

The Janus-like behaviour of sulfur in substituted diquinoline inclusion crystal structures†‡

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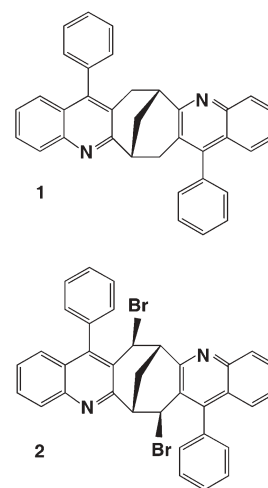
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The crystal structures of the methylene-bridged diquinolines **1,2** are compared to those of their newly synthesised thia-substituted analogues **9,10**. As expected from our molecular design, neither non-brominated compound **1** nor **9** shows inclusion properties, but the dibrominated structures **2** and **10** act as versatile lattice inclusion host molecules. All our crystal structures of the methylene-bridged compounds **1,2** contain an (EF)₆ centrosymmetric dimeric building block, built from three different types of aryl edge-face (EF) interactions. The crystal structures of the thia-compounds **9,10** also involve (EF)₆ dimers, but fall into two distinct types. In one group, the sulfur atom effectively mimics the methylene group and isostructural compounds result across the two series. The second group is comprised of structures that are markedly dissimilar between the two series, even though the sulfur substituent does not play an overt role in the molecular packing. These similarities and differences are examined in crystal engineering terms.

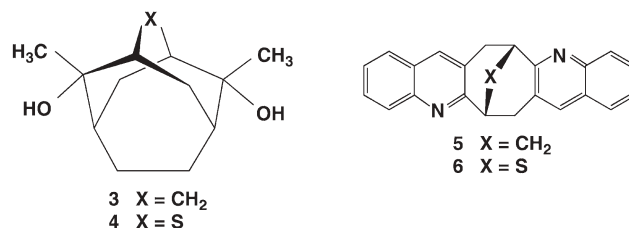
Introduction

Recently, we have been carrying out a systematic crystal engineering study of bridged diquinoline systems in order to understand their molecular inclusion properties. The parent compound **1**, for example, shows no host properties but its dibromo derivative **2** is an excellent lattice inclusion host, and these were expected outcomes from our molecular design.¹ Despite this behavioural difference, both racemic **1** and **2** form closely related dimeric brick-like units that pack together in their crystal structures.² Opposite enantiomers self-assemble by means of three different aromatic edge-face interactions^{3,4} (EF₁–EF₃) to form centrosymmetric (EF)₆ bricks, as illustrated in Fig. 1 for **2**.

In this paper we report the outcomes of replacing the methylene group at the centre of the alicyclic linker group of **1** and **2** by a sulfur atom. It is known that sometimes this action can lead to sulfur mimicking methylene and thereby resulting in formation of an isostructural solid. In other cases, however, entirely different crystal structures result. From our own research, crystallisation of diols **3** and **4** from chloroform is an example of the former behaviour, with both racemic diols yielding isostructural inclusion compounds of type (host)₄·(CHCl₃) in space group *I*4₁/*acd*.^{5,6} In contrast, the racemic diquinoline **5** crystallised solvent-free from methanol in space group *P*1̄,⁷ whereas racemic **6** formed the inclusion compound (6)₆·(CH₃OH) in *R*3̄. The guest was associated with the aromatic rings of the host, rather than the sulfur atom.



Hence the sulfur did not play a dominant role as a supramolecular synthon in this crystal structure.⁸



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Results and discussion

Preparation and crystallisation of the thiadiquinolines **9** and **10**

The two target molecules were synthesised as illustrated in Scheme 1. Two equivalents of commercial 2-aminobenzophenone **7** were condensed with one of 9-thiabicyclo[3.3.1]nonane-2,6-dione^{9,10} **8** by means of Friedländer condensation.^{11,12} The

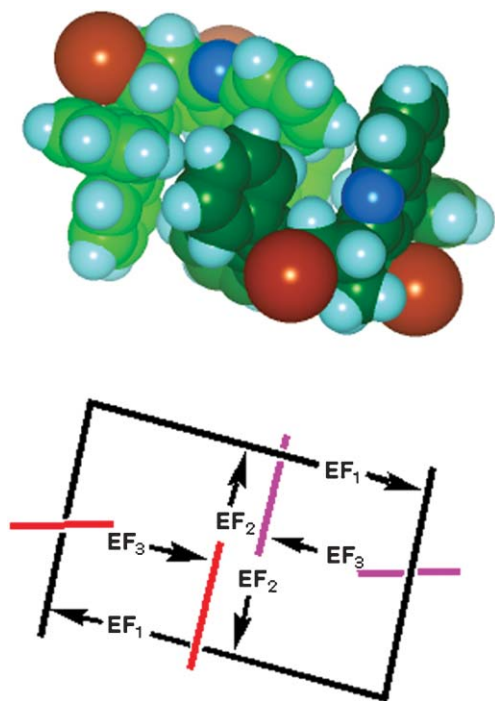


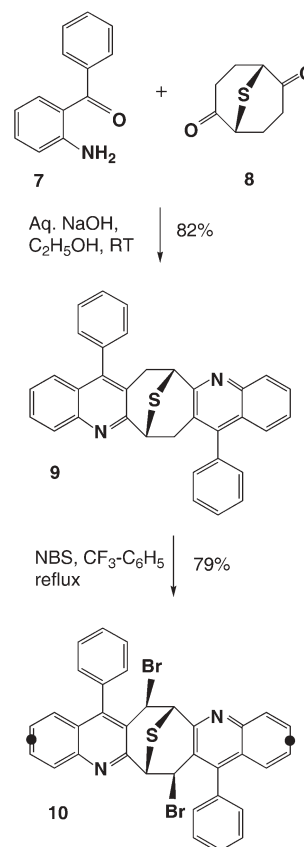
Fig. 1 Molecular and diagrammatic representations of the centrosymmetric (EF)₆ building block present in crystal structures of the dibromo diquinoline **2**. Atom codes in the molecular structure: C green (opposite enantiomers light or dark), H light blue, N dark blue, Br brown. In the diagrammatic representation, the protruding pendant phenyl groups are coloured red (upper surface) or purple (lower surface).

