Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Synthesis and Supramolecular Behaviour of 2,7-Dibromo-9-alkynylfluorenols

Rahman Hosseinzadeh[a]; Wilhelm Seichter[b]; Tayebeh Sanaeishoar[a]; Edwin Weber[b]
[a] Department of Chemistry, University of Mazandaran, Babolsar, Iran [b] Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Freiberg, Germany

To cite this Article Hosseinzadeh, Rahman , Seichter, Wilhelm , Sanaeishoar, Tayebeh and Weber, Edwin(2007) 'Synthesis and Supramolecular Behaviour of 2,7-Dibromo-9-alkynylfluorenols', Supramolecular Chemistry, 19: 6, 353 — 364
To link to this Article: DOI: 10.1080/10610270600955157
URL: http://dx.doi.org/10.1080/10610270600955157

Supramolecular Chemistry, September 2007 Vol. 19 (6), pp. 353–364

Taylor & Francis
Taylor & Francis Group

Synthesis and Supramolecular Behaviour of 2,7-Dibromo-9-alkynylfluorenols

RAHMAN HOSSEINZADEH[a,*], WILHELM SEICHTER[b], TAYEBEH SANAEISHOAR[a] and EDWIN WEBER[b]

[a]*Department of Chemistry, University of Mazandaran, Babolsar, Iran;* [b]*Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg, Germany*

(Received 27 June 2006; Accepted 17 July 2006)

Two host compounds 2,7-dibromo-9-ethynyl-9-fluorenol (1) and 2,7-dibromo-9-trimethylsilylethynyl-9-fluorenol (2) were synthesized and their inclusion properties studied. Crystals of the host compounds show interesting change of colour from yellow to colourless upon guest complexation. To determine this phenomenon the crystal structures of guest-free compounds and five selected clathrates, involving diethylamine, triethylamine, pyridine, and 1,4-dioxane as the guest, have been determined by X-ray diffraction. The various modes of supramolecular interaction observed in these crystals are used as a basis for explaining colour changes accompanying guest inclusion.

Keywords: 9-Alkynyl-9-fluorenols; Crystalline inclusion compounds; Organic guests; Decolouration phenomenon; Supramolecular interactions; X-ray crystal structure determinations

INTRODUCTION

Organic molecules capable of forming crystalline host-guest inclusion compounds, designated as clathrates or lattice inclusions [1,2], are a particular section of crystal-engineering [3–7]. They have become of increasing importance in the past few years due to the potential uses for analytical problems and in materials science including sensor technology [8–14]. They serve also as useful models for studying interatomic interactions and other aspects of molecular recognition [3–7,15,16]. Molecules containing the fluorene moiety, especially when functionalized by a hydroxy group at the 9-position of the fluorene unit, have proved to be successful hosts that form clathrates with a variety of organic guests [17–22]. Substitution of the fluorene moieties at the 2- and 7-positions by halogen atoms also gives rise to successful host compounds [23–25]. Moreover, fluorene containing hosts have been shown to provide guest specific solid-state fluorescence [26].

This has stimulated the study of potential inclusion behaviour and crystal structures of the fluorene compounds **1** and **2**. They are related rigid constitutions featuring an assembly of very different non-covalently interacting groups incorporated into one single molecule, respectively, thus enabling different kinds of supramolecular synthons [27] involving hydrogen bonding, π-stacking and halogen contacts [16,28] which may compete with the functional groups of a guest solvent. Hence, the potential multi-operating compounds **1** and **2** are promising tests both in crystal-engineering and crystalline inclusion formation, including prospective change of colour attributed to the supramolecular construction.

We describe the synthesis and crystal structure of the unsolvated compounds **1** and **2**, report their inclusion behaviour and give detailed structural information of five inclusion compound of **1** (**1a**, **1b**) and **2** (**2a**, **2b**, **2c**), being related to changes of colour on solvent inclusion.

RESULTS AND DISCUSSION

Preparation and Properties of Compounds

The host compound **1** was prepared by treatment of its trimethylsilyl derivative **2** with K_2CO_3 in THF-MeOH. Compound **2** was synthesized from trimethylsilylethyne and 2,7-dibromo-9-fluorenone with *n*-BuLi as a base. In order to show the inclusion properties, the host compounds **1** and **2** were

*Corresponding author. Fax: + 98-11252-42002. E-mail: r.hosseinzadeh@umz.ac.ir

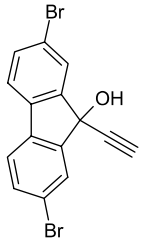
ISSN 1061-0278 print/ISSN 1029-0478 online © 2007 Taylor & Francis
DOI: 10.1080/10610270600955157

TABLE I Crystalline inclusion compounds (host:guest stoichiometry ratios†)

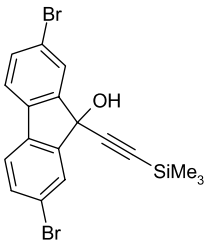
Guest Solvent‡	Host compound	
	1	**2**
$HNEt_2$	1:1	1:1
NEt_3	1:1	1:1
Pyridine	¶	2:1
Piperidine	1:1	¶
1,4-Dioxane	2:1	–

† Host: guest chemical composition ratios were determined by ^{1}H NMR integration; where possible, confirmed by single crystal structure analysis. ‡ MeOH, EtOH, acetonitrile, nitromethane, ethyl acetate, Et_2O, dichloromethane and toluene, which were also tested, yielded no inclusion compounds on recrystallization. ¶ Difficult to crystallize.

crystallized from various kinds of potential guest solvents, including alcohols, amines, aprotic polar and apolar compounds, to yield the inclusion crystals listed in Table I.



1



2

1a = **1** · 1,4-dioxane (2:1)

1b = **1** · diethylamine (1:1)

2a = **2** · diethylamine (1:1)

2b = **2** · triethylamine (1:1)

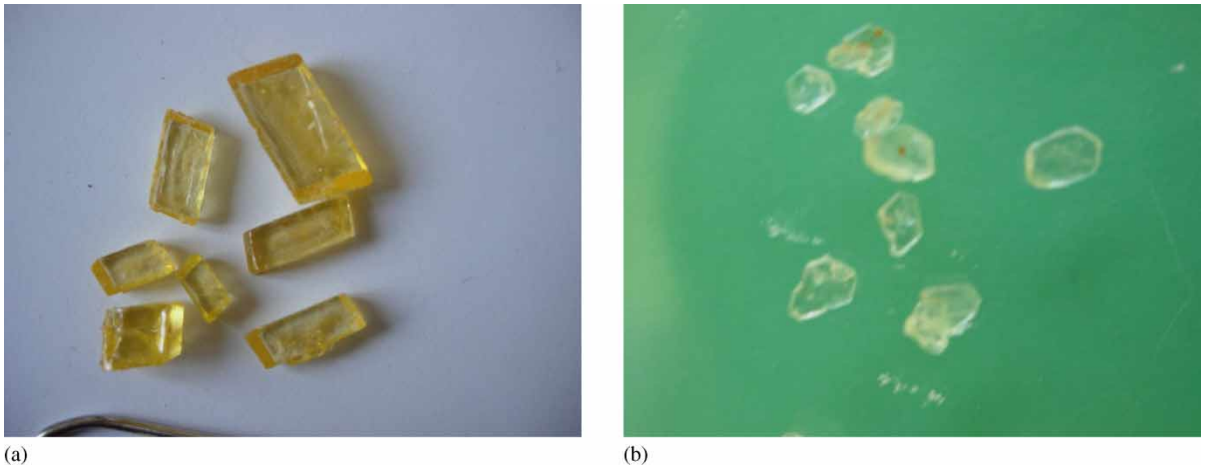
2c = **2** · pyridine (2:1)

The host compound **1** is a yellow microcrystalline material which shows interesting change of colour from yellow to colourless upon guest complexation with diethylamine. On the other hand, complexation of **1** with 1,4-dioxane resulted in no perceptible colour change. The guest-free compound **2** is also a yellow crystalline material leading to fading of colour upon complexation with several guest solvents, including diethylamine, triethylamine, and pyridine. An example is illustrated in Fig. 1. While these changes of colour relate to recrystallization experiments from guest solutions, a similar colour change is readily detectable by absorption of guest vapours from a saturated atmosphere. For example, when the yellow guest-free crystals of **2** were placed in a vessel saturated with triethylamine vapour at room temperature for 8 h, the colour of the crystals completely turned from yellow to colourless. During the absorption of triethylamine, the crystal structure of guest-free **2** simultaneously changed with changing of colour. This phenomenon was confirmed by powder X-ray diffraction, showing rather different powder pattern of **2** against the inclusion compound which has formed (Fig. 2), corresponding with data calculated from single crystal analysis [29].

