

Balance of forces between various contacts in crystal structures of two isomeric benzo-condensed dibromodihydroxy-containing compounds

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ABSTRACT: Various forces influence the formation of a crystal structure and sometimes an unstable balance between different supramolecular interactions is the reason for polymorphism. Four crystal structures relating to the interplay between bromine contacts, aromatic interactions, hydrogen bonding and the influence of the solvent used in the crystallization process are reported. In this context **1** and **2** were synthesized as model compounds both containing two hydroxy groups and two bromophenyl substituents in a *cis* configuration attached at different sides to the basic 9,10-dihydroanthracene subunit. Variation in the position of the bromo substituents in **1** and **2** allows further comparison with reference to interaction modes and crystal packing. A variety of interactions (O—H···O, O—H···Br, Br···Br) are realized in two crystal modifications of **1**, **1A** and **1B**, with similar molecular geometry but considerably different packing relationships. The balance of forces between the possible contacts and their endeavour to control the crystal packing is influenced by the solvent which is used for crystallization. Modification **1A** crystallized from pure toluene, whereas for **1B** toluene with a trace of chloroform was used. In pure chloroform **1** includes solvent molecules in a host lattice, forming a clathrate structure **1C** [**1**·CHCl₃ (1:1)] with packing motifs similar to the structure **1B**. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: Crystal structure; balance of forces; benzo-condensed dibromodihydroxy compounds; polymorphism

INTRODUCTION

Investigations of the characteristic behaviour of different functional groups and their influence on the packing arrangement in crystal structures are of great interest in crystal engineering.¹ The knowledge of the strength and orientation of the interaction between functional groups gives the possibility for a design of organic solids² with desired properties, thus having applications in materials science.

Hydrogen bonds with different functional groups (O—H, N—H_x and sometimes also C—H_x) have been well studied.³ To compare such interaction systems, the description with synthons⁴ in supramolecular synthesis or through a set of graphs⁵ is helpful. Unlike hydrogen bonds, knowledge of the influence of halogen atoms on crystal packing and their interactions with other halogen atoms, nucleophilic and electrophilic groups and aro-

matic π -systems is still at an early stage^{6,7} and the nature of these contacts is under current discussion.⁸

For the analysis of halogen contacts, early work was done with simple halogen compounds including Cl₂, Br₂ and I₂ and comparative studies between halogen-substituted benzene derivatives,⁹ showing that halogen atoms are able to form various important interactions with preferential ranges of contact distances and angles, relatively easy to describe between pairs of identical halogens (Cl···Cl, Br···Br, I···I) and mixed pairs (Br···Cl, Cl···I, Br···I). On the other hand, halogen atoms form short contacts with nitrogen, oxygen and sulphur. Moreover, halogen atoms could act as a hydrogen acceptor (electron donor) in hydrogen bonds (a good historical overview is given in Ref. 1).

Depending on the geometric parameters, two types of halogen···halogen interactions are distinguishable.¹⁰ In the first type (A), both carbon—halogen bonds form a nearly colinear arrangement, so that the contact angles Θ_1 (C—Br1···Br2) and Θ_2 (C—Br2···Br1) are equal and around $160 \pm 10^\circ$. This molecular arrangement normally contains a centre of inversion between the halogen atoms and is typical of triclinic structures.¹¹ In the second type (B), one of the two angles is $170 \pm 10^\circ$ and the other to $90 \pm 10^\circ$. Type B is characteristic of monoclinic and orthorhombic space groups.¹¹ The

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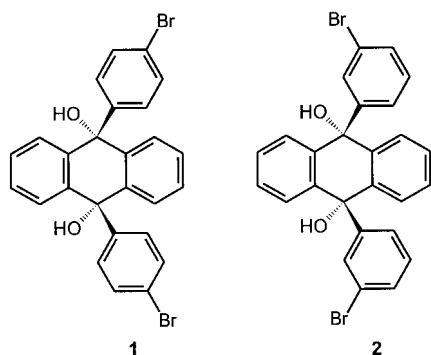
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halogen atoms are correlated by a screw axis or a glide plane.

The preference to form one of these two types of halogen...halogen interactions changes with the polarizability of the halogen atoms. A CSD study¹² of hundreds of crystal structures indicated that the chlorine atom (as one of the hardest halogen atoms, smaller and less polarizable than bromine and iodine) forms both types of contacts in the same ratio. Bromine atoms (as a soft atom, easy to polarize) prefer the perpendicular type (B) and this tendency is also present in the contacts of molecules with iodine atoms.

For further investigation of halogen contacts, model compounds are desirable which have a more complex structure than the simple benzene derivatives but being indicative of these interactions including also competition with groups supporting hydrogen bonds and π -interactions. Moreover, for controlling geometry, variation of the position of the halogen substituents is aimed for. These properties are ascribed to compounds **1** and **2** (Scheme 1), an x-ray structural study of which is reported here.



Scheme 1

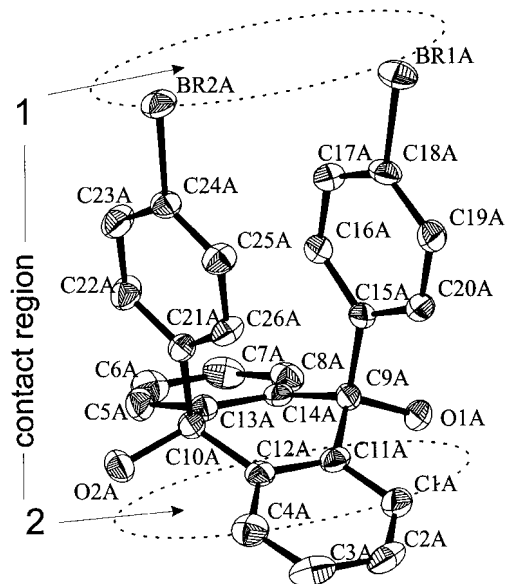


Figure 1. Molecular structure of the dibromo dihydroxy compound **1** showing the numbering system. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. A C_2 -pseudo-symmetry axis runs through the centre of the cyclohexa-1,4-diene moiety. Two regions of potential contact groups are distinguishable: region 1 around the bromine atoms being polarizable (soft) and region 2 formed by the two hydroxy groups

RESULTS AND DISCUSSION

Compounds **1** and **2** were synthesized in moderate yields from anthraquinone and the respective dibromobenzene using a lithium organic reaction. Both compounds contain two hydroxy groups and two bromophenyl substituents in a *cis* configuration attached at different