resulting thiaquinoline derivative **9** was obtained in 82% yield. Benzylic bromination using *N*-bromosuccinimide (NBS) in trifluoromethylbenzene then afforded the dibromo analogue **10**. The highly regio- and stereo-selective outcomes of such NBS substitution reactions have been discussed by us in recent publications.^{13,14}

In accord with the design principles that we have outlined previously,^{1,15,16} the parent thiaquinoline **9** gave no indication of including guest molecules, but its dibromo analogue **10** was a versatile host molecule. Single crystal structures of the carbon disulfide, dichloromethane, tetrahydrofuran, 1,1,2,2-tetrachloroethane and chlorobenzene inclusion compounds of **10** were solved. Determinations were also carried out on the solvent-free crystals of both compounds **9** and **10**, and numerical details of all these crystal structures are presented in Table 1.

Analysis of the crystal structures

All five of the lattice inclusion compounds of **10** crystallised in space group $P\bar{1}$. The carbon disulfide, dichloromethane, tetrahydrofuran, and 1,1,2,2-tetrachloroethane compounds had a host : guest stoichiometry of 1 : 1, but the stoichiometry of the chlorobenzene inclusion compound was 1 : 2. The apohost structure of **10** was present in $C2/c$, and the solvent-free structure of **9** crystallised in space group $P2_1/c$. When these crystal structures of the thia-substituted diquinolines were compared to those containing the central methylene



Scheme 1 Synthesis of the thiaquinoline derivatives **9** and **10**.

group, they fell into three groups: (i) crystals that were isostructural; (ii) one that could only be compared indirectly; and, (iii) crystal structures that were different.

The isostructural crystal structures

The crystal structure of the non-brominated compound **9** is isostructural in $P2_1/c$ with that of its non-S analogue **1**.¹⁷ Both structures contain centrosymmetric (EF)₆ bricks (Fig. 2) that differ slightly from those of their brominated analogues (Fig. 1) due to the values of the torsion angles present between the phenyl groups and the aryl wings. These angles are discussed in greater detail later in this paper.

The bricks of **9** associate by means of EF and offset face-face (OFF) interactions to generate the arrangement illustrated in Fig. 3. This packing results in chains of homochiral molecules of **9** running along the *b* direction. Adjacent chains have the opposite handedness.

The crystal structure of (10)·(CS₂) shown in Fig. 4 is isostructural with the corresponding non-S structure (2)·(CS₂).¹⁷ It also has many similarities with the structure of (2)·(CHCl₃), and to a lesser extent with that of (2)·(*p*-xylene), already published.² The building block present in all of these solids is the type of centrosymmetric (EF)₆ brick illustrated in Fig. 1, and their chief difference is the subtle changes in the manner by which the three types of guest molecules are incorporated as a result of the variation in guest size and shape.

The structure of the inclusion compound (10)·(CH₂Cl₂), illustrated in Fig. 5, is also the same as its non-S analogue

Table 1 Numerical details of the solution and refinement of the crystal structures

Compound	9	10	10 and carbon disulfide	10 and dichloromethane	10 and tetrahydrofuran	10 and 1,1,2,2-tetrachloroethane	10 and chlorobenzene
Formula	C ₃₄ H ₂₄ N ₂ S	C ₃₄ H ₂₂ Br ₂ N ₂ S	(C ₃₄ H ₂₂ Br ₂ N ₂ S) · (CS ₂)	(C ₃₄ H ₂₂ Br ₂ N ₂ S) · (CH ₂ Cl ₂)	(C ₃₄ H ₂₂ Br ₂ N ₂ S) · (C ₄ H ₈ O)	(C ₃₄ H ₂₂ Br ₂ N ₂ S) · (C ₂ H ₂ Cl ₄)	C ₃₄ H ₂₂ Br ₂ N ₂ S · (C ₆ H ₅ Cl) ₂
Formula mass	492.61	650.4	726.6	735.4	722.5	818.3	875.5
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.7356(15)	21.421(8)	9.964(5)	10.085(4)	10.204(5)	10.067(5)	10.001(6)
<i>b</i> /Å	26.301(4)	8.159(1)	10.551(5)	10.509(4)	10.564(5)	10.289(5)	10.437(5)
<i>c</i> /Å	10.4093(18)	17.182(6)	15.788(8)	15.811(6)	15.804(7)	17.046(7)	20.029(8)
<i>α</i> /°	90	90	104.96(3)	106.24(2)	104.64(3)	76.54(3)	78.18(3)
<i>β</i> /°	109.840(4)	116.29(2)	99.56(3)	100.09(2)	99.74(3)	88.64(3)	77.99(3)
<i>γ</i> /°	90	90	97.30(3)	92.01(2)	93.26(3)	85.93(3)	83.90(2)
<i>V</i> /Å ³	2507.1(7)	2692(2)	1556(1)	1578(1)	1616(1)	1713(1)	1997(1)
<i>Z</i>	4	4	2	2	2	2	2
<i>D</i> _{calc} /g cm ^{−3}	1.31	1.60	1.55	1.55	1.48	1.59	1.46
<i>μ</i> /mm ^{−1}	0.156	3.089	2.810	2.811	2.584	2.750	2.234
No. of intensity meas.	17399	2375	5402	5536	5676	6007	7015
No. of indep. obsd. ref.	5766	1795	3166	3277	2792	4087	3804
No. of reflections (<i>m</i>)	5766	1795	3166	3277	2792	4087	3804
Variables (<i>n</i>) in final ref.	334	149	197	196	198	225	226
<i>R</i> = Σ Δ <i>F</i> /Σ <i>F</i> _o	0.058	0.047	0.064	0.060	0.065	0.053	0.059
<i>R</i> _w = [Σ <i>w</i> Δ <i>F</i> ² /Σ <i>w</i> <i>F</i> _o ²] ^{1/2}	0.120	0.073	0.071	0.077	0.082	0.064	0.075
<i>s</i> = [Σ <i>w</i> Δ <i>F</i> ² /(<i>m</i> − <i>n</i>)] ^{1/2}	0.902	1.75	1.85	1.64	1.68	1.83	1.63
Crystal decay	none	none	4%	none	22%	none	39%
Min., max. trans. coeff.	0.98, 0.99	—	0.49, 0.73	0.60, 0.69	0.52, 0.75	0.51, 0.75	0.56, 0.79
<i>R</i> for mult. meas.	0.094	0.022	0.042	0.039	0.059	0.014	0.027
Largest peak in final diff. map/e Å ^{−3}	0.24	0.73	1.21	1.17	1.53	0.81	1.05

