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VERSATILE PACKING MODES OF 9-SUBSTITUTED 9-FLUORENOLS. X-RAY CRYSTAL STRUCTURES OF 9-METHYL-, 9-PHENYL-, 9-(1-NAPHTHYL)- AND 9-(2-BIPHENYLYL)FLUOREN-9-OL

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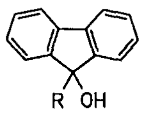
The four studied semi-rigid fluorenol derivatives differ only in the size of the 9-substituents. All four compounds crystallize with two molecules per asymmetric unit and with relatively low crystallographic symmetry [$P\bar{1}$ for the 9-methyl derivative (1) and $P2_1/n$ for the 9-(1-phenyl) (2), 9-(1-naphthyl) (3) and 9-(2-biphenylyl) (4) derivatives]. Crystal data: 1, $a = 8\cdot779(1)$, $b = 11\cdot570(1)$, $c = 11\cdot747(1)$ Å, $\alpha = 91\cdot197(5)$, $\beta = 104\cdot345(4)$, $\gamma = 105\cdot848(6)^\circ$; 2, $a = 8\cdot425(1)$, $b = 13\cdot819(1)$, $c = 23\cdot902(2)$ Å, $\beta = 95\cdot87(1)^\circ$; 3, $a = 15\cdot679(4)$, $b = 8\cdot567(2)$, $c = 23\cdot884(17)$ Å, $\beta = 92\cdot60(6)^\circ$; 4, $a = 7\cdot770(6)$, $b = 33\cdot766(10)$, $c = 13\cdot649(4)$ Å, $\beta = 95\cdot30(1)^\circ$. Nevertheless, the packing modes are different. The 9-methylfluoren-9-ol molecules, forming H-bonded tetramers with full H-bond saturation, give rise to the lowest packing coefficient among the four compounds. The crystals of the 9-phenyl derivative are built up of H-bonded dimers, whereas those of the bulky 9-naphthyl and 9-diphenylyl derivatives consist of single molecules only. The latter two compounds, however, have a denser packing than the two that contain H-bonded aggregates. The crystal structures are held together mainly by ordinary Van der Waals forces. In the case of 9-biphenylylfluoren-9-ol, the structure seems to be stabilized also by weak H-bond-type interactions from the alcoholic hydroxyl group to the π-electron cloud of an aromatic ring in the neighbouring molecule [the O···centroid distances are $3\cdot182(3)$ and $3\cdot248(4)$ Å, and in the 9-naphthyl derivative the OH groups are involved in some short ($\sim 3\cdot3$ Å) intermolecular approach, possibly indicating an electrostatically favourable packing for that compound.

INTRODUCTION

Whether molecules are capable of forming a dense or loose crystalline packing, or no stable crystal at all, depends on various parameters including the size and shape and polarity or the H-bonding capability of the molecular species under discussion.[1] A knowledge of the principles of aggregate formation is important in the engineering of crystals[2] and in the design of crystalline hosts.[3] In general, molecules which pack only badly are inclined to crystallize with a second component to fill the free space; hence they are potential clathrate formers.[4]

H-bonds between polar groups, if available in reasonable geometries, will determine a crystalline structure,[5] but less polar intermolecular interactions