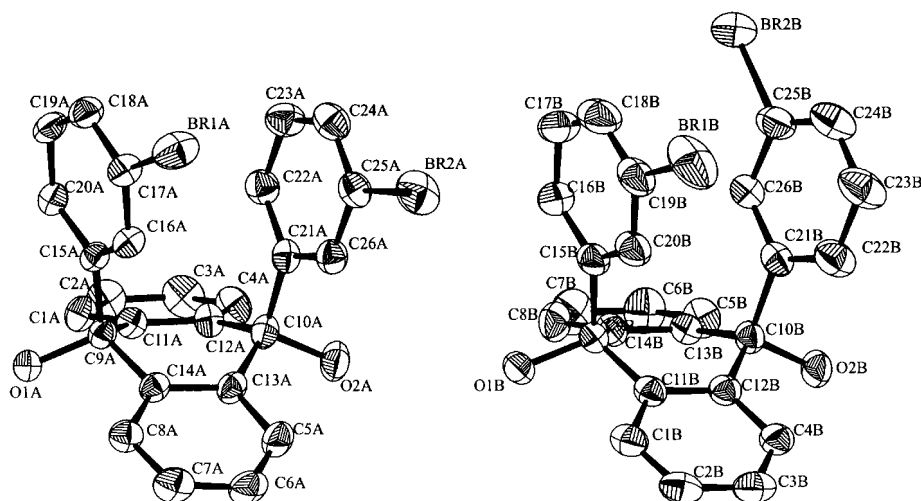


Figure 2. Molecular structure of the dibromo dihydroxy compound **2** showing the numbering system. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. A C_2 -pseudo-symmetry axis runs through the centre of the cyclohexa-1,4-diene moiety. Two conformers are distinguishable depending on the orientation of the bromines

Table 1. Crystal data and some selected experimental details from the crystal structures of compounds **1** and **2**

Identification code	1A	1B	1C	2
Host:guest ratio	No	No	[1 ·CHCl ₃ (1:1)]	No
Crystallized from	Toluene	Toluene with a trace of chloroform	Chloroform	Toluene
Formula	C ₂₆ H ₁₈ O ₂ Br ₂	C ₂₆ H ₁₈ O ₂ Br ₂	C ₂₆ H ₁₈ O ₂ Br ₂ ·CHCl ₃	C ₂₆ H ₁₈ O ₂ Br ₂
Formula weight	522.22	522.22	641.59	522.22
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> -1	<i>Cc</i>	<i>Pbcn</i>	<i>C2/c</i>
<i>Unit cell dimensions:</i>				
<i>a</i> (Å)	13.701(3)	13.3880(1)	16.486(1)	28.194(2)
<i>b</i> (Å)	14.752(3)	24.770(3)	13.7484(6)	16.738(1)
<i>c</i> (Å)	21.790(4)	12.742(3)	22.4129(4)	18.618(1)
α (°)	73.34(3)	90	90	90
β (°)	89.83(3)	96.47(2)	90	97.453(6)
γ (°)	88.17(3)	90	90	90
Volume (Å ³)	4217.0(15)	4198.6(1)	5080.1(4)	8712.1(12)
<i>Z</i>	8	8	8	16
<i>D</i> _c (mg m ⁻³)	1.645	1.652	1.678	1.593
Absorb. μ (mm ⁻¹)	3.865	5.060	7.144	4.877
<i>F</i> (000)	2080	2080	2544	4160
Crystal size (mm)	0.2 × 0.2 × 0.15	0.41 × 0.38 × 0.33	0.3 × 0.32 × 0.25	0.4 × 0.3 × 0.26
Crystal habit	Colourless	Colourless	Transparent	Colourless
Temperature (K)	195(2)	195(2)	293(2)	293(2)
Radiation used [λ (Å)]	Mo K α , 0.71073	Cu K α , 1.5418	Cu K α , 1.5418	Cu K α , 1.5418
sin θ/λ	0.7135	0.6262	0.5777	0.5878
Index ranges	<i>h</i> (0,19) <i>k</i> (-20,21) <i>l</i> (-30,30)	<i>h</i> (0,16) <i>k</i> (0,30) <i>l</i> (-15,15)	<i>h</i> (0,19) <i>k</i> (0,15) <i>l</i> (0,25)	<i>h</i> (0,33) <i>k</i> (0,19) <i>l</i> (-21,21)
Reflections collected	45729	4341	4566	7682
Independent reflections	23991	4204	4084	7398
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	14951	4176	3269	5914
Refinement method	Full-matrix/ <i>F</i> ²	Full-matrix/ <i>F</i> ²	Full-matrix/ <i>F</i> ²	Full-matrix/ <i>F</i> ²
Data/restraints/parameters	23991/5/1374	4204/2/552	4084/0/317	7398/0/554
Absorption correction	No correction	No correction	DIFABS ²⁵	DIFABS ²⁵
Goodness of fit on <i>F</i> ²	1.011	1.083	1.080	1.039
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0477	0.0648	0.0749	0.0749
<i>R</i> 1 (all data)	0.0997	0.0650	0.094	0.090
<i>wR</i> 2 (all data)	0.1017	0.1633	0.1733	0.2027
Final $\Delta\rho_{\max}/\Delta\rho_{\min}$ (eÅ ⁻³)	0.67/-0.97	3.23/-1.78	0.80/-1.05	1.57/-1.49
Diffractometer	Nonius Kappa-CCD	Enraf-Nonius CAD4	Philips PW 1100	Philips PW 1100
Data collection mode	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Decay (%)	No decay	3	No decay	No decay

sides to the basic 9,10-dihydroanthracene subunit. The variation in the position of the bromine atoms in **1** and **2** will allow the influence of the bromine atoms on the crystalline packing mode relative to the interactions between the hydroxy and the aryl groups to be compared.

Perspective views of the molecules of **1** and **2** are shown in Figs 1 and 2, respectively, including the numbering schemes of the atoms. The diol compound **2** exists in two conformers, depending on the direction of the C—Br bond. The absence of flexible aliphatic groups lead to a rigidity in conformation and a block-like molecular structure owing to the plane aromatic systems. These types of block compounds tend to crystallize in a optimal closest-packed model. In addition, the solvent used in the crystallization process gives rise to a strong influence on the packing motif depending on the polarity. Toluene, as an apolar solvent used in the crystallization

of diol **1**, leads to the crystal structure **1A**. For the polymorphic structure **1B**, toluene was used with a trace of chloroform. In pure chloroform compound **1** includes the solvent as guest in a host lattice with a ratio of 1:1 and crystallizes with the clathrate structure **1C** [**1**·CHCl₃ (1:1)] with packing motifs slightly similar to **1B**.

Crystal data and selected experimental details are given in Table 1 and selected conformational features, bromine contacts and H-bond geometries are summarized in Tables 2–5.

Molecular structures

Based on the *cis* configuration in both molecules **1** and **2**, two potential contact regions are distinguishable (Fig. 1): one (region 1) which is around the two bromine atoms

being rather polarizable (soft) and the other (region 2) including the two hydroxy groups having a high affinity to form hydrogen bonds. These features provide them with the ability to form intermolecular interactions with soft partners in region 1, such as bromine or chlorine atoms (structure **1C**), or hard partners in region 2, e.g. an oxygen atom.

The central cyclohexa-1,4-diene ring in both dibromo containing diols **1** and **2** shows a boat- conformation in the *cis* configuration and therefore the 9,10-dihydroanthracene unit has a roof-shaped geometry. The double-substituted ring carbons C9 (sp^3) and C10 (sp^3) occupy the edges of the boat and form nearly tetrahedral angles with all substituents. In contrast, the molecular geometry in various crystal structures of the *trans*-diol compound¹³ is determined by a nearly flattened central cyclohexa-1,4-diene ring. The *trans*-diol possesses a linear molecular geometry with the phenyl groups in opposite directions and a planar 9,10-dihydroanthracene unit. However, the diols **1** and **2** with a *cis* configuration indicate a parallel arrangement of the substituted phenyl groups, showing distances between the planes from 3.7 to 4.0 Å and a small lateral offset (angle between the longitudinal axis are from 5 to 10°). As an indicator for the geometry of the phenyl groups, the intramolecular Br...Br distances are very similar in crystal structures **1B**, **1C** and **2**, amounting to 4.5 Å.