(2)·(CH₂Cl₂).¹⁷ Once again, the core host packing is due to the centrosymmetric (EF)₆ brick previously described in the two published structures.²

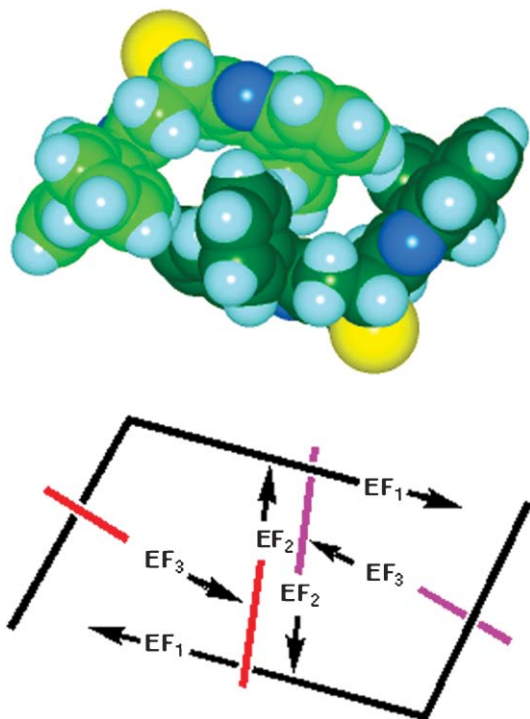


Fig. 2 The centrosymmetric (EF)₆ dimer present in the crystal structure of **9**. This should be compared with Fig. 1, which illustrates the slightly different building block used in the crystal structures of the brominated analogues **2** and **10**. The atom coding is identical but with the addition of S yellow.

One crystal structure that cannot be directly compared

We were unable to obtain crystalline material when the non-S compound **2** was crystallised from 1,1,2,2-tetrachloroethane, and so a direct comparison with (10)·(CHCl₂–CHCl₂) cannot be made. Once again, the host molecules assemble into the same centrosymmetric (EF)₆ bricks that stack along the *b* and *c* directions. As can be seen in Fig. 6, however, the resulting crystal structure is significantly different to the previous two cases, due to rotation of the bricks around *a*. Previously, one aryl wing of the host lay approximately in the *ac* plane, but this is no longer the case here. The *c* dimension is also increased to accommodate the larger guests.

Dissimilar crystal structures of 10

When the dibrominated non-S compound **2** was crystallised from tetrahydrofuran, the solvent-free (apohost) material was produced. This substance crystallised in space group *P*2₁/*c*, but its crystal structure was related to those of its inclusion compounds. In common with these, the host molecules assembled into centrosymmetric (EF)₆ dimers that then stacked together.¹⁷ In contrast to this behaviour, the thia-derivative gave crystals of (10)·(C₄H₈O) from a tetrahydrofuran solution. This structure is presented in Fig. 7. It is essentially the same as those of (10)·(CS₂) and (10)·(CH₂Cl₂), with only minor dimensional differences being present.

Major behavioural differences were also observed when **2** and **10** were crystallised from solutions in chlorobenzene, from which the compounds (2)·(C₆H₅Cl) and (10)·(C₆H₅Cl)₂ were obtained, respectively. The structure of the (2)·(C₆H₅Cl) compound is analogous to the others so far described here, except that the unit cell adopts a more orthogonal nature with all three cell angles near 90° [*α* 90.30(3), *β* 90.04(3), *γ* 90.42(3)°].

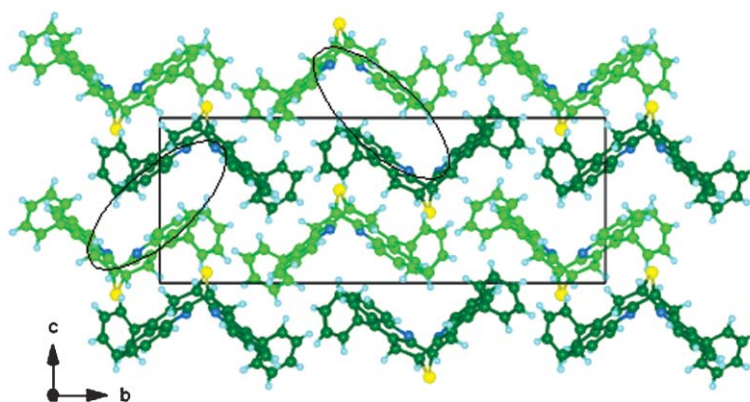


Fig. 3 Part of the crystal structure of the non-brominated thiadiquinoline **9** projected onto the *bc* plane. Two bricks are highlighted by the ellipses.