Considering these results, detailed single crystal X-ray diffraction studies of the different free hosts and their inclusion compounds seemed to be appropriate for attempting to understand the reasons for the observed colour changes.

Structural Study

This study includes determination of the crystal structures of compounds **1**, **1a**, **1b**, **2** and **2a**–**2c**. Basic crystallographic information for these structures is listed in Table II. Perspective views of the molecules **1** and **2** are depicted in Fig. 3 and packing illustrations of **1a**, **1b**, **2a**–**2c** are presented in Figs. 4–10. Geometric parameters of possible intermolecular connections involving H bonds and halogen contacts or $\pi \ldots \pi$ interactions are listed in Tables III and IV, respectively.



(a) (b)

FIGURE 1 Photographs of crystals of guest-free **2** (a, yellow) and inclusion compound **2c** (b, colourless). Colour in online version.

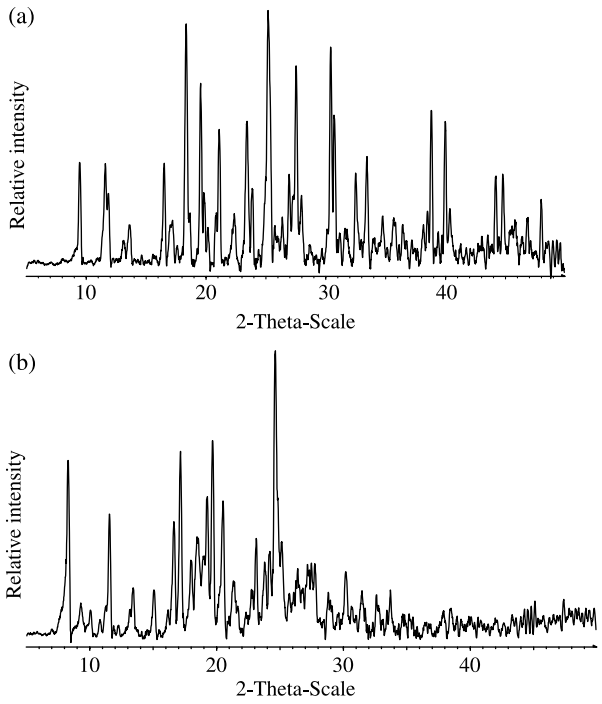


FIGURE 2 Powder diffractograms of (a) unsolvated host compound **2** and (b) its inclusion compounds with triethylamine (**2b**).

Crystal Structures of the Solvent Free Compounds 1 And 2

The molecular structures of **1** and **2** including the atomic numbering scheme are shown in Fig. 3. According to the low degree of conformational freedom, the ethynylfluorenols feature approximate mirror symmetry, which in their solid phase structures is only disturbed by the coordinating hydroxy group, and in the case of **2** by the conformation of the ethynyl trimethylsilyl residue. The observed bond lengths and angles are in the range of expected values and in good agreement with the structure of 9-ethynyl-9-fluorenol reported previously [30,31].

Crystallization of **1** from methylene chloride yields yellow crystals of the space group $P-1$ ($Z=2$). The packing structure, which is depicted in Fig. 4, exhibits several types of non-covalent interactions between molecules. With the exception of the acidic ethynyl hydrogen and the less accessible oxygen, the molecule satisfies the whole potential for intermolecular association. Linear hydrogen bonded chains [C(9)—H(9A)...Br(2) 3.04 Å] being linked to double strands via O—H...Br [*d*(H1)...Br(1) 2.87 Å] and Br...Br interactions [3.585(4) Å] are the basic supramolecular motifs of the crystal structure [27,32,33]. Aromatic π...π contacts with centroid distances of 3.698(2) and 3.717(3) Å between the fluorenyl moieties make up the dominating binding element between the molecular double strands [34]. A view of the crystal packing along the *b*-axis shows a typical layer arrangement of molecules. Because of different binding modes between molecules of consecutive layers, their order can be described as A–B–A–B...-type.

Recrystallization of the trimethylsilyl (TMS) substituted ethynylfluorenol **2** from CH_2Cl_2 yields yellow rhombic crystals of the monoclinic space group $P2_1/c$ ($Z=4$). The attachment of the bulky TMS group to the ethynyl unit is associated with a major change in the crystal lattice structure and in the pattern of intermolecular interactions (Fig. 5). In a more detailed description, the mode of hydrogen bonding differs from that of **1** in that the ethynyl group of **2** acts as acceptor for a short O—H...π hydrogen bond [O(1)—H(1)...π 2.46 Å, 170.9°] [32,33]. Taking into account this stronger interaction, the crystal can be regarded as consisting of molecular dimers, which in turn are linked by weaker Br...Br contacts with an interatomic distance of 3.592(1) Å. The C—Br...Br—C geometry with angles $\theta_1 = 173.2(1)°$ and $\theta_2 = 98.4(1)°$ is a typical 'type II' interaction as classified by Desiraju [3,35]. The fluorenyl units of the molecules stack along the *a*-axis by means of offset face-to-face (OFF) interactions [34] which exhibit centroid distances of 3.703(2) and 3.794(2) Å between aromatic rings.

Crystal Structures of the Inclusion Compounds Of 1 And 2

In order to elucidate how inclusion formation affects supramolecular binding patterns, in particular those between host molecules, potentially being connected with the colour change, we succeeded to grow crystals containing guest species of different hydrogen bond donor/acceptor capabilities.

Crystallization of **1** from 1,4-dioxane yields yellow prisms which proved to be a 2:1 host-guest compound (space group *P*-1) with the guest molecule located on the symmetry center 1/2, 1/2, 1/2. The crystal is composed of discrete 2:1 host-guest aggregates in which the components are linked by a conventional O—H...O hydrogen bond [*d*(O...H 1.98 Å] [36]. Neither the ethynyl hydrogen nor the bromine atoms are involved in intermolecular cross-linking. Thus, a relevant stabilizing element of the structure can be seen in the formation of face-to-face stacks of aromatic building blocks which extend in the direction of the crystallographic *a*-axis (Fig. 6).