1 R = Me

2 R = Ph

3 R = 1–Naphthyl

4 R = 2–Biphenylyl

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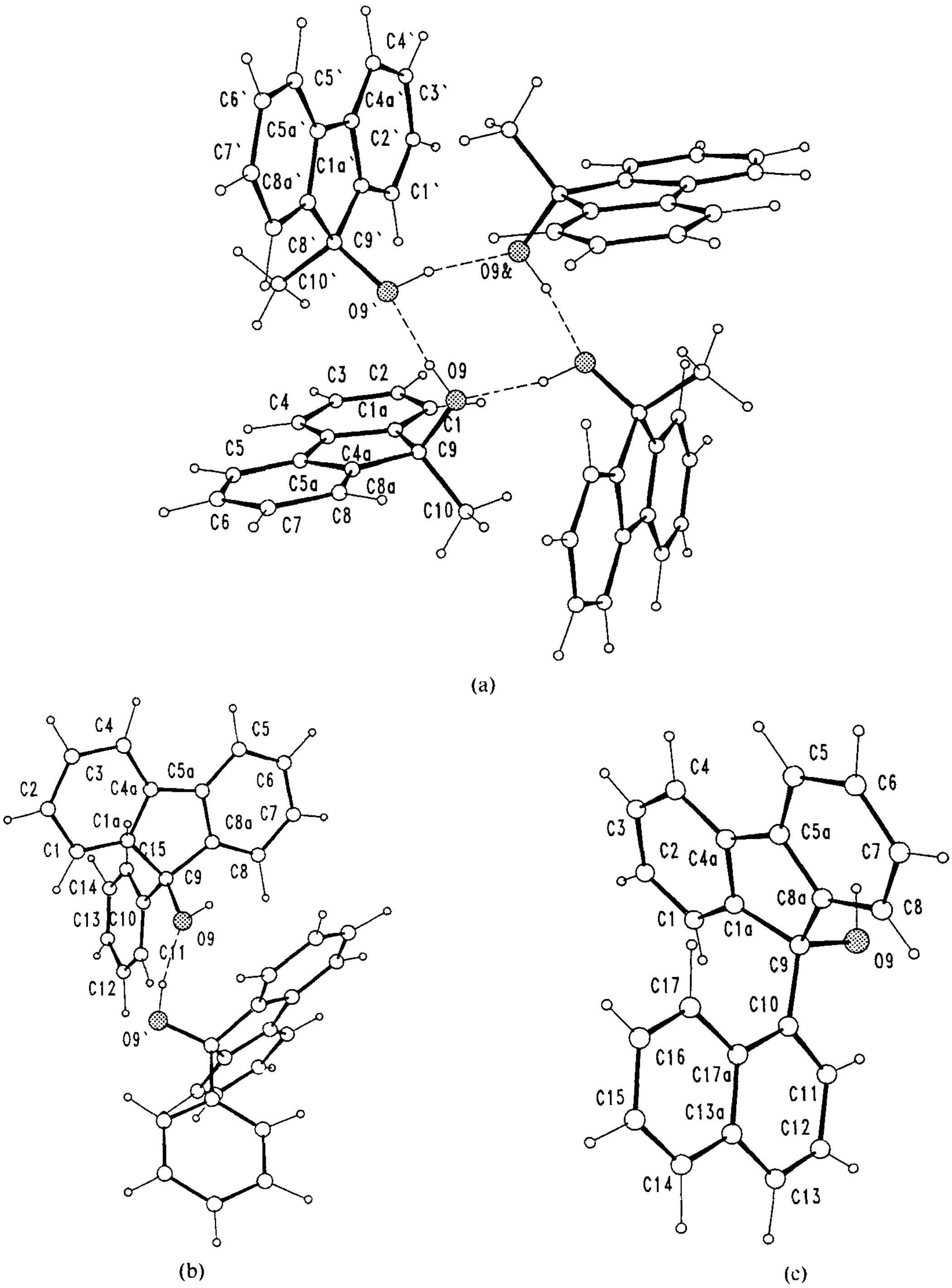
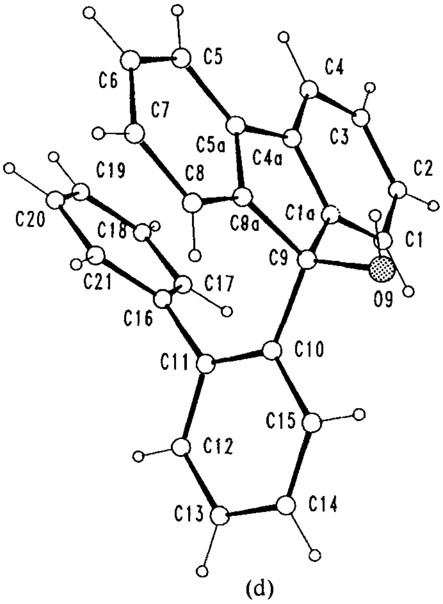