The four independent molecules in crystal structure **1A** are divided in two groups. Molecules C and D present a nearly identical geometry, whereas molecules A and B differ in some special aspects of the molecular structure. The differences are concentrated in the geometry of the phenyl groups and are indicated by the intramolecular Br...Br distances in the molecules [A 4.308(1); B 4.955(1); C 4.495(1); D 4.422(1) Å].

The diol **2** differs from diol **1** in the position of the bromine atoms, resulting in the existence of two conformations of **2**. There are two possibilities to orientate the bromine atoms in the parallel arrangement of the *meta*-substituted phenyl groups, facing each other. Either both bromine atoms point in the same direction [Br...Br = 4.456(1) Å] or in opposite directions [Br...Br = 5.598(2) Å]. The conformers were found in the unit cell with a ratio of 1:1. On the whole, the molecular geometries of **1** and **2** in the structures **1A**, **1B**, **1C** and **2** are similar. Nevertheless, the crystal structures **1A** and **1B** are polymorphic.

Polymorphism

Various forces influence the formation of a crystal structure and sometimes an unstable balance between different molecular interactions is the reason for polymorphism. On the other hand, strong and rigid interactions avoid changes in crystal structures and the formation of different crystalline modifications of one

chemical compound. Although polymorphism is a well known crystallographic phenomenon,¹⁴ no model exists to predict the polymorphic behaviour of chemical compounds. Basically two reasons for polymorphism are distinguishable: (1) the deviation of the molecular arrangement at a minimum of energy or thermodynamic equilibrium and (2) a variety of possible association modes or packing relations of the molecules, i.e. geometric reasons. The latter incorporates the molecular structure, the conformation and configuration of the compound. For special cases the term conformation-polymorphism is used.¹⁵ Historical studies of polymorphism concern with differences in crystal structures, depending mainly on temperature.¹⁴ Much less studied are transitions caused by pressure or the solvent used in the crystallization process. The compounds may be covered by solvent molecules connected at functional groups, forming hydrogen bonds, especially with polar aprotic (acetone, dimethylformamide, dimethyl sulphoxide) or polar protic solvents (alcohols, amines). Additionally, the solvent molecules are able to act as a preorganizer in solution, predetermine the crystal structure or be included in supramolecular host-guest crystals, which increase the number of possible polymorphic structures. In that kind of clathrate structure¹⁶ the host molecules change their association modes to fit guest molecules, indicating that the host assemblies are pseudo-polymorphs or guest-dependent polymorphs.¹⁷

Packing arrangement

The molecular geometry of **1** in the two polymorphic structures **1A** and **1B** is very similar. However, the packing arrangement is completely different, thus showing polymorphism. The following driving forces, which influence the mode of packing, are to be considered as possible reasons for the polymorphism here (under constancy of temperature and pressure): (a) bromine contacts in region 1, (b) hydrogen bonding of the hydroxy groups in region 2, (c) tendency to achieve a closest packed structure, including π - π stacking, and (d) type of solvent used in the crystallization process. The two polymorphic structures yield colourless crystals that are not distinguishable with the help of a microscope or by melting-point. They were achieved by variation of the crystallization solvent, as mentioned above. These two polymorphic structures do not form a polymorphic pair, where one crystal structure could be transferred into another by simple heating. A transfer is only possible by decomposition/dissolution of the crystal structure.

In the crystal structure **1A** (Fig. 3, Table 2) two types of O—H...O hydrogen bonds are distinguishable according to the direction of interaction: type E (equatorial) and type A (axial). A few hydroxy groups (O1B, O1D) participate in hydrogen bonds of type E and join adjacent molecules to infinite chains. Phenyl rings in a nearly

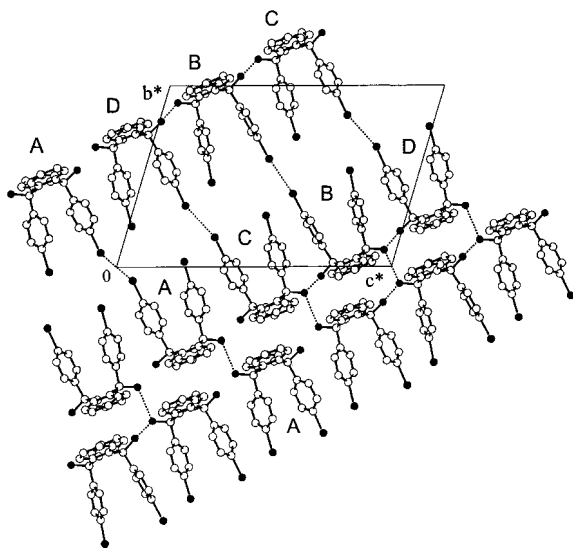


Figure 3. View along the a -axis of the packing arrangement in the triclinic crystal structure **1A**, the first modification of **1**. The four independent molecules are labeled A–D. Hydrogen atoms are omitted and contacts are depicted by dotted lines. The molecules in **1A** are joined into infinite chains via O—H \cdots O hydrogen bonds (equatorial type). Pairs of these chains are joined into ladders by O—H \cdots O hydrogen bonds (axial type). The ladders form cross-links by means of linear Br \cdots Br contacts to yield sheets

parallel orientation support this arrangement, resulting in a perfect molecule fitting in the chain. Each independent molecule A, B, C and D contains one hydroxy group (O1A, O1B, O1C and O1D) which participates in hydrogen bonds of type A and acts as hydrogen donor. This hydrogen bonding joins pairs of the chains into ladders (Fig. 4). The ladders are stabilized by the O—H \cdots π interactions of each independent molecule by the O2A, O2B, O2C and O2D hydroxy groups. These interactions with an aromatic ring of the 9,10-dihydroanthracene unit of a neighbouring molecule are of the ‘edge’ rather than the ‘centroid’ type (Table 2). The ladders form cross-links by means of linear Br \cdots Br contacts to yield sheets. Only the bromine atoms indicated by the number 2 are involved in these contacts.

The Br2A \cdots Br2A* and Br2B \cdots Br2B* contacts are related by a centre of symmetry, whereas the Br2C \cdots Br2D and Br2D \cdots Br2C are not related by symmetry, but contain equal distances and angles. The same relationships between the four independent molecules are to be found in the four hydrogen bonds of type A. The hydrogen bonds O1A \cdots O1A* and O1B \cdots O1B* are related by a centre of symmetry and contain different O \cdots O distances [2.978(4) and 3.005(4) Å, respectively], whereas the hydrogen bonds O1C \cdots O1D and O1D \cdots O1C, of the same type of interaction, have no symmetry relation but identical O \cdots O distances. However, the hydroxy hydrogen atoms H1CO—(O1C) and H1DO—(O1D) are oriented in distinct directions and were located on the difference electron density map. The hydroxy hydrogen H1CO acts in the hydrogen bond (axial, type A) O1C—H1CO \cdots O1D, whereas H1DO form a hydrogen bond O1D—H1DO \cdots O2B (equatorial, type E).