Upon recrystallization of **1** from diethylamine, colourless crystals containing the components in the stoichiometric ratio 1:1 are formed. The inclusion compound crystallizes in the uncommon orthorhombic space group *Cmca* with one half host and one half guest molecule in the asymmetric entity of the unit cell, i.e. both molecules are bisected by a crystallographic mirror plane. The fluorenyl moiety

TABLE II Crystallographic and structure refinement data of the compounds studied

Compound	**1**	**1a**	**1b**	**2**	**2a**	**2b**	**2c**
Empirical formula	$C_{15}H_8Br_2O$	$C_{15}H_8Br_2O{\cdot}0.5\ C_4H_8O_2$	$C_{15}H_8Br_2O{\cdot}C_4H_{11}N$	$C_{18}H_{16}Br_2OSi$	$C_{18}H_{16}Br_2OSi{\cdot}C_6H_{15}N$	$C_{18}H_{16}Br_2OSi{\cdot}C_4H_{11}N$	$2\ C_{18}H_{16}Br_2OSi{\cdot}C_5H_5N$
Formula weight	364.03	408.09	437.17	436.22	537.41	509.36	951.54
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*Cmca*	$P2_1/c$	$P2_1/n$	*P*-1	*P*-1
A (Å)	6.8393(2)	7.4735(2)	17.794(4)	8.0898(3)	10.5643(5)	10.2914(6)	10.9113(5)
B (Å)	9.2309(3)	8.3532(2)	8.491(2)	21.0969(8)	12.7131(7)	11.9832(7)	11.9255(5)
c (Å)	10.4131(3)	13.7359(4)	24.414(5)	10.5662(4)	18.7903(11)	12.0879(7)	15.7731(7)
α (°)	84.387(2)	98.797(2)	90.0	90.0	90.0	61.055(3)	78.449(2)
β (°)	85.275(1)	97.214(2)	90.0	100.805(2)	99.545(3)	65.548(3)	88.921(2)
γ (°)	82.105(1)	113.289(1)	90.0	90.0	90.0	71.206(3)	86.983(2)
V (Å^3)	646.46(3)	761.84(4)	3688.7(14)	1771.36(12)	2488.7(2)	1173.54(12)	2008.01(15)
Z	2	2	8	4	4	2	2
F(000)	352	400	1744	864	1096	516	948
D_c (g cm^{-3})	1.870	1.779	1.574	1.636	1.434	1.441	1.574
μ (mm^{-1})	6.253	5.321	4.399	4.643	3.320	3.516	4.103
Temperature (K)	298(2)	298(2)	93(2)	93(2)	93(2)	93(2)	153(2)
Measured reflections	24711	31740	39632	46369	71502	46910	86197
θ-range (°)	2.2–32.4	2.7–36.5	2.3–37.0	1.9–35.2	1.9–38.9	2.0–36.1	1.3–36.3
Index ranges $\pm h$, $\pm k$, $\pm l$	$-10/10$, $-13/13$, $-15/15$	$-12/12$, $-13/13$, $-22/22$	$-30/30$, $-14/13$, $-35/41$	$-13/13$, $-34/34$, $-17/17$	$-18/18$, $-21/21$, $-33/33$	$-17/16$, $-19/19$, $-19/20$	$-18/18$, $-19/19$, $-26/26$
No. of unique reflections	4644	7388	4794	7880	14360	11137	19433
R_{int}	0.0258	0.0296	0.0366	0.0339	0.0394	0.0283	0.0291
No. of refined parameters	164	191	121	203	269	254	459
No. of F^2 values used $[I > 2\sigma(I)]$	3296	4153	3136	6389	9891	8700	14000
$R_1[I > 2\sigma(I)]$	0.0328	0.0448	0.0531	0.0247	0.0329	0.0288	0.0291
wR_2 $[I > 2\sigma(I)]$	0.1076	0.1352	0.1469	0.0543	0.1254	0.0894	0.0984

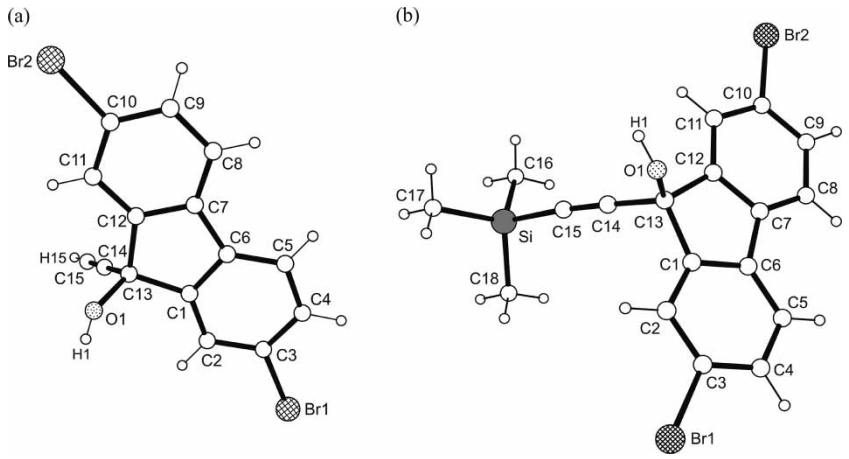


FIGURE 3 Molecular structure and numbering scheme of (a) 2,7-dibromo-9-ethynyl-9-fluorenol (**1**) and (b) 2,7-dibromo-9-trimethylsilylethynyl-9-fluorenol (**2**).

deviates significantly from planarity which should be ascribed to packing effects. Because both inclusion components act as hydrogen bond donors and acceptors, the crystal structure of **1b** consists of infinite supramolecular strands of alternating host and guest molecules which run along the crystallographic *b*-axis (Fig. 7). The H . . . A distances within the molecular chains are 1.76 Å for O(1)—H(1) . . . N(1G) and 2.19 Å for N(1G)—H(1G′) . . . O(1) connections, respectively. The centroid distance of 3.793(4) Å between the aromatic molecule parts of adjacent strands suggests appreciable $\pi \ldots \pi$ interactions [34].

A different situation is found in the inclusion compound of **2** with diethylamine (Fig. 8). The structure consists of discrete 2:2 host-guest aggregates in which the functional groups form an eight-membered cyclic hydrogen bond system [graph set $R_2^2(8)$] [37], with O(1)—H(1) . . . N(1G) and N(1G)—H(1G′) . . . O(1) hydrogen bond lengths of 1.85 and 2.37 Å, respectively. The C—C—N—C torsion angles within the guest molecule adopt the energetically favourable *anti*

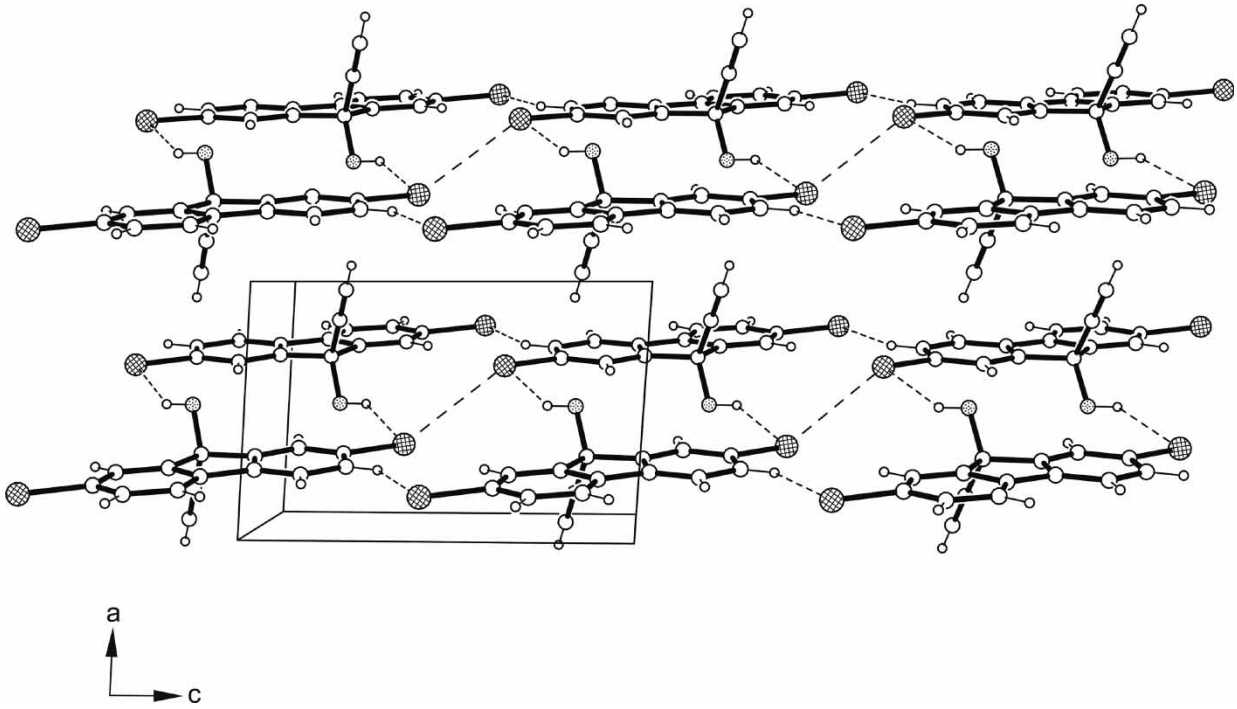


FIGURE 4 Packing diagram of **1** viewed down the crystallographic *b*-axis.