(a)

(b)

(c)

Figure 1. Perspective views of (a) the H-bonded tetramers of molecule **1**, (b) the H-bonded dimers of **2**, (c) the single molecule of **3** and (d) the single molecule of **4**, with crystallographic numbering of the atoms. Oxygen atoms are shaded and the solid and dashed lines represent covalent and hydrogen bonds, respectively. In the case of **4**, only one of the two disorder sites of H(9) is included



(d)

Figure 1. (*Continued*)

such as aryl–aryl contacts may also dominate.[6,7] Moreover, it is known from recent studies[8] that O—H···aryl hydrogen bonds are also possible as an intermediate of the two interaction types, which shows that the crystal packing is governed by a delicate interplay of contacts.

Here we report crystal structures of a series of selected compounds [9-methyl- (**1**), 9-phenyl- (**2**), 9-naphthyl- (**3**) and 9-(2-biphenylyl)fluroen-9-ol (**4**)], which may shed some light on the problem. Earlier investigations have shown that 9-aryl-substituted fluoren-9-ols and related bridged triarylmethanols are efficient clathrate hosts.[9] In this context, the present studies may also explain the influence of the substituents on the clathrate-forming properties of this compound family.

RESULTS AND DISCUSSION

Perspective views of the H-bonded aggregates of **1** and **2** and of the single molecules of **3** and **4** are shown in Figure 1(a)–(d), including the numbering schemes of the atoms. Crystal data and selected experimental details are given in Table 1 and selected conformational

Table 1. Crystal data and some selected experimental details for compounds **1–4** (Esds where given, are in parentheses)

Parameter	1	2	3	4
Formula	$C_{14}H_{12}O$	$C_{19}H_{14}O$	$C_{23}H_{16}O$	$C_{25}H_{18}O$
M_{wr}	196·25	258·32	308·38	334·42
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Unit cell dimensions				
a (Å)	8·779(1)	8·425(1)	15·679(4)	7·770(6)
b (Å)	11·570(1)	13·819(1)	8·567(2)	33·766(10)
c (Å)	11·747(1)	23·902(2)	23·884(17)	13·649(4)
α (°)	91·197(5)	90·0	90·0	90·0
β (°)	104·345(4)	95·87(1)	92·60(6)	95·30(4)
γ (°)	105·848(6)	90·0	90·0	90·0
V_c (Å^3)	1109·5(2)	2768·2(3)	3205(3)	3566(5)
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	8	8	8
D_c mg m^{-3})	1·1748(2)	1·2397(2)	1·278(1)	1·246(1)
$F(000)$	416	1088	1296	1408
Temperature (K)	291 ± 1	291 ± 1	158 ± 1	296 ± 1
Radiation used (λ, Å)	Cu Kα (1·54183)	Cu Kα (1·54183)	Mo Kα (0·71069)	Cu Kα (1·54184)
μ (cm^{-1})	5·33	5·49	0·71	5·40
No. of reflections measured	4295	5969	6239	6534
θ_{max}(°)	70	70	25	65
N_{tot} (unique, non-zero)	3753	4565	5399	5271
N_{ref} [with $I/\sigma(I) > 3$]	2846	3267	3477	4224
$N_{variables}$	289	391	435[a]	451
$R(=\Sigma\|\Delta F\|/\Sigma\|F_0\|)$	0·071	0·042	0·043	0·076
$wR(=[\Sigma w\|\Delta F\|^2/\Sigma w\|F_0\|^2]^{1/2}$	0·107	0·059	0·053	0·105
Weighting: g in SHELX[b]	0·00020	0·00020	0·000384	–[c]
Final $\Delta\rho_{max}$, $\Delta\rho_{min}$(eÅ^{-3})	0·29, –0·26	0·16, –0·17	0·25, –0·22	0·34, –0·35

[a] In the case of 3 the 'blocked full-matrix least-squares' refinement technique[11] had to be used owing to the large number of refined variables; two blocks, each with 219 variables, were refined in consecutive cycles.