Closer inspection of the four independent molecules in the asymmetric unit shows that the longitudinal axis of molecule A has a special orientation (Fig. 4) with the short interactions of its hydroxy groups with bromine and the long distances to the hydroxy groups of adjacent molecules in the chain that attracts attention (Table 2). The longitudinal axis of the 9,10-dihydroanthracene subunit of molecule A is not parallel in relation to the orientation of the other molecules in the chain. The network of hydrogen bonds in the chain (type E) is interrupted around the molecule A. The prolongation of the expected hydrogen bonds O1A \cdots O2D and O2A \cdots O1C by 1.0 and 1.5 Å, respectively, is combined with a contraction of the intermolecular distances to bromine atoms. Consequently, the deviation in the orientation of the longitudinal axis gives the possibility for the hydroxy groups O1A and O2A to form two O \cdots Br contacts. Moreover, these contacts are the only ones which produce an interaction between the sheets and join them.

This competitive behaviour of all possible interactions is caused by a willingness of the hydroxy groups to compromise. The hydroxy hydrogen atoms are saturated

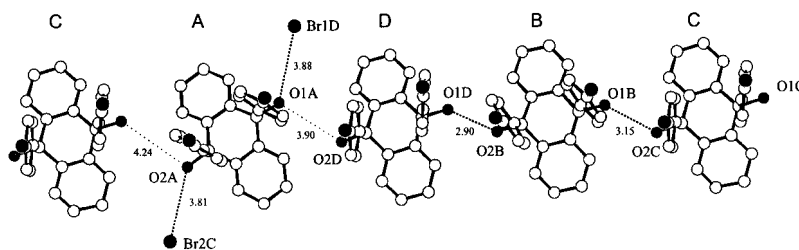


Figure 4. Part of the chain formed by O—H \cdots O hydrogen bonds in **1A** illustrating the special orientation of the molecule A. The longitudinal axis of the 9,10-dihydroanthracene subunit of molecule A is not parallel in relation to the orientation of the other molecules in the chain. The network of hydrogen bonds in the chain is interrupted around the molecule A and give the possibility to form two O \cdots Br contacts. The four independent molecules are labeled and the values of contact distances are donor \cdots acceptor distances

Table 2. Bond lengths (Å) and bond angles (°) of H-bonds^a classified in two types of interactions (equatorial direction, type E, forming a chain and axial direction, type A, forming a ladder), linear Br···Br and O···Br contacts in the crystal structure of **1A** (Esds are in parentheses)

Atoms involved ^b (symmetry code)	Distance			Angle ^c		
	D—H	H···A	D···A	D—H···A	⟨ Θ 1	⟨ Θ
<i>Chain: O—H···O type E</i>						
O1B—H1By···O2C (vi)	0.73(3)	2.49(5)	3.155(4)	152(7)	120.9(2)	135.8(2)
O1D—H1DO···O2B	0.83(3)	2.13(3)	2.897(3)	155(3)	121.2(2)	142.4(2)
O1A···O2D	—	—	3.901(3) ^d	—	104.6(2)	132.3(2)
O2A···O1C	—	—	4.220(3) ^d	—	113.4(2)	114.2(2)
<i>Ladder: O—H···O type A</i>						
O1A—H1Ax···O1A(i)	0.68(3)	2.30(3)	2.978(4)	171(8)	115.1(2)	115.1(2)
O1B—H1Bx···O1B(v)	0.70(3)	2.32(3)	3.005(4)	167(8)	114.9(2)	114.9(2)
O1C—H1CO···O1D(vii)	0.75(3)	2.24(3)	2.976(3)	167(3)	114.3(2)	114.5(2)
<i>Plane: Br···Br linear</i>						
Br2A···Br2A (viii)	—	—	3.398(1)	—	155.1(1)	155.1(1)
Br2B···Br2B (ix)	—	—	3.459(2)	—	161.5(1)	161.5(1)
Br2C···Br2D (x)	—	—	3.387(1)	—	149.3(1)	163.1(1)
<i>O—H···Br</i>						
O1A—H1Ay···Br1D(iii)	0.67(3)	3.23(3)	3.884(2)	166(8)	121.0(2)	113.1(2)
O2A···Br2C (iv)	—	—	3.814(3)	—	140.5(2)	106.8(1)
<i>O—H···C (aromatic)</i>						
O2A—H2AO···C7D(xi)	0.66(3)	2.70(3)	3.331(4)	164(3)	116.9(2)	—
O2A—H2AO···C6D(xi)	0.66(3)	2.80(3)	3.445(4)	167(3)	95.1(2)	—
O2B—H2BO···C7C(vii)	0.70(3)	2.61(3)	3.294(4)	164(3)	113.2(2)	—
O2B—H2BO···C8C(vii)	0.70(3)	2.88(3)	3.534(4)	156(3)	126.8(2)	—
O2B—H2BO···C6C(vii)	0.70(3)	2.97(3)	3.624(4)	157(3)	91.6(2)	—
O2C—H2CO···C7B(vii)	0.65(2)	2.76(3)	3.367(4)	156(3)	116.8(2)	—
O2C—H2CO···C6B(vii)	0.65(2)	3.01(2)	3.587(4)	150(3)	94.1(1)	—
O2D—H2BO···C7A(xi)	0.71(3)	2.76(3)	3.453(4)	164(3)	98.6(2)	—
O2D—H2BO···C8A(xi)	0.71(3)	2.94(3)	3.637(4)	168(3)	115.9(2)	—

^a All hydroxyl hydrogen atoms were located on the difference electron density map.

^b (i) $-x, -y, -z + 1$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x, -y, -z + 1$; (v) $-x + 1, -y + 1, -z + 2$; (vi) $x, y + 1, z$; (vii) $-x + 1, -y, -z + 2$; (viii) $-x, -y + 1, -z$; (ix) $-x + 1, -y + 2, -z + 1$; (x) $-x + 1, -y + 1, -z + 1$; (xi) $-x + 1, -y, -z + 1$.

^c angles: ⟨ Θ 1, C9/C10—O···O*⟩; ⟨ Θ 2, C9/C10—O*···O⟩; ⟨ Θ 3, C18/C24—Br···Br*⟩; ⟨ Θ 4, C24/C18—Br*···Br⟩; ⟨ Θ 5, C9/C10—O···Br⟩; ⟨ Θ 6, C18/C24—Br···O⟩; ⟨ Θ 7, C10—O2···C (aromatic).

^d These two contact distances are greater than the sum of the van der Waals radii. Nevertheless, they are presented in the table for a better understanding of the interactions in the packing arrangement (see Fig. 4).

with one interaction: O1A and O1C form hydrogen bonds of type A (axial), whereas O2A and O2D shows O—H···π interactions. Only the electron lone pairs of the oxygen with partly nucleophilic character remain active for further interaction. Consequently, it seems to us that for the formation of a second contact, both bromine atoms and lone pairs of hydroxy groups are acceptable.