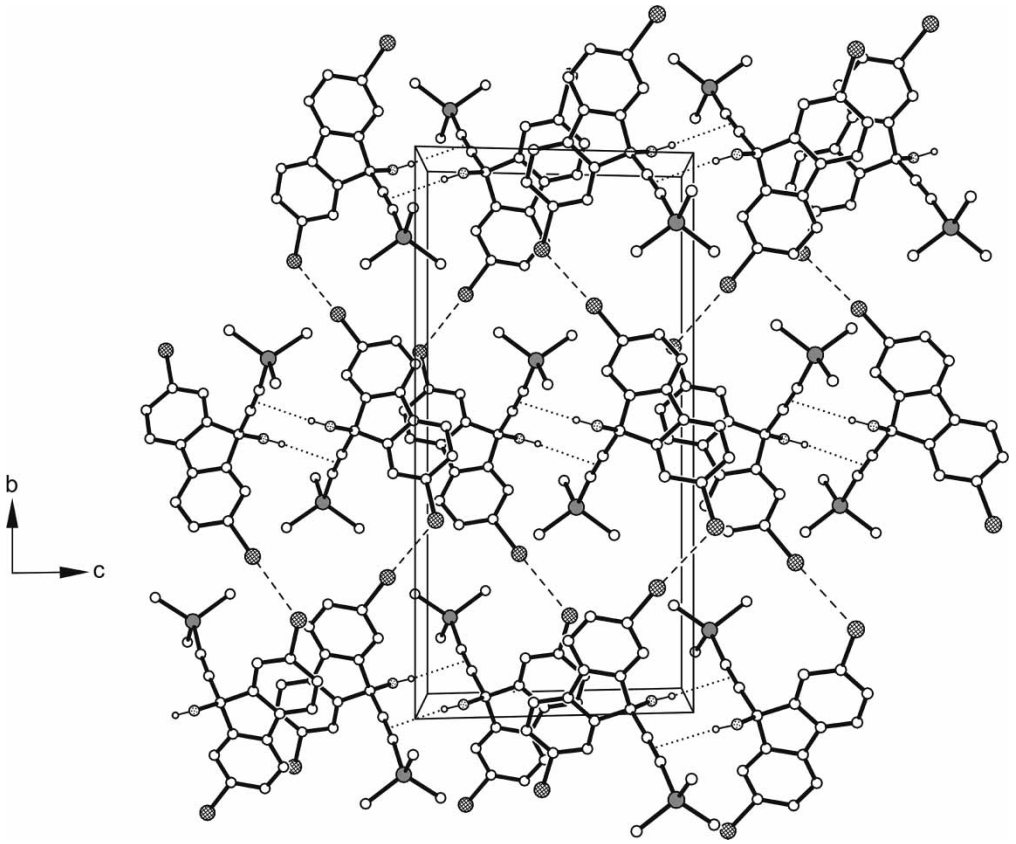


FIGURE 5 Packing diagram of **2** viewed down the crystallographic *a*-axis.

(173.8°) and *gauche* (−68.7°) conformation. The host-guest aggregates stack along the *a*-axis by means of aromatic OFF interactions [34] thus forming chain-like assemblies with centroid distances of 3.874(2) Å between the interacting aromatic moieties. The crystal structure is further stabilized by Br . . . Br contacts which form a so-called Type I geometry [3,35] (Br . . . Br 3.555 Å, C-Br . . . Br 139.9°) thus linking the supramolecular chains in direction of the crystallographic [110] plane, while the second bromine atom of each host molecule does not cooperate in interaction.

The **2** . . . triethylamine (1:1) complex (**2b**) crystallizes in the monoclinic space group $P2_1/n$ with one host and one guest molecule in the asymmetric unit. Although the guest molecule lacks a strong donor site, hydrogen bonded strands are the basic supramolecular elements, the structure of which resembles those observed in inclusion compound **1b**. Within the molecular strands, the guest accepts one conventional hydrogen bond [O(1)—H(1) . . . N(1) 1.91 Å, 170.1°] [36] to a host molecule and a weaker contact [C(2G)—H(2G3) . . . O(1) 2.48 Å, 156.4°] [32,33] in which one of the methyl hydrogens is linked with a second host (Fig. 9). Also the present structure is stabilized by π . . . π contacts between aromatic units having a centroid distance of 3.814(2) Å [34].

The crystal structure of the **2** . . . pyridine (2:1) inclusion compound (**2c**), which has the space group *P*-1, contains two symmetry-independent host molecules and one pyridine molecule. Due to the given stoichiometric ratio, the structure is composed of 2:1 host-guest units which form the hydrogen bond motif O—H(host 1) . . . O—H(host 2) . . . N(guest). In this unit, the host molecules are inclined at an angle of 51.69(2)°. A view of the crystal packing along the *c*-axis reveals layers of host molecules (Fig. 10). The molecular arrangement within the layer reveals that aromatic π . . . π interactions [34] with centroid–centroid separations of 3.638(3) and 3.642(3) Å between pairs of parallel fluorenyl moieties, supported by weak C—H . . . Br hydrogen bonds [*d*(H . . . Br) 2.92–3.05 Å] [32,33], contribute significantly to the stabilization of the structure. The guest molecules are accommodated in closed cavities created by the trimethylsilyl residues of four host molecules.

CONCLUSION

Two 2,7-dibromo-9-alkynylfluorenols, **1** and **2**, were synthesized and their inclusion properties have been studied revealing a strong tendency to include guest amines and by way of exception also 1,4-dioxane in case of **1**, whereas simple alcohols and common aprotic dipolar or polar compounds failed to be

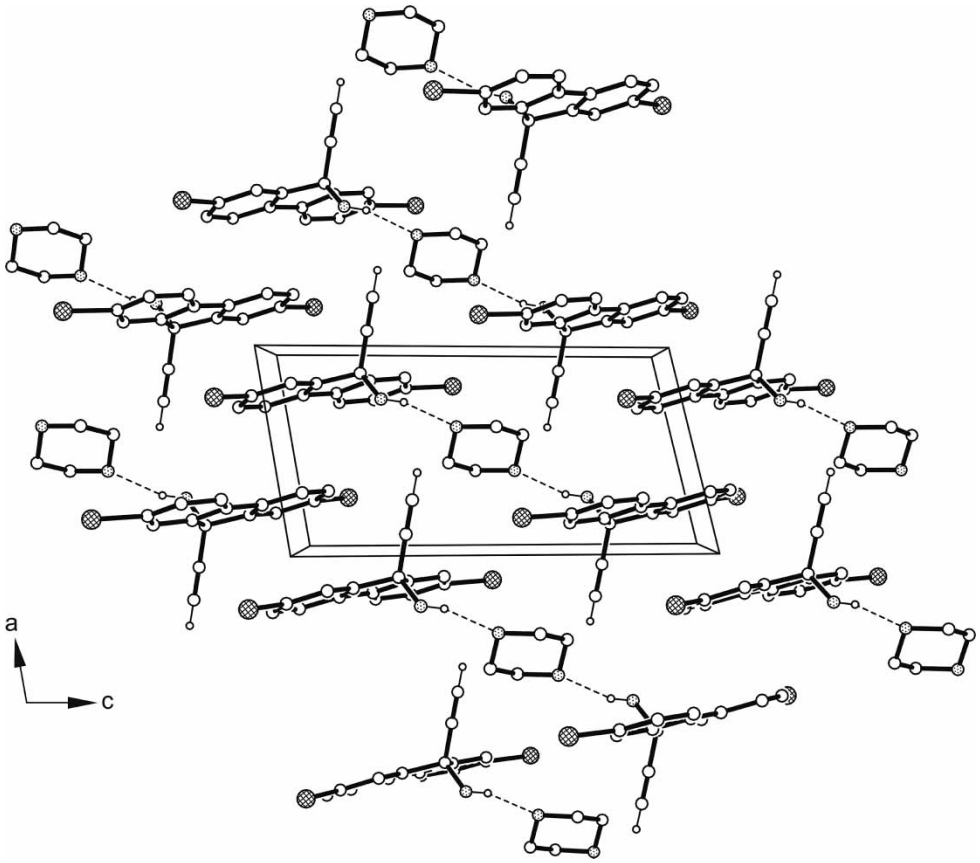


FIGURE 6 Packing diagram of the crystal inclusion of **1** with 1,4-dioxane (2:1) viewed down the crystallographic *b*-axis.