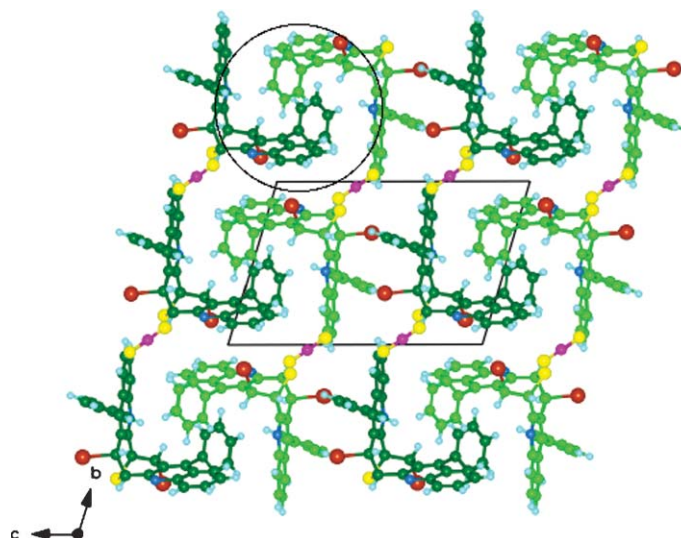


Fig. 4 Part of the crystal structure of **(10)·(CS₂)** projected onto the *bc* plane. Atom coding: guest C purple. The CS₂ guest molecules associate at the corners of the dimeric (EF)₆ brick. The circle highlights one brick in this structure.

The chlorobenzene molecules are, once again, associated with the corners of the (EF)₆ bricks.¹⁷

The structure of **(10)·(C₆H₅Cl)₂** is illustrated in Fig. 8. In this crystal the angles are similar to those in the other structures of **10**, but *c* has increased further to accommodate an additional guest molecule. Rotation of the (EF)₆ bricks is rather similar to that present in **(10)·(CHCl₂–CHCl₂)**. One independent set of guest molecules (coloured black) remains associated with the corners of the (EF)₆ bricks. However, a second independent set of guests (coloured purple) lie in the *ab* plane, such that the direct brick contacts along *c* have been removed and the remaining stacks of bricks are now separated into layers in the *ab* plane.

As previously reported, **(2)·(CHCl₃)** is formed when the non-S compound is crystallised from chloroform.² The structure of this compound is related to those containing CS₂ or CH₂Cl₂. In contrast, crystals of the apohost structure of **10** were obtained from chloroform. This material crystallises in space group *C2/c*. It has a structure entirely different from the apohost form of **2** and, indeed, from all the other compounds found in these two series. The molecules do not

assemble into bricks. Instead, the crystal structure is made up of homochiral layers in which the S apices all point in the same direction (up or down, in Fig. 9). Adjacent molecules along *b* tuck (*exo*- to *endo*-) into their neighbour, and molecules in the adjacent layers point in the opposite direction.

Comparison of the structures

Some numerical values for the crystal structures are compared in Table 2. The molecular structures of these diquinolines are flexible due to the presence of the bicyclic linker group, and one means of comparison is the fold angle (defined by the sulfur atom and the two black dots shown on the structure in Scheme 1). The values for the five inclusion compounds of **10** (85.8–88.5°) are consistent, and not atypical for those of related diquinoline compounds. The packing coefficients (67.0–69.4%) are also uniform. The fold angle for the apohost **10** (98.1°) is about ten degrees higher than the other compounds, and its packing coefficient (70.1%) is slightly higher. In contrast, the fold angle of the non-brominated precursor **9** is higher still (102.9°) but its packing coefficient is

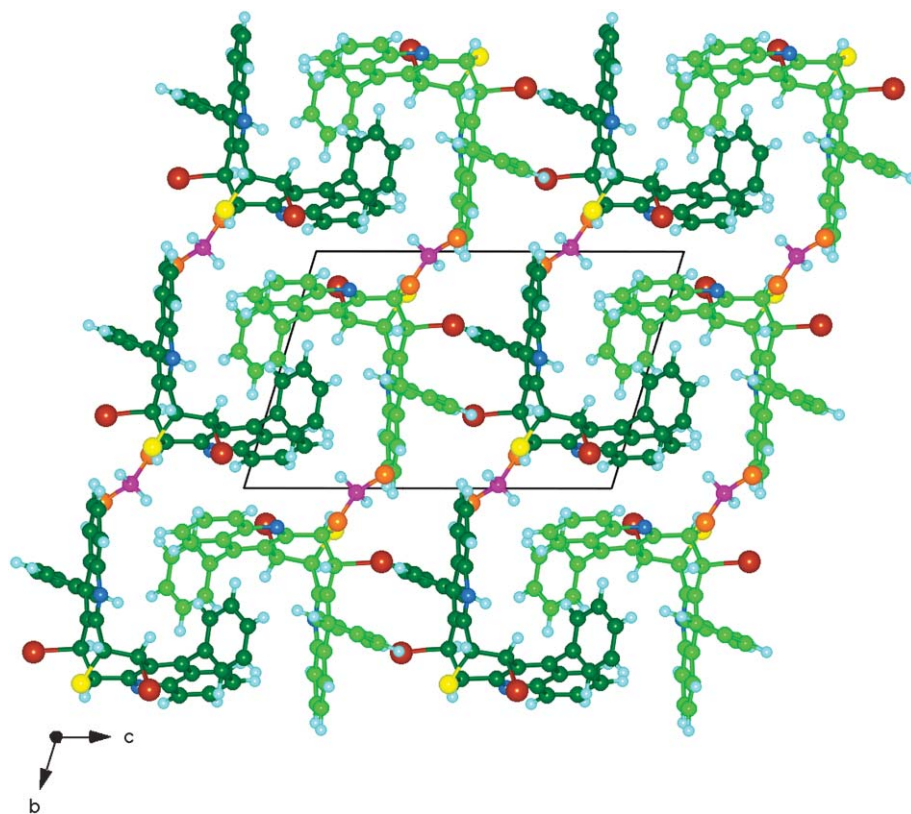


Fig. 5 Part of the crystal structure of $(10) \cdot (\text{CH}_2\text{Cl}_2)$ projected onto the bc plane. Atom code: guest C purple, guest Cl orange. The CH_2Cl_2 guest molecules are located at the corners of the centrosymmetric host dimeric $(\text{EF})_6$ bricks. Only the major disorder component of the guest is shown.