The packing arrangement of the monoclinic crystal structure **1B**, the second modification of **1**, presents a layer structure (Fig. 5, Table 3). The dimer mode in polymorph **1B** shows O—H···O and O···Br contacts for linking two molecules, twisted with respect to each other. This arrangement is supported by optimum packing of a substituted phenyl group into the concave 9,10-dihydroanthracene unit. In the crystalline modification **1B** all three possible contacts (O—H···O, O—H···Br, Br···Br), including the perpendicular Br···Br interaction, are present to form a high degree of connection, but only in layers. No linear Br···Br contact is present. The dimers are arranged by two four-centre closed loops (Fig. 6) to give aggregated blocks. These blocks of dimers are

arranged like a brick pattern in one sheet. Interactions with the layers above and underneath are reduced to disperse van der Waals contacts. The two closed loops differ in the participating atoms. One loop involves three hydroxy groups and one bromine atom (ring 1, Fig. 6) and the other three bromine atoms and one hydroxy group (ring 2, Fig. 6).

Crystallization of diol **1** in pure chloroform lead to the clathrate structure **1C** [**1**·CHCl₃ (1:1)], where **1** is the host including the solvent as a guest (Fig. 7, Table 4). At a first approximation, the clathrate structure is determined by the mode of dimer formation, similar to **1B**. This typical association pattern of twisted molecules, linked by an O—H···O hydrogen bond and an O—H···Br contact (Table 4), combined with an optimal packing of a phenyl group in the concave 9,10-dihydroanthracene unit, exists between the host molecules. Closer inspection of the molecular packing shows that the basic dimer motif is enlarged to a chain, indicating a zig-zag pattern. The empty edges in the chain are occupied by the guest molecules to form an infinite molecular column. These

Table 3. Bond lengths (Å) and bond angles (°) in O···H—O bond^a interactions, and O···Br and Br···Br contacts in the crystal structure of **1B** (Esds, where given, are in parentheses)

Atoms involved ^b (symmetry code)	Distance			Angle ^c		
	D—H	H···A	D···A	D—H···A	⟨ Θ	⟨ Θ
<i>Ring 1</i>					⟨ Θ 1	⟨ Θ 2
O2A—H2AO···O2B	0.84(-)	2.09(-)	2.859(9)	151(-)	120.2(5)	135.4(5)
O2B—H2BO···O1B (i)	1.05(13)	1.82(13)	2.811(8)	157(11)	123.2(5)	138.7(5)
O1B—H1BO···Br1B (i)	0.88(13)	2.53(14)	3.398(6)	168(10)	114.8(4)	91.6(3)
O2A···Br1B (ii)	—	—	3.186(6)	—	123.5(4)	160.7(3)
<i>Ring 2</i>					⟨ Θ 3	⟨ Θ 4
O1A—H1AO···Br2B	0.89(14)	2.62(14)	3.487(6)	165(11)	87.9(3)	113.6(4)
O1A···Br1A (iii)	—	—	3.093(6)	—	131.0(5)	160.6(3)
Br1A···Br2A (iii)	—	—	3.826(1)	—	79.5(3)	160.0(3)
Br2A···Br2B (ii)	—	—	3.699(1)	—	85.1(3)	159.0(3)

^a The H positions are derived from difference electron density calculations, except H2AO, and are not refined.

^b (i) $x, -y, z + 0.5$; (ii) $x, y, z + 1$; (iii) $x, -y + 1, z - 0.5$.

^c Angles: ⟨ Θ 1, C9/C10—O···O*/Br; ⟨ Θ 2, C9/C10/C18—O*/Br···O; ⟨ Θ 3, C9/C18/C24—O/Br···Br*; ⟨ Θ 4, C18/C24—Br*···O/Br.

columns are the dominant structure motif in **1C**, where no layer structure exists.

As was shown in crystal structure **1B**, the *cis* configuration favour the formation of four-centre closed loops. In the present crystal structure **1C** the interaction motif is similar, but the fourth member of the loop is chloroform acting with its perpendicular geometry as an edge in the ring of contacts. The guest solvent is C—H···O hydrogen bonded to host molecule **1** with C27···O1 = 3.104(7) Å.

A CSD analysis (ca 100 entries) of hydrogen bonds involving hydrogen of chloroform and oxygen has been published,¹⁸ suggesting an average C···O distance of 3.32 Å. The smallest value was about 3.0 Å. Hence, the intermolecular C···O distance in **1C** of 3.104(7) Å is slightly smaller than the average, but in a normal range.

Two chlorine atoms interact with a bromine and

complete the contact ring. In Table 4, all possible contacts in **1C** are summarized. However, the contacts of chlorine and oxygen are insignificant, according to their small contact angle Θ 2. Hence, in crystal structure **1C** the interactions of chlorine atoms are reduced to contacts with bromine atoms.

Considering Fig. 7 with removed chloroform, a zig-zag chain of host molecules remains besides an empty channel. Joining the two depicted zip-like chains by lateral movement produces a structure with four-centre closed loops, in a manner similar to **1B**, but different in the type of ring members. In the theoretical loop, there is an even number of oxygen and bromine atoms (2 + 2), whereas in the structure **1B** both rings contain only odd numbers (3 + 1) and (1 + 3).

In the crystal structure of compound **2** (Fig. 8, Table 5) two molecules A and B with different conformations

Table 4. Bond lengths (Å) and bond angles (°) in O···H—O bond^a interactions, and O···halogen and Br···Cl contacts in the clathrate crystal structure **1C** [**1**·CHCl₃ (1:1)] (Esds are in parentheses)

Atoms involved ^b (symmetry code)	Distance			Angle ^c		
	D—H	H···A	D···A	D—H···A	⟨ Θ	⟨ Θ
<i>Hydrogen bonds</i>					⟨ Θ 1	⟨ Θ 2
O1—H1ox···O2 (i)	0.82(8)	2.23(9)	2.902(7)	139(8)	135.6(5)	128.9(5)
O2—H2ox···Br2 (i)	0.60(9)	3.11(9)	3.695(5)	172(13)	102.3(3)	99.79(2)
C27—H27···O1 (iii)	0.90(5)	2.22(2)	3.104(7)	165(5)	—	134.2(4)
<i>O···Cl</i>					⟨ Θ 3	⟨ Θ 4
O1···Cl2	—	—	3.773(5)	—	156.2(3)	54.5(2)
O1···Cl3	—	—	3.841(6)	—	129.8(3)	52.4(3)
O2···Cl2	—	—	3.781(6)	—	133.4(3)	81.5(2)
O2···Cl3	—	—	3.859(5)	—	163.3(3)	79.2(3)
<i>Br···Cl</i>					⟨ Θ 5	⟨ Θ 6
Br2···Cl2 (iii)	—	—	3.679(6)	—	135.1(3)	105.1(4)
Br2···Cl3 (iii)	—	—	3.871(7)	—	159.8(3)	98.2(4)
Br1···Cl1 (iv)	—	—	3.880(6)	—	154.1(4)	113.9(4)

^a The H positions are derived from difference electron density calculations and are not refined.