included (Table I). An interesting finding of guest specific colour change from yellow of the uncomplexed crystalline hosts to colourless or fading, being connected with the solvent inclusion, gave rise to a detailed study of crystal structures, suggesting potential facts about this phenomenon.

The crystal structures of the free host compounds are typical of complex systems of weak supramolecular interactions [3,4,32–34], involving the expected range of Br . . . Br, C—H . . . Br and π-stacking interactions, but also O—H . . . Br and O—H . . . π contacts in **1** and **2**, respectively, while the usual hydrogen bridges [36] formed between hydroxyl groups are not found, probably due to packing effects. Thus, a number of different weaker interactions rather than formation of few strong hydrogen bonds is dominating the lattice structures of unsolvated **1** and **2**. On the other hand, in each of the inclusion compounds of **1** and **2** that have been studied by X-ray diffraction (**1a**, **1b**, **2a**–**2c**), the host hydroxy groups are used to form conventional hydrogen bonds (O—H . . . O, O—H . . . N and N—H . . . O) [36] to the guest molecules, taking the place of the formerly weaker inter-host supramolecular contacts.

The most interesting point, however, is related to the mode of π-stacking [34] between the fluorenyl units, showing the formation of continuously π-stacked fluorenes in cases of **1**, **1a** and **2** (cf. Fig. 4), whereas isolated dimers of π-stacked fluorenes are found in **1b** and **2a**–**2c** (cf. Fig. 7), corresponding to the yellow and colourless crystals, respectively. Hence, the colour change of the crystals from yellow to colourless upon guest complexation may be attributed to the transformation of the continuous stacks of fluorenes to dimers. A similar phenomenon was recently observed for a series of fluorene containing propargylallenes [38–40]. This behaviour of a specific colour change on solvent inclusion shows good promise for the development of colouring sensor materials based on crystalline inclusion chemistry [41–43].

EXPERIMENTAL

Measurements and Materials

Melting points were determined with a hot-stage microscope (VEB Dresden Analytik) and are uncorrected. The IR spectra are measured as KBr pellets with a Perkin-Elmer FT-IR 1600 spectrometer. ^{1}H and ^{13}C spectra were recorded using a Bruker DPX 400 instrument (internal standard TMS). Elemental analyses were performed with a Heraeus CHN rapid analyzer.

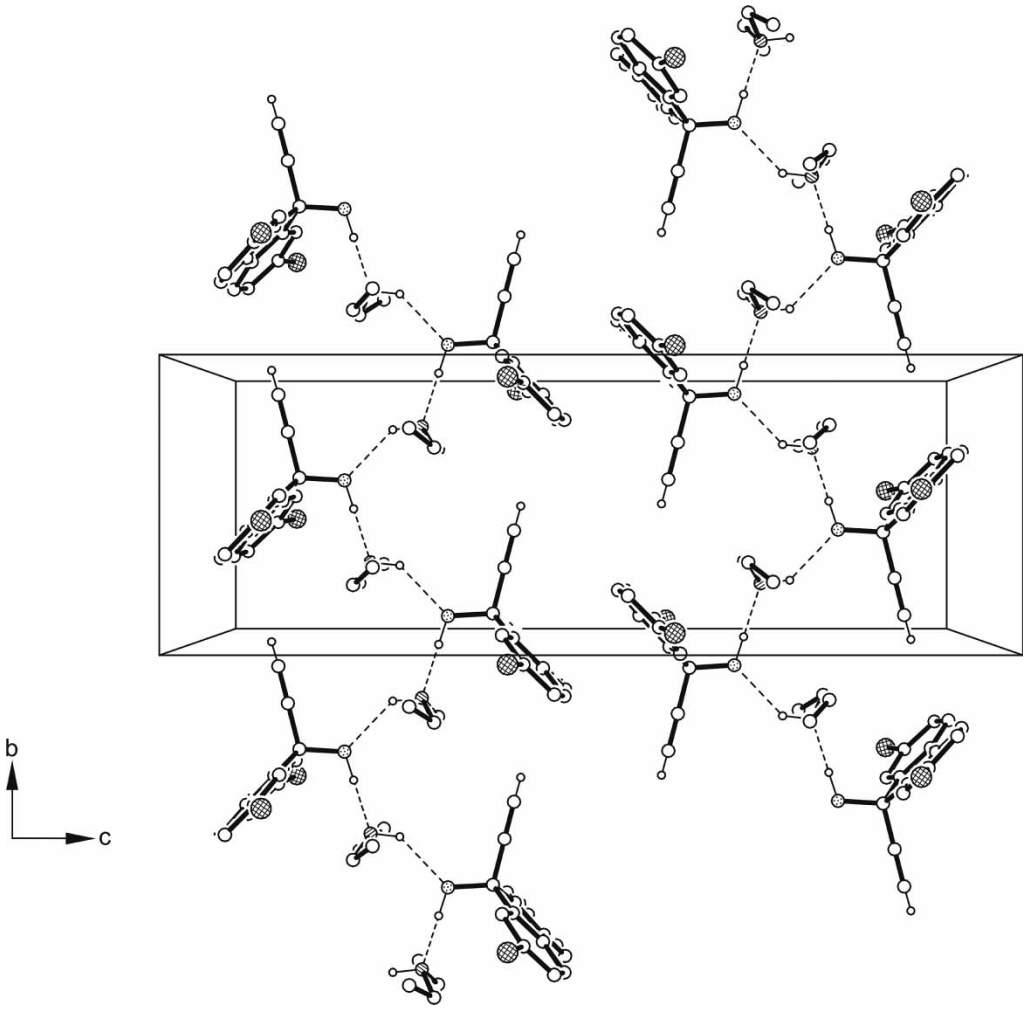


FIGURE 7 Packing diagram of the **1**...diethylamine (1:1) inclusion compound (**1b**) viewed down the crystallographic *a*-axis.

Starting compounds 2,7-dibromo-9-fluorene [44] and 2,7-dibromo-9-fluorenone [45] were prepared according to literature procedures. Fluorene and trimethylsilylethyne were purchased from Acros.