[b] Weights of the structure factors in SHELX[13] are estimated as $w = [\sigma^2(F) + gF^2]^{-l}$.

[c] Weights of the structure factors in the refinement of 4 were estimated as $4F_0{}^2/\sigma(F_0{}^2)^2$ (according to the computer software SDP-PLUS[15]).

Table 2. Selected conformational features of compounds **1**–**4** (Esds are given in parentheses)

Parameter	Molecules	1	2	3	4
The nine C atoms of the fluorene rings are co-planar within (Å)	Unprimed	0·085	0·104	0·128	0·060
	Primed	0·090	0·072	0·110	0·065
Dihedral angle between the two benzene ring planes in the fluorene moieties (°)	Unprimed	1·9(1)	4·0(1)	2·0(1)	1·6(2)
	Primed	2·9(1)	2·7(1)	1·9(1)	2·0(2)
Dihedral angle between the LS planes through the fluorene moiety and the aryl substitutent (°)	Unprimed	—	94·8(1)	84·20(4)	87·2(1)[a]
	Primed	—	88·7(1)	85·86(4)	83·8(2)[a]

[a] In the case of the biphenylyl substituent in **4**, the dihedral angle is calculated between the plane through one phenyl ring of the biphenyly group [which is bonded to C(9)] and the fluorene moiety.

Table 3. Bond lengths (Å) and bond angles (°) in possible H-bond interactions in crystals of **1**, **2** and **4** (Esds, where given[a], are in parentheses)

			Distance			Angle
Compound	Atoms involved	Symmetry	O···acceptor	O—H	H···acceptor	O—H···Acceptor
1	O(9)—H(9)···O(9′)	x, y, z	2·732(3)	0·93	1·84	161
	O(9′)—H(9′)···O(9)	$-x, 1-y, 1-z$	2·730(4)	0·98	1·78	162
2	O(9′)—H(9′)···O(9)	x, y, z	2·845(2)	0·98	1·88	170
4	O(9)—H(9a)···centroid[b]	$1+x, y, z$	3·182(3)	0·99	2·61	117
	O(9)-H(9b)···centroid	$1+x, y, z$	3·182(3)	0·95	2·36	145
	O(9′)—H(9′a)···centroid	$1+x, y, z$	3·248(4)	1·04	2·36	143
	O(9′)—H(9′b)···centroid	$1+x, y, z$	3·248(4)	0·96	2·73	115

[a] The H positions are derived from difference electron density calculations and are not refined (see text).

[b] 'Centroid' means the centre of the C(16)—C(17)—C(18)—C(19)—C(20)—C(21) aromatic rings (unprimed and primed) in **4**.

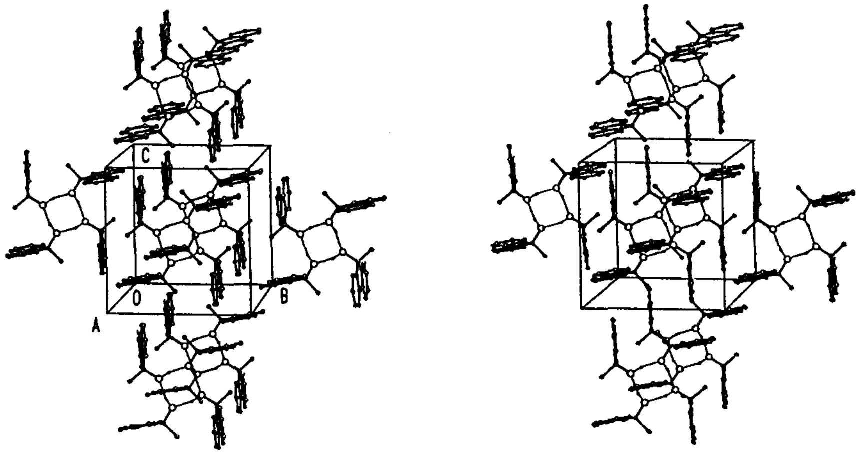


Figure 2. Stereo packing illustration of **1**. The carbon-bonded H atoms are omitted for clarity. Thin lines represent H-bonds