^b (i) 0.5 -x, 0.5 + y, z; (ii) x, y + 1, z; (iii) -x + 1, -y, -z; (iv) 0.5 + x, 0.5 - y, -z.

^c Angles: ⟨ Θ 1, C—D···A; ⟨ Θ 2, C—A···D; ⟨ Θ 3, C9/C10—O···Cl; ⟨ Θ 4, C27—Cl···O; ⟨ Θ 5, C18/C24—Br···Cl; ⟨ Θ 6, C27—Cl···Br.

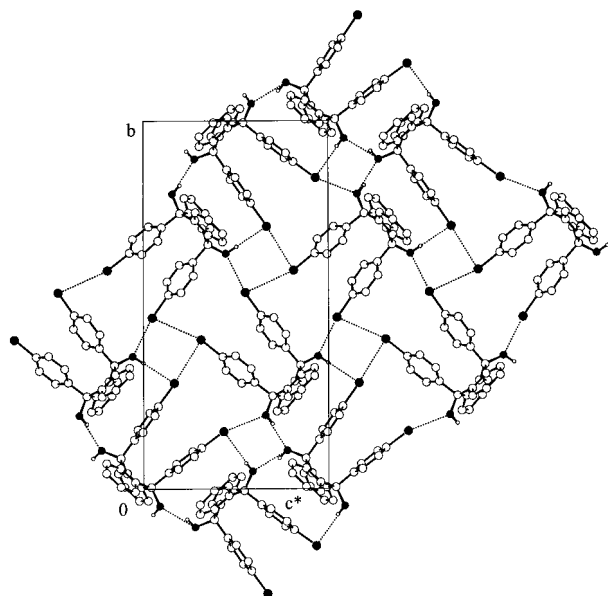


Figure 5. View along the *a*-axis of the packing arrangement in one plane of the monoclinic crystal structure **1B**, the second modification of **1**. In this modification the molecules form dimers via an O—H···O hydrogen bond and an O···Br contact. Blocks of dimers are arranged like a brick pattern. Two different four-centre closed loops among three blocks are the dominant motif of interaction between these dimers (see Fig. 6). Contacts and hydrogen bonds are depicted as dotted lines

adopt the same mode of dimer as in **1B** and **1C**. Two molecules are twisted to each other and a bromine-substituted phenyl group fit into the concave roof-shaped 9,10-dihydroanthracene unit. Additionally the molecules are connected by a hydrogen bond O1A···O1B. Whereas the analogous diol **1** was capable of forming bromine contacts, owing to the *para* position of the halogen, the *meta* position of the bromine atoms in both conformations of **2** prevents this contact.

Dimer motifs are joined into a four-membered ring of molecules. These molecules are linked together by four hydrogen bonds surrounding a centre of symmetry. Each hydroxy group, specified by the number 1, participates in two hydrogen bonds and also acts as hydrogen donor and acceptor. Therefore, the oxygens have exhausted both options to form contacts, i.e. the hydrogen atom is involved in a hydrogen bond, in the same way as the electron lone pair, as a hydrogen acceptor. From the geometric point of view, this four-centre closed loop of cooperative hydrogen bonds is comparable to the ring systems in **1B**. On the other hand, the atoms involved are different. In the crystal structure of **2** the atoms of the four-center closed loop are identical, which is fairly common, for example, for crystal structures of phenol compounds.¹⁹

The four-membered intermolecular ring systems are connected via outside-located hydroxy groups (O2B) and by a linear Br···Br contact (Br1B) to adjacent molecules,

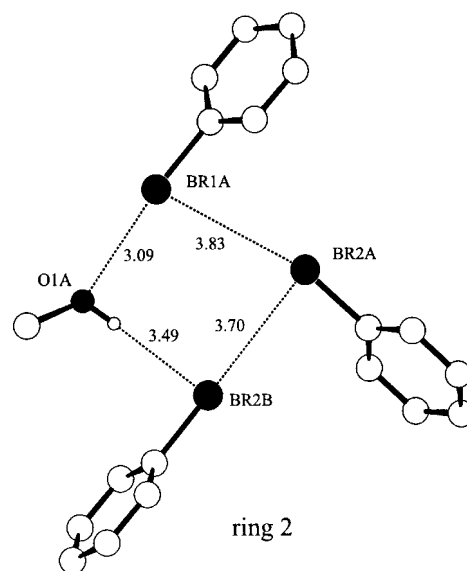
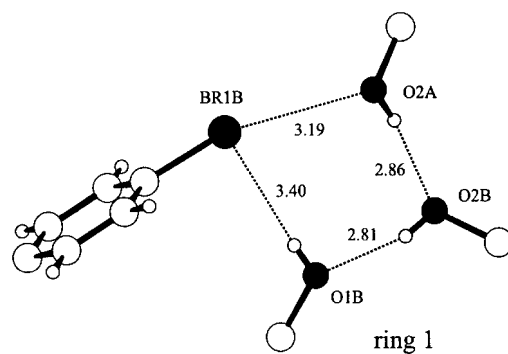


Figure 6. The two types of four-centre closed loops among three blocks of dimers are dominant in the structure **1B**. One of them is formed by three hydroxy groups and one bromine but the other involves three bromine atoms and one hydroxy group. The values of distances indicate donor···acceptor distances. Depicted hydroxy hydrogen atoms were located on the difference Fourier map, except H2AO—(O2A). Contacts and hydrogen bonds are depicted as dotted lines

which are involved in the same type of intermolecular rings. As a result of these two and their two symmetry-equivalent interactions, each of the planar ring motifs is part of a large association. The contacts spread out as a layer structure in the *ac*-plane. Significant contacts between these layers are not present.

Influence of the solvent

Calorimetric titration of compound **1** with toluene shows no complexation or aggregation between **1** and the solvent. In contrast, chloroform appears to interact with the diol, using the chlorine atoms and the hydrogen such as shown in the clathrate structure of **1C**. However, the

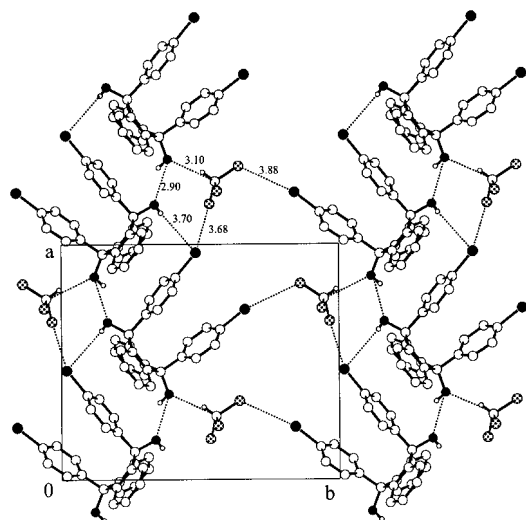


Figure 7. View along the *c*-axis of the packing arrangement of planes in the orthorhombic clathrate structure **1C** [**1**·CHCl₃ (1:1)]. This clathrate, crystallizing from pure chloroform, presents a dimer mode similar to **1B** (Fig. 5). The packing arrangement shows only small difference due to the included solvent causing a swelling effect in the crystal packing. In addition, the host molecules are arranged into a chain rather than into separated dimers. The values of distances indicate donor···acceptor distances. Depicted hydroxy hydrogen atoms were located on the difference Fourier map. Contacts and hydrogen bonds are depicted as dotted lines