Synthesis of 2,7-Dibromo-9-trimethylsilylethynyl-9-fluorenol (2)

To a solution of trimethylsilylethyne (2.8 mL, 20 mmol) in dried diethylether (80 mL) was added dropwise *n*-butyllithium (11.3 mL, 18 mmol, 1.6 M in hexane) at −60°C under argon. The mixture was stirred for 30 min, and allowed to warm to room temperature. Stirring was continued at room temperature for 30 min. The resulting mixture was added dropwise via canule to a suspension of 2,7-dibromofluorenone (5.41 g, 16 mmol) in dried diethylether (150 mL) at −40°C. The mixture was stirred at room temperature for 2 h and then quenched with sat. aqueous NH_4Cl. The organic layer was separated, washed with water and sat. aqueous NaCl, dried over Na_2SO_4, and evaporated to yield the raw product. After addition of *n*-hexane (200 mL), the precipitate was filtered und dried to yield 6.3 g (91%) of compound **2**. Mp (from CH_2Cl_2): 215–216°C; IR (KBr): $\tilde{\nu} = 3462$ (OH), 1628, 1449, 1250, 1059, 859 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 0.14$ (s, 9 H), 2.61 (s, 1 H), 7.44 (d, $J = 8.0$ Hz, 2 H), 7.52 (dd, $J = 8.0$, 2.0 Hz, 2 H), 7.90 (d, $J = 2.0$ Hz, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = -0.24$ (Si—CH_3), 74.50 (C—OH), 90.06 (C≡C), 103.13 (C≡C), 121.58 (CH), 122.53 (C—Br), 127.90 (CH), 132.95 (CH), 137.18 (C), 148.58 (C). Anal. Calcd for $C_{18}H_{16}Br_2OSi$ (%): C, 49.56; H, 3.70. Found C, 49.60; H, 3.47.

Synthesis of 2,7-Dibromo-9-ethynyl-9-fluorenol (1)

To a solution of **2** (5.0 g, 11.5 mmol) in THF-MeOH (1:1, 100 mL), K_2CO_3 (8.0 g, 57 mmol) was added and the mixture stirred at room temperature for 2 h. After filtration, the filtrate was evaporated under reduced pressure. The residue was dissolved in EtOAc (50 mL). The solution was washed with water, then with sat. aqueous NaCl, and dried over Na_2SO_4. Evaporation under reduced pressure yielded compound **1** (96%). Mp (from CH_2Cl_2): 205–206°C; IR

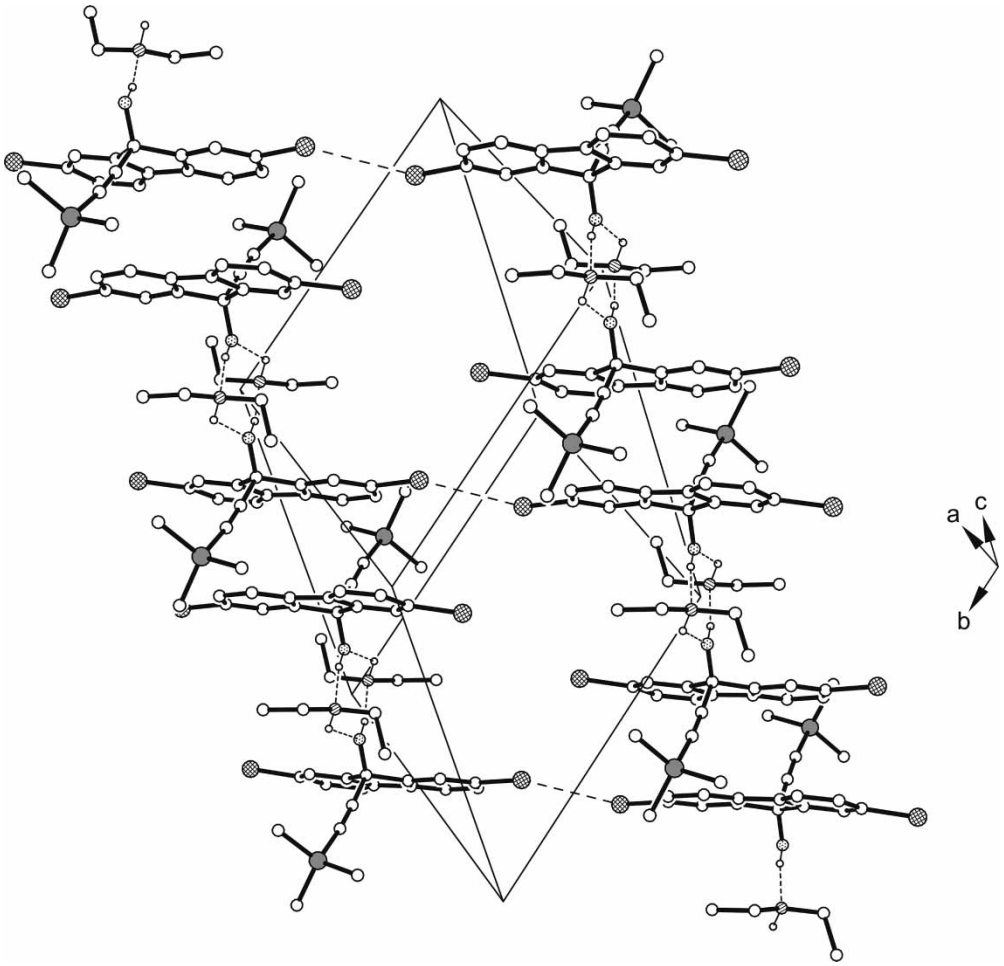


FIGURE 8 Packing diagram of the **2**...diethylamine (1:1) inclusion compound (**2a**).

(KBr): $\tilde{\nu} = 3457$ (OH), 1629, 1452, 1062, 1008, 817 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 2.55$ (s, 1H), 2.59 (s, 1 H), 7.45 (d, $J = 8.0$ Hz, 2 H), 7.54 (dd, $J = 8.0$, 1.6 Hz, 2 H), 7.82 (d, $J = 1.6$ Hz, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 72.73$ (C≡C), 74.04 (C—OH), 82.44 (C≡C), 121.67 (CH), 122.60 (C—Br), 127.90 (CH), 133.18 (CH), 137.11 (C), 148.08 (C). Anal. Calcd for $2C_{15}H_8Br_2O{\cdot}C_4H_8O_2$ (%): C, 50.04; H, 2.96. Found C, 49.92; H, 2.89.

General Procedures for Formation of the Crystalline Inclusion Compounds

Host compounds **1** and **2** were dissolved under heating in a minimum amount of the respective guest solvents. After leaving the mixture for several hours at room temperature, the crystals formed were filtered, washed with CH_2Cl_2–hexane (1:1), and dried under reduced pressure (1 h, 15 torr, room temperature). Host-guest stoichiometric ratios were determined by ^{1}H NMR integration.

X-ray Crystallography

X-ray diffraction studies of the solvent-free structures (**1**, **2**) and of the crystal inclusions (**1a**–**b**, **2a**–**c**) were carried out on a Bruker-AXS APEX2 diffractometer with a CCD area detector ($\lambda_{MoK\alpha} = 0.71073$ Å, graphite monochroator). Frames were collected with ω and ϕ rotation at 5 or 10 s per frame. Reflection intensities were corrected for Lorentz and polarization effects. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT [46]). Structure solution, refinement and data output were carried out with the SHELXTL program package [47]. All non-hydrogen atoms were refined anisotropically. With the exception of the hydroxy hydrogens in **1b** and **2**, and the amino hydrogens in **1b** and **2b,** all other hydrogens were included in the models in calculated positions and were refined as constrained to bonding atoms. The crystal data and experimental parameters are summarized in Table II. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 608995