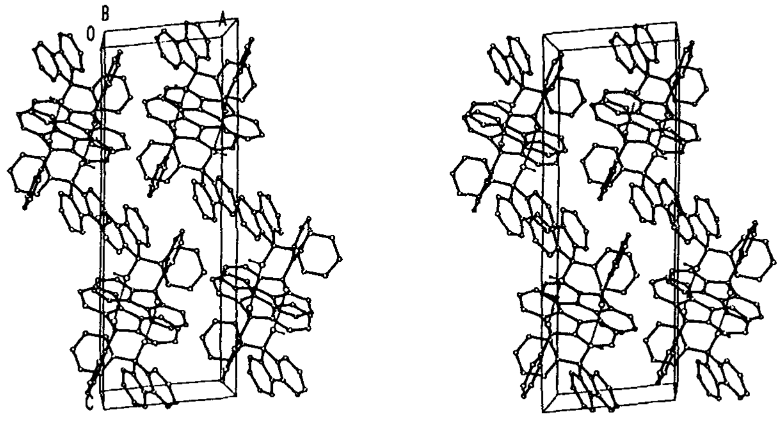


Figure 3. Stereo packing diagram of crystal **2**. The carbon-bonded H atoms are omitted for clarity. Thin lines represent H-bonds

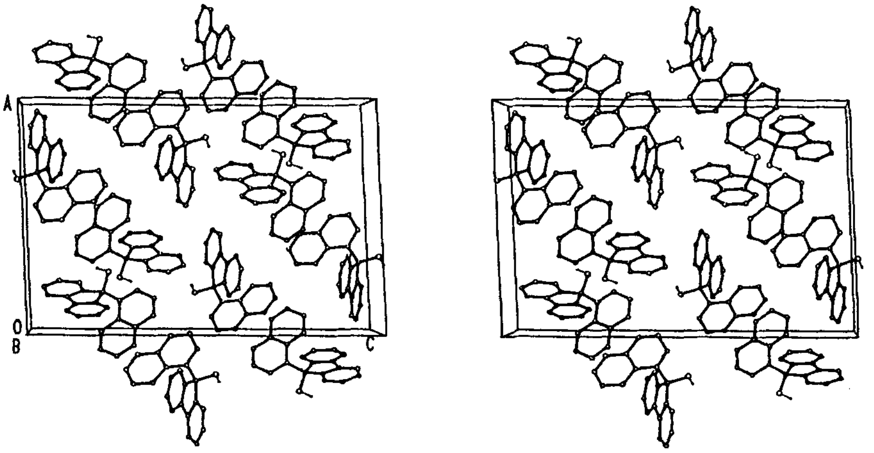


Figure 4. Stereo illustration of the packing arrangement of **3**. The carbon-bonded hydrogens are omitted for clarity

features and H-bond geometries are presented in Tables 2 and 3, respectively. Stereoscopic illustrations of the various packing modes are shown in Figures 2–5.

Molecular structures

It is noteworthy that all four structures contain two molecules per asymmetric unit. Corresponding bond distances and bond angles in the eight crystallographically independent molecules presented here generally conform to each other and are comparable to those previously published for related molecules.[9] The conformations are also similar [Figure 1(a–d)]. The phenyl substituents in **2**, the naphthyl groups in **3** and also one phenyl ring [which is bonded to C(9)] in each biphenylyl moiety of **4** are approximately perpendicular to the respective fluorene moiety. The two six-membered ring planes of each biphenylyl group of **4** are tilted through a 81·4(2)° and 83·8(2)° in the unprimed and primed molecule, respectively.