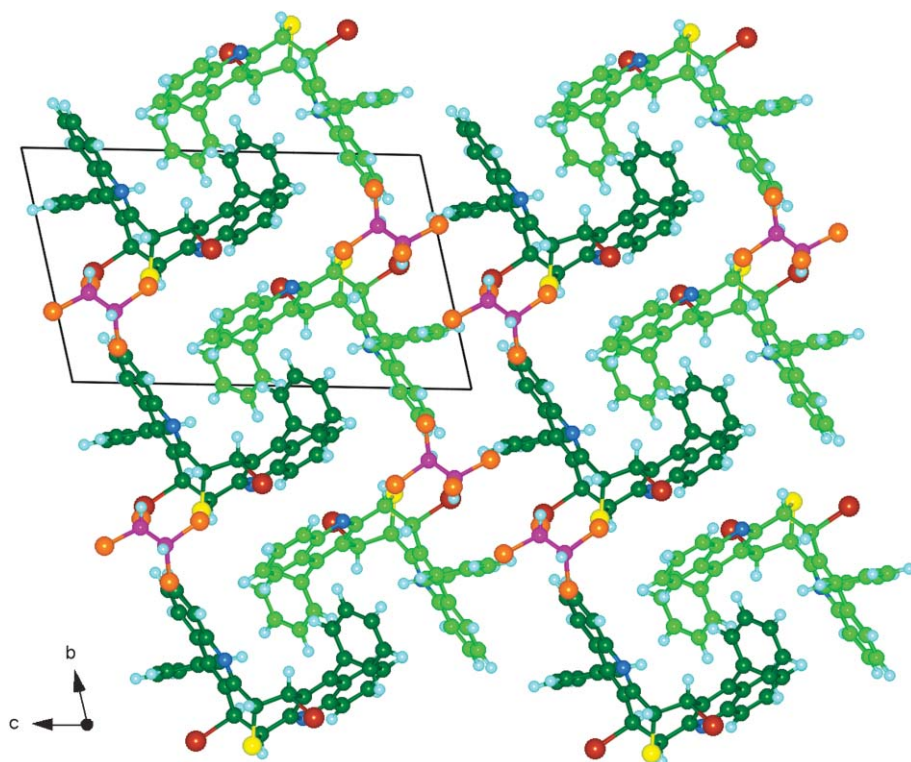


Fig. 6 The crystal structure of $(10) \cdot (\text{CHCl}_2\text{-CHCl}_2)$ projected onto the bc plane. The orientation of the $(\text{EF})_6$ bricks is rotated compared to the previous two structures shown in Figs. 4 and 5, to accommodate the bulkier guest.

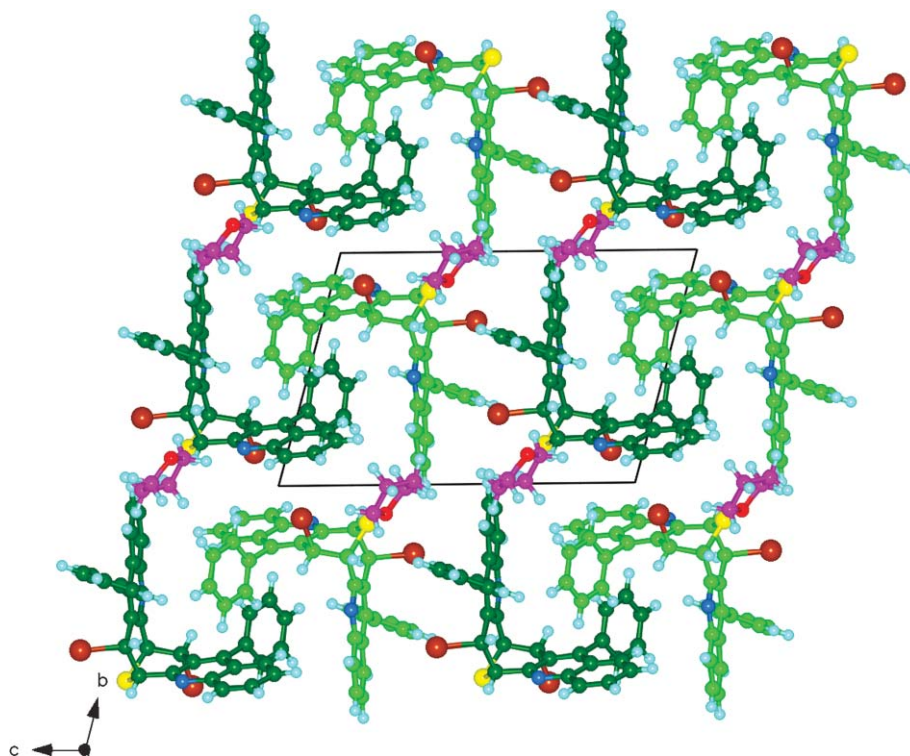


Fig. 7 The crystal structure of the inclusion compound $(10) \cdot (C_4H_8O)$ with its guest atoms represented as C purple, H light blue, and O red. Its close similarity to the solids $(10) \cdot (CS_2)$ (see Fig. 4 and Table 1), and $(10) \cdot (CH_2Cl_2)$ (see Fig. 5 and Table 1), should be noted.