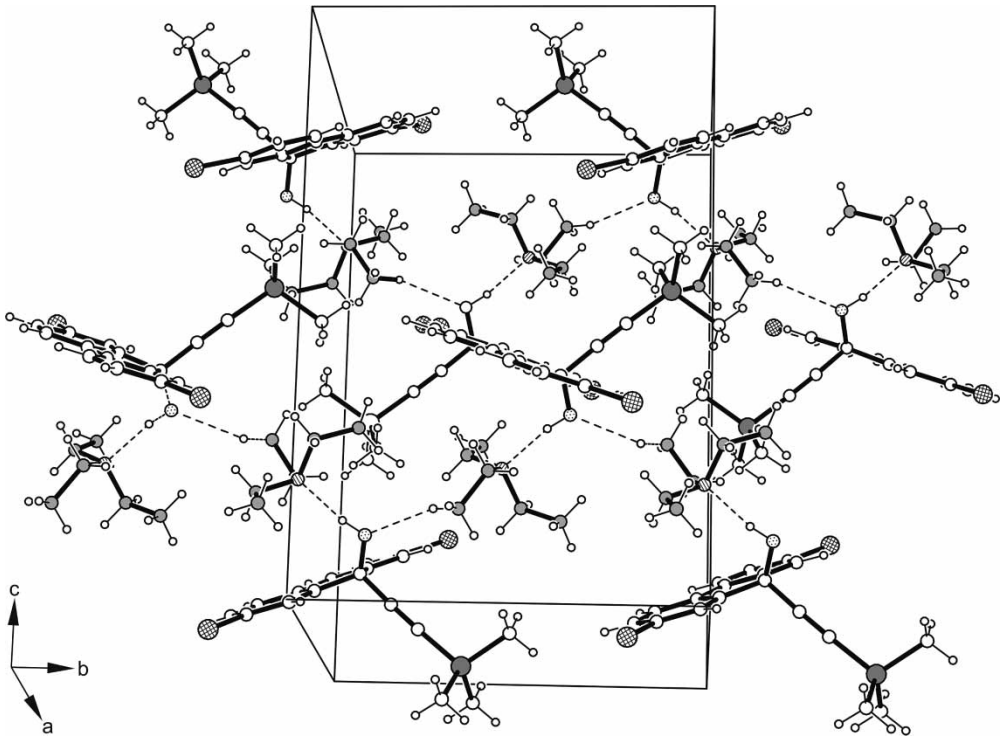


FIGURE 9 Packing diagram of the **2** . . . triethylamine (1:1) inclusion compound (**2b**). Guest molecules distinguished by shading of carbon atoms.

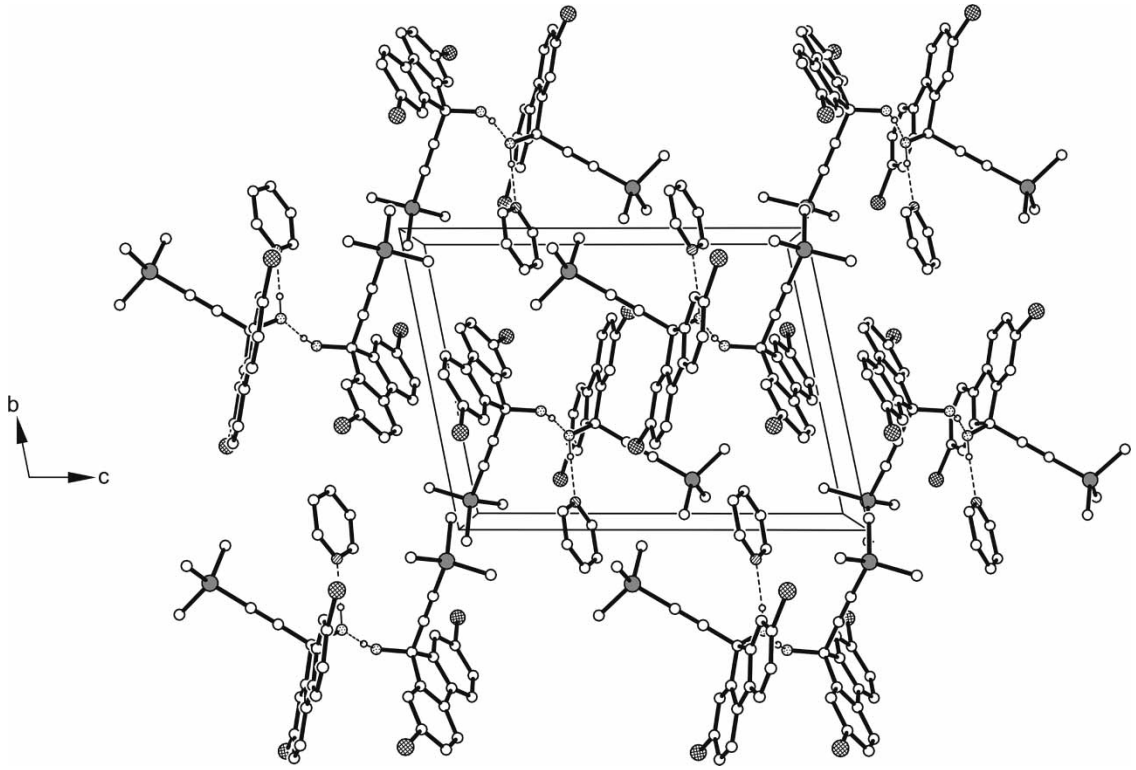


FIGURE 10 Packing diagram of the **2** . . . pyridine (2:1) inclusion compound (**2c**).

TABLE III Distances (Å) and angles (°) of hydrogen bonds and possible halogen…halogen interactions of the compounds examined (esd's in parentheses)

Atoms involved D—H…A (C—Br…Br)	Symmetry	Distances D—H	Distances D…A	Angle H…A (Br…Br)	Angle D—H…A (C—Br…Br)
1					
O(1)—H(1)…Br(1)	$1-x, 1-y, 2-z$	0.82	3.504(2)	2.87	135.9
C(9)—H(9A)…Br(2)	$x, y, 1+z$	0.96	3.792(2)	3.04	36.6
C(10)—Br(1)…Br(1)	$1-x, 1-y, 3-z$			3.59	147.0
1a					
O(1)—H(1)…O(1G)	x, y, z	0.82	2.773(4)	1.98	161.0
C(9)—H(9)…O(1)	$x, -1+y, z$	0.93	3.376(3)	2.48	162.6
C(2G)—H(2GB)…Br(2)	$2-x, 1-y, 1-z$	0.97	3.798(5)	3.03	136.7
C(1G)—H(1GA)…Br(1)	$1-x, 1-y, -z$	0.97	3.853(5)	2.95	156.2
1b					
O(1)—H(1)…N(1G)	x, y, z	0.93	2.692(4)	1.76	179.7
N (1G)—H(1G')…O(1)	$x, 0.5+y, 0.5-z$	0.92	2.951(3)	2.19	139.7
2					
C(3)—Br(1)…Br(2)	$2-x, 0.5+y, 1.5-z$			3.59	98.4
C(10)—Br(2)…Br(1)	$2-x, -0.5+y, 1.5-z$			3.59	173.2
C(16)—H(16A)…Br(2)	$3-x, -y, 2-z$	0.98	3.908(1)	3.03	149.2
C(18)—H(18C)…Br(1)	$1+x, 0.5-y, 0.5+z$	0.98	3.795(1)	3.02	136.6
O(1)—H(1)…$\pi_{(3)}$†	$2-x, -y, 2-z$	0.84	3.289(1)	2.46	170.9
2a					
O(1)—H(1)…N(1)	$-1+-x, -1+y, z$	0.84	2.678(2)	1.85	170.8
N(1)—H(1')…O(1)	$1-x, 1-y, z$	0.91	2.978(2)	2.37	124.9
C(3)—Br(1)…Br(1)	$1-x, -1-y, 1-z$			3.56	39.9
C(17)—H(17B)…Br(2)	$-x, -1-y, -z$	0.98	3.882(2)	2.99	152.6
2b					
O(1)—H(1)…N(1)	$0.5+x, 1.5-y, 0.5+z$	0.84	2.740(2)	1.91	170.1
C(2G)—H(2G3)…O(1)	$1-x, 1-y, 1-z$	0.98	3.398(2)	2.48	156.4
2c					
O(1)—H(1)…N(1G)	$x, -1+y, z$	0.84	2.697(2)	1.87	167.3
O(1A)—H(1A)…O(1)	x, y, z	0.84	2.746(2)	1.91	170.9
C(11A)—H(11A)…Br(1)	$-1+x, y, z$	0.95	3.829(2)	2.92	159.6
C(18)—H(18C)…Br(2)	$-x, 1-y, 1-z$	0.98	3.846(2)	3.05	139.2
C(18A)—H(18F)…Br(2A)	$1+x, y, z$	0.98	3.923(3)	3.02	153.5

† π means the centre of the corresponding ethynyl group C(14)—C(15).