Packing relationships

The 9-substituted fluoren-9-ol derivatives **1**–**4** are bulky, irregularly shaped molecules containing an alcoholic OH group that is capable of intermolecular H-bond interactions. These features provide them with the ability to form inclusion compounds with a variety of different solvents.[9a] Nevertheless, they can be crystallized also without guests. Kitaigorodsky[1] has demonstrated that molecules without inner symmetry elements attain the closest packing in the space groups

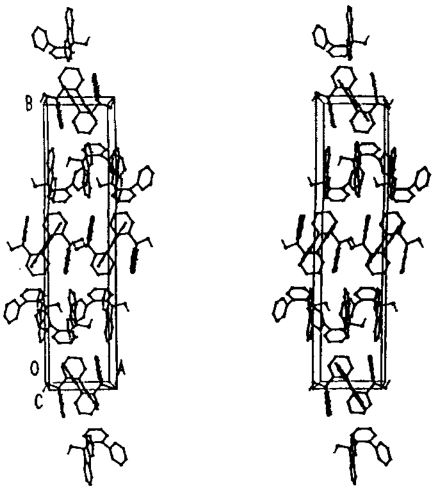


Figure 5. Stereo packing illustration of crystal **4**. The carbon-bonded H atoms are omitted for clarity

$P\bar{1}$, $P2_1$, $P2_1/c$, Pca, Pna and $P2_12_12_1$. Note also that in organic chemical crystallography a remarkable predominance of space group $P2_1/c$ (or $P2_1/n$) has been observed. In agreement with these observations, the four fluoren-9-ol derivatives **1**–**4** were found to crystallize in space groups $P\bar{1}$ (**1**) and $P2_1/n$ (**2**, **3** and **4**). The packing coefficients (i.e. the ratio of the space occupied by a molecule to the space allotted in the unit cell, estimated according to the crude method of Kitaigorodsky[1]) is 0.69 for **1**, 0·72 for **2**, 0·74 for **3** and 0·73 for **4**; these ratios are within the 0·65–0·77 interval characteristic for normal close-packed organic crystals.[1]

The four fluorenol derivatives differ only in the size of the 9-substituents. It is notable, however, that molecules **3** and **4** with the relatively large naphthyl and biphenylyl substituents exhibit denser packing than compounds **1** and **2** with the smaller 9-methyl and 9-phenyl groups (Figures 2–5). At the same time, inspection of the H-bond interactions in the crystals shows conspicuous differences between them. In crystals of 9-methylfluoren-9-ol, tetramer aggregates are formed around the centre of symmetry via H-bond interactions [Figure 1(a)]. The optimum close packing of these large tetramer units gives rise to the lowest density among the four crystals. We have seen previously in the structure of the 9-phenylfluoren-9-ol : benzene (8 : 3) complex[9a] that the 9-phenyl derivative can also form tetramers in the same way as the 9-methyl analogue. The guest-free crystals of **2**, however, contain H-bonded dimers only, where the primed OH group functions as a proton donor and the unprimed group is a proton acceptor. Hence neither the requirement for maximum saturation of the hydrogen bonds nor the 'maximum acceptor rule,' postulated a few years ago,[5b,10] is fulfilled in this structure. Nevertheless, in the **2**·benzene (8 : 3) complex the benzene guests fill up the voids between the huge host tetramers, resulting in a packing coefficient of 0·69. It seems probable that the H-bonded tetramer aggregates of the 9-phenyl derivative cannot reach close packing without guests and, according to Kitaigorodsky's assumption,[1] no crystallization will occur if the shape of the molecule (or aggregate) is such that no packing can be effected with a packing coefficient above 0.6. Consequently, the packing mode in crystal **2** is determined by a compromise between the potential energies of dense packing on the one hand and hydrogen bonding on the other. The H-bonded oligomers of **1** and **2** are held together by weak Van der Waals' forces. The packing of the dimers of **2**, however, seems to be stabilized also by π–π interactions between neighbouring fluorene moieties (cf. Figure 3).