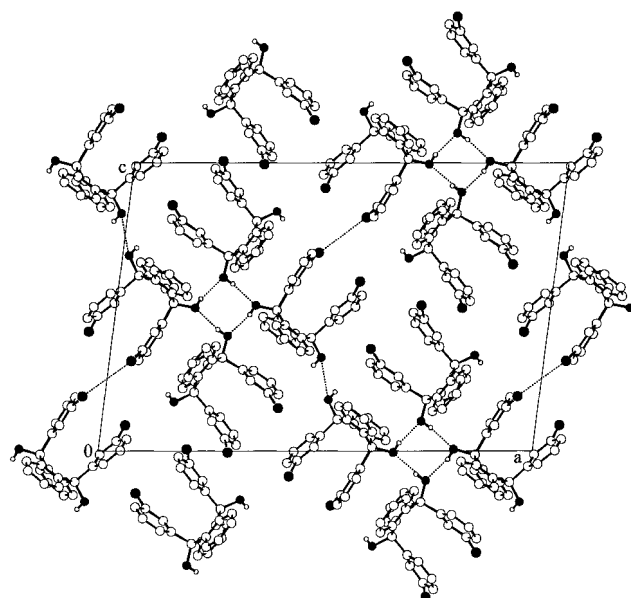


Figure 8. View along the *b*-axis of the monoclinic crystal structure **2** showing the packing arrangement of one plane. Planar four-centre rings dominate the crystal structure. The rings contain four cooperative hydrogen bonds with one phenyl group of each molecule being oriented into the concave roof-shaped 9,10-dihydroanthracene moiety of a neighbouring molecule. Depicted hydroxy hydrogen atoms were located on the difference Fourier map. Contacts and hydrogen bonds are depicted as dotted lines

determined enthalpy of complexation of **1** with chloroform is small (4 KJ mol⁻¹) and thus rather unspecific, i.e. no detailed information about the position of the interaction can be deduced. Nevertheless, this value is indicative of a small association. A question is whether the solvent molecule supports an assembly of two molecules or avoids contacts by saturation of the functional groups. As a good approximation, weak contacts of the chlorine atom in region 1 (bromine atoms) and a C—H···O hydrogen bond in region 2

(hydroxy groups) with their preorganizing influences seem to be the reason for the polymorphism of **1** and the formation of different crystal structures **1A** and **1B**.

CONCLUSION

The block-like dibromodihydroxy-containing compounds prefer to crystallize in layer structures. Optimum

Table 5. Bond lengths (Å) and bond angles (°) in O···H—O bond^a interactions, and O···Br and Br···Br contacts in the crystal structure of **2** (Esds are in parentheses)

Atoms involved ^b (symmetry code)	Distance			Angle ^c		
	D—H	H···A	D···A	D—H···A	⟨Θ	⟨Θ
<i>Hydrogen bonds</i>						
O1A—H10A···O1B	0.74(7)	2.04(7)	2.769(6)	170(8)	⟨Θ 1 115.5(3)	⟨Θ 2 152.8(3)
O1B—H10B···O1A (i)	0.73(8)	2.02(9)	2.726(5)	160(9)	116.7(3)	147.7(3)
O2B—H20B···O2B (ii)	0.62(9)	2.39(9)	2.737(8)	113(9)	159.6(3)	159.6(3)
<i>O···Br</i>						
O2A···Br2B (iii)	—	—	4.088(6)	—	⟨Θ 3 140.7(6)	⟨Θ 4 90.5(6)
<i>Br···Br</i>						
Br1B···Br1B (iii)	—	—	3.871(2)	—	⟨Θ 5 121.2(2)	⟨Θ 6 121.2(2)

^a The H positions are derived from difference electron density calculations and are not refined.

^b (i) $-x + 0.5, -y + 0.5, -z$; (ii) $-x + 1, y, 0.5 - z$; (iii) $-x + 1, y, -z - 0.5$.

^c Angles: ⟨Θ 1, C9/C10—O···O*; ⟨Θ 2, C9/C10—O*···O; ⟨Θ 3, C9/C10—O···Br; ⟨Θ 4, C18/C24—Br···O; ⟨Θ 5, C18/C24—Br···Br*; ⟨Θ 6, C18/C24—Br*···Br.

packing, realized by fitting a phenyl group into a concave 9,10-dihydroanthracene moiety, and nearly planar four-centre closed loops are the dominant motifs in the crystal structures. Generally, five different types of loops are possible, differing in the number of participating bromine atoms or hydroxy groups (Br:OH = 4:0, 3:1, 2:2, 1:3, 0:4). The absence of a crystal structure containing four-centre closed loops only with bromine atoms (4:0) or with a balanced ratio (2:2) of both functional groups indicates the instability of these even arrangements when a planar ring motif is required from optimum packing relationships. As shown elsewhere,^{4b} a cluster of four bromine atoms is arranged in a tetrahedral fashion with distances between any two bromine atoms of 3.91 Å. Mixed rings with different members (bromine atoms and hydroxy groups) in an odd ratio (1 + 3 or 3 + 1) seem to be favoured in planar arrangements.

Short O...Br contacts (3.1–3.2 Å) contain C—O...Br angles of about $125 \pm 10^\circ$ and C—Br...O angles of about $160 \pm 10^\circ$. This indicates that the part of the bromine atom situated opposite to the covalent bromine carbon bond interacts with the laterally attached electron lone pair of the oxygen. The hydroxy hydrogen atom in such arrangements adopts a perpendicular orientation to the direction of this O...Br interaction. Longer O...Br contacts (3.4–3.8 Å) contain contact angles both in the range 90 – 120° .

In the case of pure bromine interactions, the contacts are shorter (3.4–3.5 Å) in a linear geometry ($\Theta 1 = \Theta 2 = 160 \pm 10^\circ$), i.e. in the bond directions, whereas longer bromine contacts of about 3.7–3.85 Å present a perpendicular geometry ($\Theta 1 = 80 \pm 10^\circ$; $\Theta 2 = 160 \pm 10^\circ$).

The variation in the position of the bromine atoms attached to the phenyl groups in the diol compound **2** results in an absence of Br...O contacts. The four-centre closed loop formed contains four cooperative hydroxy groups. However the packing relationship of **2** is similar, according to the fit of the bromophenyl group into the concave 9,10-dihydroanthracene unit of a neighbouring molecule.

Thus, for crystallization of compounds the right choice of a suitable solvent is not a parameter to be neglected. A sensitive balance of forces between various contacts and their endeavour to determine and control the mode of association are influenced by the solvent of crystallization, and lead to polymorphism or guest-dependent polymorphism.

EXPERIMENTAL

Synthesis. Melting-points were determined with a hot-stage microscope (VEB Dresden Analytik) and are uncorrected. ¹H and ¹³C NMR spectra were recorded using a Bruker MSL 300 (300 MHz) instrument. The chemical shifts (δ) are reported as ppm relative to SiMe₄.