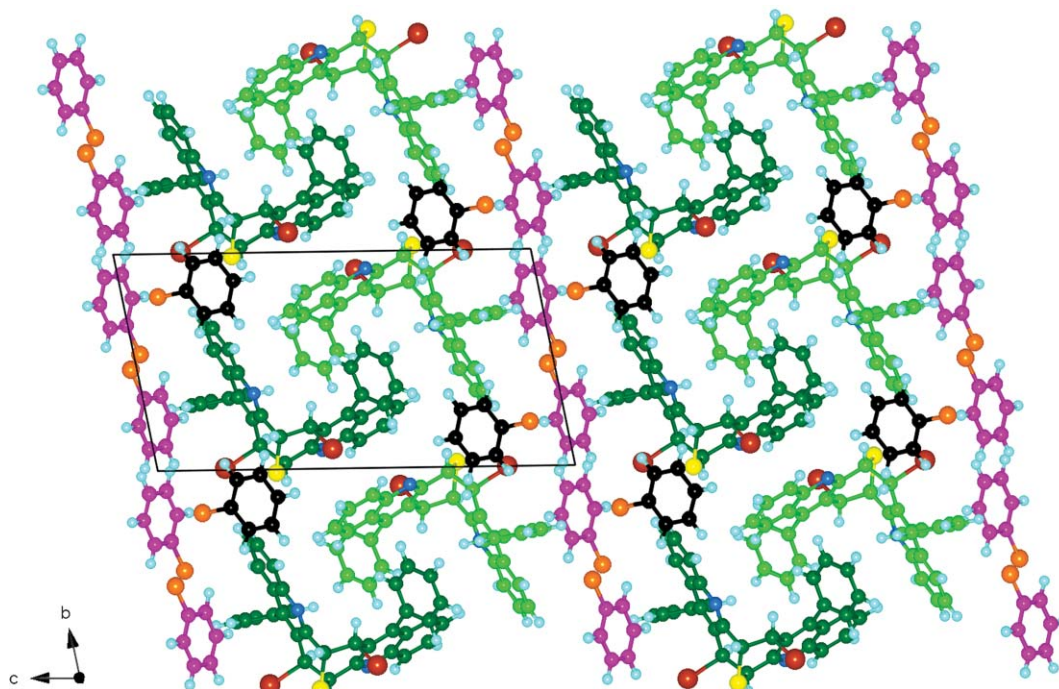


Fig. 8 Crystal structure of $(10) \cdot (C_6H_5Cl)_2$ projected onto the bc plane. The two independent chlorobenzene molecules are differentiated using black or purple C atoms. The stacks of $(EF)_6$ bricks and purple guest molecules comprise alternating layers in the ab plane. Only the major disorder components of the guests are shown.

similar to those of the inclusion compounds of **10**. These variations illustrate how the conformational mobility designed into the central linker group can be utilised to

modify the crystal packing when required. Fold angle values for diquinolines with bicyclo[3.3.0]octane or bicyclo[3.3.1]nonane linkers normally lie between 80 and 115°,

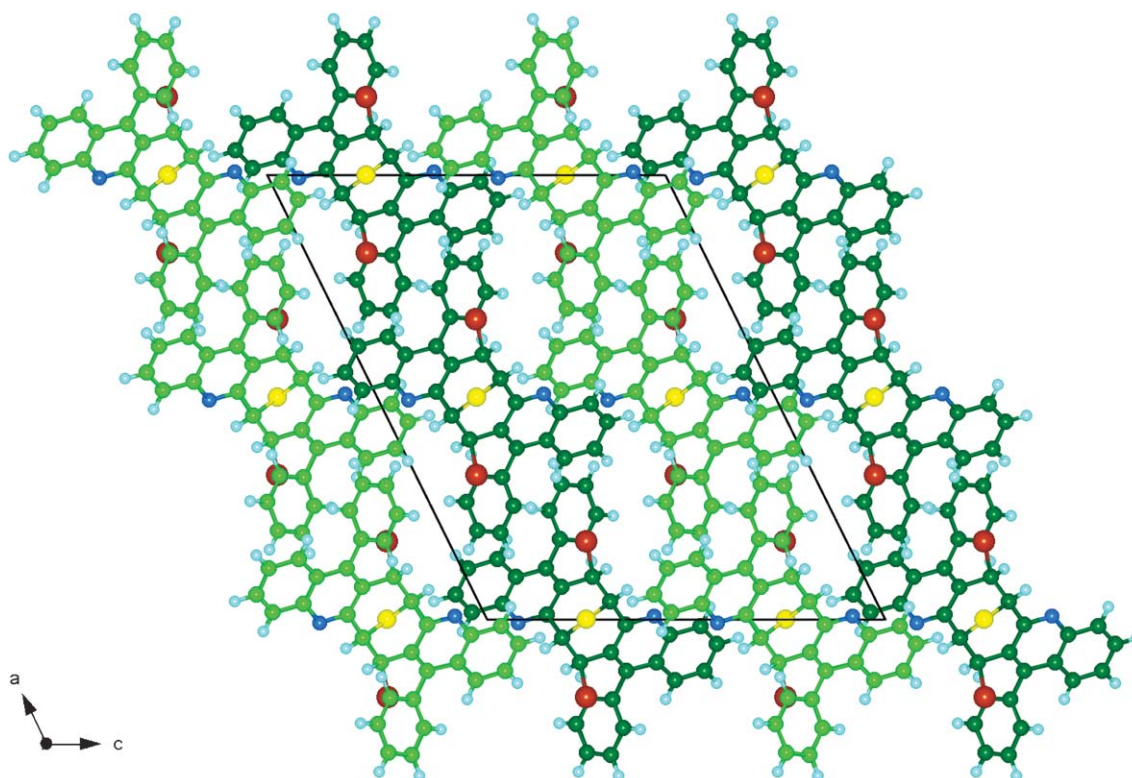


Fig. 9 Part of the crystal structure of solvent-free **10** showing the homochiral layers of molecules in the *ab* plane.

Table 2 Comparison of the crystal structures of **9** and **10**

Properties/Guest	9	10	10/CS₂	10/CH₂Cl₂	10/C₄H₈O	10/C₂H₂Cl₄	10/C₆H₅Cl
Host fold angle ^a	102.9	98.1	88.5	85.8	85.8	88.0	87.2
Packing coefficient/%	68.3	70.1	69.3	68.4	69.4	68.7	67.0
Torsion angles <i>t</i> ₁ , <i>t</i> ₂ /° ^b	71.9	108.0	95.4	93.5	89.4	97.9	95.0
	89.8	108.0	107.5	106.7	106.1	105.4	104.7

^a The angle at the S atom subtended by the two sites marked by black circles on structure **10** in Scheme 1 ^b The angles between the plane of the pendant phenyl groups and the plane of the diquinoline wings

and so the behaviour here of the apohost is by no means exceptional.

