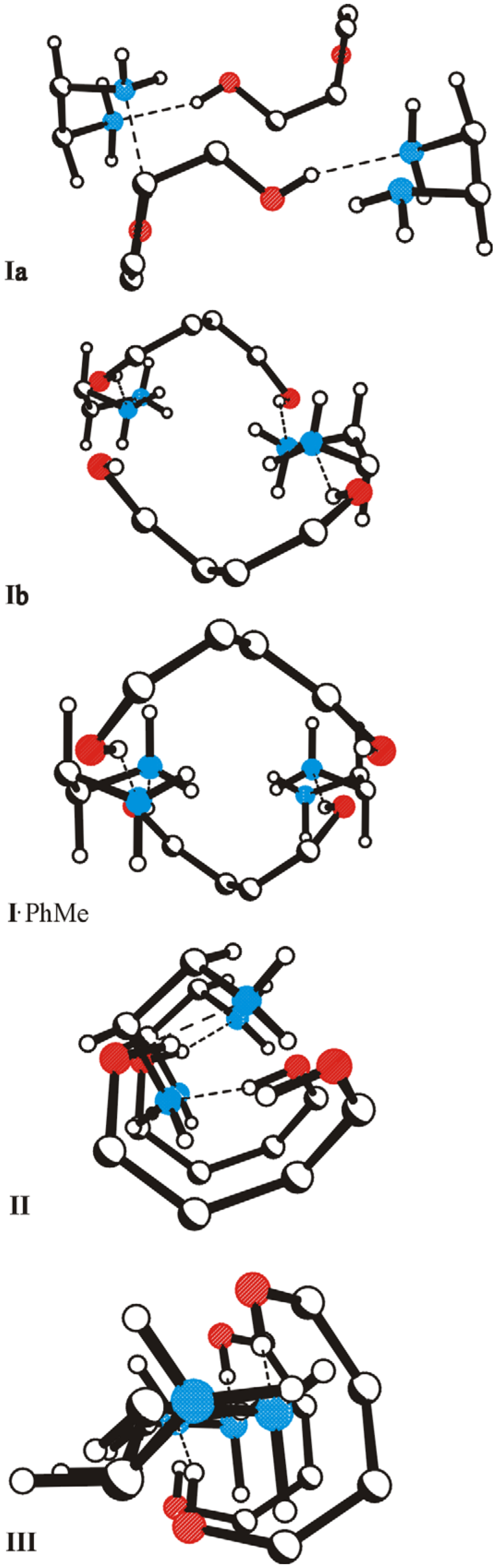

Figure 4. Covalent and hydrogen bonds forming the backbones of supramolecules in two symmetry independent aggregates **Ia** and **Ib**, **I**·PhMe (toluene molecules omitted for clarity), **II**, and **III** (compare Fig. 3).

86[48] and refined by full-matrix least squares using SHELXL-93.[49] All H atoms of BINOL (except for the H1 and H1′ protons in (*S*)-**1**·(*R*,*R*)-**2** (**II**) which were located from ΔF-maps and refined) were calculated from the molecular geometry (C–H 0.93 and O–H 0.82 Å) and their U_{iso} have been related to thermal vibrations of their carriers. The H atoms of NH_2 groups in four diamines were located from difference maps and all were included in the refinements. All other H atoms were calculated from the molecular geometry (C–H 0.97 Å, and $U_{iso}(H) = 1.3–1.5U_{eq}(C)$). The absolute configurations of all compounds were known á priori from the chemical information about the substrates investigated, and the correct configurations were assigned after solving the structures. The selected information about the crystal structures, experiments and structures solutions and refinements are summarized in Table 3. Supplementary crystallographic data for this paper in the form of CIF files CCDC 626328 (for **I**), 626327 (for **I**·PhMe), 626326 (for **II**) and 626325 (for **III**) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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