The IR spectra were recorded on a Nicolet Model 510 FT-IR spectrometer.

Compounds 1 and 2. General procedure. The respective dibromobenzene (1,4-dibromobenzene for **1**, 1,3-dibromobenzene for **2**; 11.8 g, 0.05 mol) was dissolved in dry diethyl ether (150 ml) at -15°C under an atmosphere of dry argon. A solution of *n*-butyllithium (1.6 M in *n*-hexane; 31.2 ml, 0.05 mol) was added dropwise with stirring during 30 min. Stirring was continued for 30 min at 0°C and then for 1 h at room temperature. After cooling the stirred solution to -15°C , fine 9,10-anthraquinone powder (2.5 g, 0.012 mol) was added portionwise under an argon atmosphere and the mixture was stirred for 2 h at room temperature, then refluxed for 4 h, cooled and hydrolysed with aqueous saturated NH₄Cl solution. The ethereal phase was separated, washed with water and dried over anhydrous MgSO₄. Evaporation of the solvent under reduced pressure and recrystallization from toluene yielded the pure compounds.

cis-9,10-Bis(4-bromophenyl)-9,10-dihydroxy-9,10-dihydroanthracene (**1**): yield 3.4 g (55%), colourless crystals, m.p. 237 – 239°C (found, C 59.53, H 3.39; C₂₆H₁₈O₂Br₂ requires C 59.79, H 3.47%); ¹H NMR (CDCl₃), δ 6.9 (4H, d, Ar-H), 7.17 (4H, d, ArH), 7.42 (4H, m, Ar-H), 7.81 (4H, m, Ar-H); ¹³C NMR (acetone-*d*₆), δ 72.1 (C-OH), 122.5 (Ar-Br), 126.7 (Ar-H), 129.2 (Ar-H), 140.6 (Ar-C), 148.3 (Ar-COH); IR (hexachlorobutadiene), $\nu = 3558, 3529, 3499, 3447, 3060\text{ cm}^{-1}$; UV (toluene), $\lambda = 247$ (peak), 260–280 nm (shoulder).

cis-9,10-Bis(3-bromophenyl)-9,10-dihydroxy-9,10-dihydroanthracene (**2**): yield 3.2 g (52%), colourless crystals, m.p. 154 – 155°C (found, C 59.87, H 3.56; C₂₆H₁₈O₂Br₂ requires C 59.79, H 3.47%); ¹H NMR (acetone-*d*₆), δ 7.0 (4H, d, Ar-H), 7.05 (2H, s, Ar-H), 7.18 (2H, m, Ar-H), 7.48 (4H, m, Ar-H), 7.85 (4H, m, Ar-H); ¹³C NMR (acetone-*d*₆), δ 74.3 (C-OH), 121.9 (Ar-Br), 127.8 (Ar-H), 130.3 (Ar-H), 141.6 (Ar-C), 149.3 (Ar-COH); IR (hexachlorobutadiene), $\nu = 3530, 3272, 3068, 2931, 2853\text{ cm}^{-1}$; UV (toluene), $\lambda = 241$ (peak), 250–280 nm (shoulder).

Crystallography. Sample preparation. Crystals suitable for x-ray investigation were prepared by slow evaporation of solutions of the respective compounds. Crystals were grown from toluene in the case of **1A** and **2**, and from toluene with a trace of chloroform in the case of **1B**. Crystallization from chloroform gave the clathrate **1C** [**1**·CHCl₃ (1:1)].

Data collection, structure analysis and refinement. Intensity data for **1A** were obtained on an Nonius Kappa instrument with a CCD detector, for **1B** on an Enraf-Nonius CAD4 instrument with a scintillation detector and for **1C** and **2** on a Philips PW 1100 diffractometer. The structures **1B**, **1C** and **2** were solved by direct methods,

using the program *SIR92*²⁰ and refined with *SHELXL93*.^{21a} For the structure **1A**, *SHELXS*^{21b} and *SHELXL97*^{21c} were used. The diagrams were prepared using *ORTEP*,²² as implemented in *PLATON*,²³ and with *PLUTON*,²⁴

In structure **1A**, the disordered hydroxy hydrogen atoms H1Ax, H1Ay and H1Bx, H1By and the hydroxy hydrogen atom H2CO were located on the difference electron density map and refined with bond length constraints. The disorder was best modeled by assigning site-occupation factors of 0.50 for the hydrogen atoms *x* and *y*. The isotropic temperature factors of these hydrogen atoms are restrained to the temperature factors of the connected oxygen, using a multiplier of 1.5. The remaining hydroxy hydrogen atoms and the aromatic hydrogen atoms were located on the difference electron density map and refined with individual isotropic temperature factors. The residual peaks of electron density are situated meanly around the bromine atoms and besides all C—O bonds.

For **1B**, the systematic absences permit the space group to be either *Cc* or *C2/c*; *Cc* was chosen and confirmed by analysis (MISSYM-algorithm, Le Page, implemented in *PLATON*²³). In addition, the structure could not be solved in space group *C2/c*. The hydroxy hydrogen atoms were located on the difference electron density map, except H2AO. The hydrogen atom H2AO was placed on the position with the highest electron density on a circle of rotation with idealized tetragonal angle to the C—O bond. The isotropic temperature factors of the hydroxy hydrogen atoms are restrained to the temperature factors of the connected oxygen atom, using a multiplier of 1.5. All the other aromatic hydrogen atoms were included in the refinement at calculated positions and were assigned isotropic temperature factors multiplied by 1.2 to those of the atoms to which they were bound and were not refined. In the final synthesis the first peaks are distributed very systematically around the bromine atoms. These residues of electron density have an average distance to the bromine atom of 0.93 Å.

To avoid decomposition of the clathrate **1C** [**1**·CHCl₃ (1:1)], a single crystal of reasonable quality and appropriate size was sealed in a glass capillary. For **1C**, the orthorhombic space group was uniquely determined by the systematic absences. For **2**, the systematic absences permit the space group to be either *Cc* or *C2/c*; *C2/c* was chosen and confirmed by analysis.

In both crystal structures, direct methods yielded a reasonable preliminary model and all non-hydrogen atoms were located on the electron density map. On account of the considerable number of heavy atom electrons in **1C** (38%, 16 bromine atoms and 24 chlorine atoms in the unit cell) and in **2** (27%, 32 bromine atoms in the unit cell) and the problems with the refinement of heavy atom structures measured at room temperature, the numerical absorption program *DIFABS*²⁵ was applied. The hydroxy hydrogen atoms were located on the

difference electron density map for both structures. The isotropic temperature factors of these hydrogen atoms are restrained to the temperature factors of the connected oxygen atom, using a multiplier of 1.5. The remaining aromatic hydrogen atoms were included in the refinement at calculated positions and were assigned isotropic temperature factors multiplied by 1.2 to those of the atoms to which they were bound and were not refined. The residual peaks of electron density in **1C** and **2** are systematically distributed around the halogen atoms.

Supplementary material. Lists of the structure factors, atomic coordinates and thermal components for non-hydrogen atoms and hydrogen atom parameters are available from E.W. on request.

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