The torsion angles between the aryl planes of the pendant phenyl groups and the diquinoline wings were also measured. These were defined as the angle relating the *exo*-edge of the phenyl ring and the portion of the diquinoline wing nearer the sulfur bridge. In the non-brominated compound **9** and its non-S analogue **1**, one of these values is near 90° but the other is far less (71.9 and 69.1°, respectively). So, in both structures, one phenyl group is rotated significantly towards the central linker group. All the structures of **10** contain torsion angles greater than 90°. In other words, the bulky substitution results in phenyl group rotation away from the bromine atom. The symmetry present in pure **10** gives only one angle of 108°, but in all its inclusion compounds there is one torsion angle in the range 94–98° and a second between 105–108°. This difference in torsion angles is the cause of the (EF)₆ brick units of **1/9** (Fig. 2) and **2**/inclusion compounds of **10** (Fig. 1) having the slightly different appearance noted earlier.

The only molecular difference between compounds **2** and **10** is replacement of the bridging methylene group by a sulfur

atom, so it is interesting to see what role this might play in the crystals of **10**. In the apohost structure, and when the guest is small (CS₂), there is no S to non-H contact under 4 Å. The larger guest compounds show only a few contacts <4 Å. In the CH₂Cl₂ compound there is a S...Cl interaction of 3.47 Å, but this involves the minor guest component only. There is no similar interaction with the major (0.74) disorder component. For the THF compound there is a S...C(4) contact of 3.87 Å, and in the C₂H₂Cl₄ case there is a S...Cl(2) interaction of 3.48 Å. Only the major guest component (0.67) in the C₆H₅Cl compound has S...C(6) = 3.64 and S...C(1) = 3.79 Å contacts.

The host bromine atoms are a further source of molecular interactions. In the CS₂ structure there is an inter-host Br(2)...Br(2) association of 3.59 Å, but none for Br(1) < 4.5 Å. There are also good C–H...Br interactions (*D* = 3.86, *d* = 2.96 Å) for Br(1) and (*D* = 3.76, *d* = 3.00 Å) for Br(2). In addition, there is a good centrosymmetric pair of Br...ring interactions from Br(1), between the brick faces, with Br...C ring distances ranging upwards from 3.53 Å. This combination of interactions is the same in the CH₂Cl₂ and THF compounds.

For the $C_2H_2Cl_4$ structure, in which the bricks are rotated, the pair of $Br\cdots ring$ interactions has been replaced by a pair of $C-H\cdots Br$ ($D = 3.71$, $d = 3.06$ Å) and ($D = 3.89$, $d = 3.42$ Å) contacts, and a $Br\cdots Br$ interaction (4.07 Å) positioned between these. All of these involve $Br(1)$. The $C-H\cdots Br(1)$ ($D = 3.78$, $d = 2.88$ Å) and the $C-H\cdots Br(2)$ ($D = 3.81$, $d = 3.01$ Å) are both retained. Each pair of guests is linked by a double (centrosymmetric) $Cl\cdots Cl$ contact of 4.19 Å. In addition, there are host–guest $Br\cdots Cl$ interactions of 3.94 , 4.00 and 4.15 Å.

For the C_6H_5Cl compound, just the $C-H\cdots Br(2)$ interaction ($D = 3.77$, $d = 3.00$ Å) is retained. There is also a $Br\cdots Br$ contact (3.61 Å) involving this Br atom (as in the CS_2 structure). The other Br atom interacts with the guests: $Br\cdots C$ ring (pink guest, ranging from 3.23 Å) and a poorer $Br\cdots C$ ring (black guest, shortest $Br\cdots C$ distance = 3.96 Å). In this structure there is also a $Cl(pink)\cdots Cl(black)$ interaction of 3.66 Å, and weak inter-guest EF contacts. These EF comprise phenyl to pink guest (from 3.68 Å), pink guest to wing (from 3.76 Å), and two EF from black guest to phenyl (one from 3.81 Å and a poorer one from 4.19 Å).

Association between pairs of aromatic wings in the apohost structure of **10** provides a good OFF interaction between layers (centrosymmetric, and hence heterochiral). Since there is only one unique wing in this structure, all of them take part in this interaction. Within the layer there is a good vertex to face (VF) interaction between phenyl rings, as illustrated in Fig. 10. The closest interaction involving S is $C-H\cdots S$ (3.07 Å) between adjacent layers. There are no $Br\cdots Br < 4.5$ Å, but there are $C-H\cdots Br$ interactions within the homochiral layer (D 3.74 ,

d 3.10 Å) and (D 3.64 , d 3.18 Å), and between the layers (D 3.85 , d 3.24 Å).

Conclusions

The results reported here confirm the Janus-like behaviour of sulfur in organic crystallography. Half of the crystal structures obtained were isostructural with their corresponding methylene-bridged analogues. This is reasonable since S and CH_2 have similar van der Waals volumes (10.8 and 10.2 Å³, respectively, using the Bondi estimates).¹⁸ This shape and size effect has been commented on by others, notably by Desiraju.¹⁹

The other half of the crystal structures here was dissimilar across the two series. Sulfur is capable of establishing supra-molecular synthons in its own right,¹⁹ and we have recently reported such an example for another diquinoline host. This centrosymmetric motif linked six host molecules by means of three different $S\cdots Br$ interactions.²⁰ In the present work, however, our analyses show that the sulfur atom is not playing an overt role in these dissimilar crystal structures which makes such behaviour difficult to rationalise.