TABLE IV Distances (Å) and angles (°) of intermolecular connections involving aromatic units of the structures examined (esd's in parentheses)

Connections	Symmetry	Distance
1		
$\pi_{(1)}$†…$\pi_{(2)}$†	$-x, 2-y, 2-z$	3.698(2)
$\pi_{(1)}$…$\pi_{(2)}$	$1-x, 2-y, 2-z$	3.717(3)
1a		
$\pi_{(1)}$…$\pi_{(1)}$	$2-x, 1-y, -z$	3.800(5)
$\pi_{(1)}$…$\pi_{(1)}$	$1-x, 1-y, -z$	3.767(5)
1b		
$\pi_{(1)}$…$\pi_{(1)}$	$-x, y, 1+z$	3.793(4)
2		
$\pi_{(1)}$…$\pi_{(1)}$	$1-x, y, 1-z$	3.703(2)
$\pi_{(1)}$…$\pi_{(2)}$	$2-x, y, 1-z$	3.794(2)
2a		
$\pi_{(1)}$…$\pi_{(2)}$	$x, -y, 1-z$	3.874(2)
2b		
$\pi_{(1)}$…$\pi_{(2)}$	$1-x, 2-y, 2-z$	3.814(2)
2c		
$\pi_{(1)}$…$\pi_{(2)}$	$1-x, 1-y, 1-z$	3.642(3)
$\pi_{(1A)}$…$\pi_{(2A)}$†	$-x, 1-y, 2-z$	3.638(3)

† π means the centre of the corresponding aryl ring, such as (1): C(1)…C(6) ring; (2): C(7)…C(12) ring; (1A): C(1A)…C(6A) ring; (2A): C(7A)…C(12A) ring.

to CCDC 609001. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

R.H. is grateful for a Georg Forster Scholarship from Alexander von Humboldt Foundation. T.S. thanks the Research Council of Mazandaran University for their partial financial support.

References

[1] *Molecular Inclusion and Molecular Recognition—Clathrates I and II, Topics in Current Chemistry*; Weber, E., Ed.; Springer-Verlag: Berlin-Heidelberg, 1988; vols 140 and 149.

[2] Bishop, R. *Chem. Soc. Rev.* **1996**, 311.

[3] Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids*; Elsevier: New York, 1989.

[4] *The Crystal as a Supramolecular Entity, Perspectives in Supramolecular Chemistry*; Desiraju, G. R., Ed.; Wiley: Chichester, 1996; vol. 2.

[5] *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Elsevier: Oxford, 1996; vol. 6.

[6] *Design of Organic Solids, Topics in Current Chemistry*; Weber, E., Ed.; Springer: Berlin–Heidelberg, 1998; vol. 198.
[7] Seddon, K. R.; Zaworotko, M. *Crystal Engineering: The Design and Application of Functional Solids*; Kluwer: Dordrecht, 1999.
[8] Weber, E. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Kroschwitz, J. I., Ed.; 4th ed. Wiley: New York, 1995; vol. 14, pp 122–154.
[9] *Separations and Reactions in Organic Supramolecular Chemistry, Perspectives in Supramolecular Chemistry*; Toda, F., Bishop, R., Eds.; Wiley: Chichester, 2004; vol. 8.
[10] *Comprehensive Supramolecular Chemistry*; Reinhoudt, D. N., Ed.; Elsevier: Oxford, 1996; vol. 10.
[11] Brehmer, T. H.; Korkas, P. P.; Weber, E. *Sensors and Actuators B* **1997**, *44*, 595.
[12] Langley, P. J.; Hulliger *J. Chem. Soc. Rev.* **1999**, *28*, 279.
[13] Matsuura, K.; Ariga, K.; Endo, K.; Aoyama, Y.; Okahata, Y. *Chem. Eur. J.* **2000**, *6*, 1750.
[14] *Crystal Design–Structure and Function, Perspectives in Supramolecular Chemistry*; Desiraju, G. R., Ed.; Wiley: Chichester, 2003; vol. 7.
[15] Weber, E. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Kroschwitz, J. I., Ed.;, 4th ed. Wiley: New York, 1998; vol. 14, pp 352–396.
[16] Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, 2000.
[17] Weber, E. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Elsevier: Oxford, 1996; vol. 6, pp 535–592.
[18] Weber, E.; Nitsche, S.; Wierig, A.; Csöregh, I. *Eur. J. Org. Chem.* **2002**, 856.
[19] Sumarna, O.; Seidel, J.; Weber, E.; Seichter, W.; Ibragimov, B. T.; Beketov, K. M. *Cryst. Growth Des.* **2003**, *3*, 541.
[20] Caira, M. R.; Nassimbeni, L. R.; Su, H.; Weber, E. *Cryst. Eng. Comm.* **2003**, *5*, 351.
[21] Caira, M. R.; Le Roex, T.; Nassimbeni, L. R.; Ripmeester, J. A.; Weber, E. *Org. Biomol. Chem.* **2004**, *2*, 2299.
[22] Caira, M. R.; Le Roex, T.; Nassimbeni, L. R.; Weber, E. *Cryst. Growth Des.* **2006**, *6*, 127.
[23] Bourne, S. A.; Nassimbeni, L. R.; Niven, M. L.; Weber, E.; Wierig, A. J. *Chem. Soc. Perkin Trans.* **1994**, *2*, 1215.
[24] Weber, E.; Wierig, A.; Skobridis, K. *J. Prakt. Chem.* **1996**, *338*, 553.
[25] Weber, E.; Meinhold, D.; Haase, R.; Seichter, W.; Rheinwald, G. *Supramol. Chem.* **2005**, *17*, 303.
[26] Scott, J. L.; Yamada, T.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1697.
[27] Desiraju, G. R. *Angew. Chem. Int. Ed.* **1995**, *34*, 2311.
[28] Schneider, H. -J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, 2000.
[29] Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453.
[30] Steiner, T.; Starikov, E. B.; Amado, A. M.; Teixeira, J. J. C. *J. Chem. Soc. Perkin Trans.* **1995**, *2*, 1321.
[31] Overgaard, J.; Waller, M. P.; Platts, J. A.; Hibbs, D. E. *J. Phys. Chem. A* **2003**, *107*, 11201.
[32] Desiraju, G. R. *The Weak Hydrogen Bond: In Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.
[33] Nishio, M. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Steed, J. W., Eds.; Marcel Dekker: New York, 2004; p 1576.
[34] Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 1210.
[35] Reddy, C. M.; Kirchner, M. T.; Gundakaram, R. C.; Padmanabhan, K. A.; Desiraju, G. R. *Chem. Eur. J.* **2006**, *12*, 2222.
[36] Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.
[37] Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N. -L. *Angew. Chem. Int. Ed.* **1995**, *34*, 1555.
[38] Tanaka, K.; Tomomori, A.; Scott, J. L. *Cryst. Eng. Commun.* **2003**, *5*, 147.
[39] Tanaka, K.; Tomomori, A.; Scott, J. L. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 294.
[40] Scott, J. L.; Tanaka, K. *Cryst. Growth Des.* **2005**, *5*, 1209.
[41] Dickert, F. L.; Haunschild, A. *Adv. Mater.* **1993**, *5*, 887.
[42] Scott, J. L.; Downie, A. P.; Asami, M.; Tanaka, K. *Cryst. Eng. Comm.* **2002**, *4*, 580.
[43] Mastuzaki, H.; Kishida, H.; Okamoto, H.; Talizawa, K.; Matsunaga, S.; Takaishi, S.; Miyasaka, H.; Sugiura, K.; Yamashita, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 3240.
[44] Sieglitz, A. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 1232.
[45] Sprinzak, Y. *J. Am. Chem. Soc.* **1958**, *80*, 5449.
[46] Bruker Analytical X-ray Systems, SAINT-NT Version 6.0 **2003**
[47] Bruker Analytical X-ray Systems, SHELXTL-NT Version 6.10 **2000**