Experimental

¹³C NMR data (100.7 MHz) were recorded using a Bruker instrument with carbon substitution information being determined using the DEPT procedure. Melting points were measured using a Büchi B-540 instrument and the HRMS data recorded using a Finnigan/MAT 95XL-T instrument. IR and ¹H NMR data are available as supplementary information.†

8,16-Diphenyl-6,7,14,15-tetrahydro-6,14-thiacycloocta[1,2-*b*:5,6-*b'*]diquinoline **9**

Commercial 2-aminobenzophenone **7** (2.04 g, 10.34 mmol) and 9-thiabicyclo[3.3.1]nonane-2,6-dione^{9,10} **8** (0.80 g, 4.70 mmol, freshly sublimed) were dissolved in ethanol (40 mL) with stirring, and then aqueous NaOH (4 mL, 2 M) was added dropwise. The solution was refluxed overnight. The precipitated product was filtered from the cooled solution and washed with cold ethanol. Crystallisation from methanol gave **9** (1.90 g, 82%), mp 220–222 °C. Calc. for $C_{34}H_{24}N_2S$ C 82.89, H 4.91, N 5.69, S 6.51. Found: C 83.32, H 4.84, N 5.74, S 6.57%; ¹³C NMR ($CDCl_3$) δ 33.42 (CH), 36.69(CH₂), 121.79(CH), 125.80(C), 126.81(CH), 127.67(CH), 127.85(CH), 128.27(C), 129.71(CH), 129.90(CH), 130.44(CH), 132.53(C), 134.91(CH), 137.12(C), 152.82(C), 159.48(C) and one Ar–H obscured; HRMS (ESI, m/z^+) Calc. for $C_{34}H_{24}N_2S$ 492.1655, Found 492.1643; Calc. for $C_{34}H_{25}N_2S$ 493.1733, Found 493.1763; Calc. for $^{12}C_{33}^{13}C_1H_{25}N_2S$ 494.1767, Found 494.1749.

7 α ,15 α -Dibromo-8,16-diphenyl-6,7,14,15-tetrahydro-6 α ,14 α -thiacycloocta[1,2-*b*:5,6-*b'*]diquinoline **10**

A solution of *N*-bromosuccinimide (0.45 g, 2.54 mmol) and **9** (0.50 g, 1.02 mmol) in trifluoromethylbenzene (40 mL) was refluxed overnight and then the resulting mixture was allowed to cool. Succinimide was filtered off, washed with additional trifluoromethylbenzene (20 mL), and then the combined

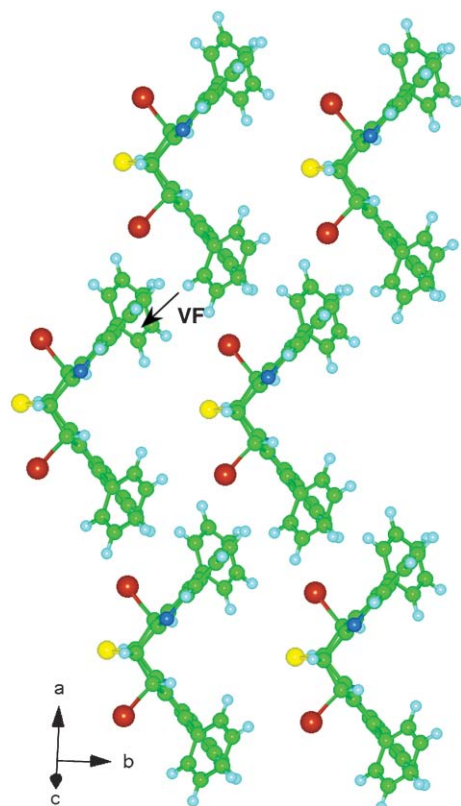


Fig. 10 Apohost crystal structure of **10** (cf. Fig. 9) illustrating the vertex to face (VF) interactions present within each homochiral layer.

filtrate was evaporated under reduced pressure to give a light-yellow solid. Crystallisation from EtOAc gave colourless crystals of **10** (0.52 g, 79%), mp 165–167 °C. Calc. for C₃₄H₂₂Br₂N₂S C 62.78, H 3.41, N 4.31, Br 24.57, S 4.93. Found C 62.98, H 3.44, N 4.32, Br 24.57, S 5.13%; ¹³C NMR (CD₃SOCD₃) δ 47.96 (CH), 52.10(CH), 124.98(C), 125.97(CH), 126.73(C), 127.79(CH), 127.96(CH), 128.37(CH), 128.67(CH), 128.72(CH), 130.17(CH), 131.22(CH), 133.44(C), 146.71 (C), 150.75(C), 151.50(C) & one Ar–H obscured; MS (EI, *m/z*⁺ >20%): 458.08 (100), 459.08 (38), 460.08 (44), 488.03 (47), 490.04 (80, M–2Br), 491.04 (30), 492.04 (30), 508.05 (50), 509.05 (20).

Structure determinations

Reflection data for the non-brominated compound **9** was recorded on a Bruker SMART CCD diffractometer, while those for the remaining six compounds were measured with an Enraf-Nonius CAD-4 diffractometer. Data were recorded at 294 K using Mo K α radiation ($\lambda = 0.7107$ Å) with scan mode = $\theta/2\theta$ (for **9**, ϕ and ω scans), $2\theta_{\max.} = 50^\circ$ (for **9**, 55°), and criteria for observed reflection = $I/\sigma(I) > 2$. Data for some crystals were corrected for absorption.^{21,22} The positions of all atoms in the asymmetric unit were determined by direct phasing (SIR92)²³ with hydrogen atoms included in calculated positions with isotropic thermal motion linked to that of the bonded atom. For **9**, the non-hydrogen atoms were refined anisotropically.²⁴ In structures containing the brominated molecule **10**, the Br atoms were refined anisotropically. The two phenyl rings of the host were refined as rigid groups each with their own TLX thermal group (where T is the translation tensor, L is the libration tensor and X is the origin of libration). The remainder of the host atoms were refined with three TLX thermal groups, except for the solvent-free structure of **10**, with half a molecule in the asymmetric unit, for which all other atoms were refined anisotropically. For the CS₂ and C₂H₂Cl₄ compounds, these guests were refined as individual anisotropic atoms. The guest molecules in the remaining inclusion structures were refined as rigid groups of the appropriate symmetry. In two crystals, the guest was disordered. In the dichloromethane compound, the guest CH₂Cl₂ had two different positions with occupancies 0.74 and 0.26. The chlorobenzene compound contained two distinct C₆H₅Cl guests, each of which was disordered (occupancies 0.70/0.30 and 0.67/0.33; coloured black and purple, respectively, in Fig. 8). The thermal motion of each guest was defined by a TLX group. Full details of refinement²⁵ can be found in the supplementary information.†

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