Similarly to compounds **1** and **2**, crystals of both the naphthyl and the biphenylyl compounds **3** and **4** contain two molecules per asymmetric unit. There are, however, no O—H···O interactions at all in the latter crystals, and the two crystallographically independent molecules in each compound do not differ significantly from each other. This is strange, because only rarely does more than one molecule occupy a general position,[1] except when molecules are dimeric owing to hydrogen bonds, or when more than one conformer is present in the crystal. However, the size and shape of molecules **3** and **4** seem to make it impossible for them to form H-bonded aggregates which can be arranged with acceptable packing density. Accordingly, they avoid H-bonds between the molecules and form crystals using weaker intermolecular interactions only. The intermolecular contact distances are generally in the same range as the sum of Van der Waals' radii. There are, however, a few exceptions worth mentioning. In the case of the diphenylyl derivative, the OH groups seem to be involved in weak H-bond-type interactions with the π-electron cloud of the neighbouring aromatic ring[8] [the C(16)···C(21) phenyl ring of the biphenylyl moiety in each molecule; cf. Fig. 5]. There is ample evidence from both experimental and theoretical treatments that lends significance to attractive interactions between π systems and H atoms.[8a–d] The possibility of steric repulsion has also been considered, though, and examined by NMR method for fluoren-9-ol.[8e] The geometric parameters, observed in the 9-biphenylylfluoren-9-ol crystal (Table 3) are comparable to those earlier published for π-electron H-bonding with water as the proton donor.[8a] Moreover, the alcoholic OH groups in **3** are involved in some short intermolecular contacts

$$\begin{gathered}[\mathrm{O(9)—C(1)}_{(1/2-x,1/2+y,1/2-z)} = 3{\cdot}267(3);\\ \mathrm{O(9)—C(2)}_{(1/2-x,1/2+y,1/2-z)} = 3{\cdot}271(3);\\ \mathrm{O(9)—C(11)}_{(1/2-x,-1/2+y,1/2-z)} = 3{\cdot}271(3);\\ \mathrm{O(9')—C(12)}_{(1-x,1-y,-z)} = 3{\cdot}314(4)\,\text{Å}],\end{gathered}$$

possibly indicating an electrostatically favourable packing for that compound.

CONCLUSION

The structures presented demonstrate the importance of close packing in organic crystal structures. The various packing modes of 9-substituted fluoren-9-ols are the result of simultaneous satisfaction of the requirements of maximum packing density and the tendency for maximum formation of H-bonds. The presence of groups suitable for H-bond interaction does not guarantee that such interactions will occur, however. H-bonds will arise only if the H-bonded aggregates can achieve a packing with acceptable density.

EXPERIMENTAL

Sample preparation and data collection. Compounds **1**,[11] **2**,[9a] **3**[9a] and **4**[9a] were prepared according to literature procedures. The crystals for x-ray studies were grown from ethanol (**1**), light petroleum (b.p. 60–90 °C) (**2**) and toluene (**3** and **4**). Single crystals of reasonable quality and appropriate size, selected for x-ray investigation, were sealed either in glue (**1**, **2**, **4**) or in a glass capillary (**3**).

Intensity data for **1**, **2** and **3** were obtained on an STOE/AED2 diffractometer, whereas an Enraf-Nonius CAD4 instrument was used for **4**. Corrections were made for background, Lorentz and polarization effects, and in the case of **4** an empirical spherical absorption correction was also applied (DIFABS).[12]

Structure analysis and refinement. Direct methods yielded reasonable preliminary models for all four structures, which were then refined by full-matrix least-squares procedures. The H atoms, except ten hydrogens of **1**, were located from difference electron density ($\Delta\rho$) maps and were held riding on their parent atoms during the subsequent calculations. Ten carbon-bonded H atoms in **1** were given geometrically predicted positions with C—H = 1·00 Å, recalculated after each cycle of the refinement. In **4** the alcoholic H atom is supposed to be disordered in both molecules. It must be noted that these H atom positions are only realistic as a hypothetical model of a peculiar H-bond interaction. Accordingly, two positions, each with 50% site occupany, were included for both H(9) and H(9′) in the structure factor calculation.

In the final refinements the non-hydrogen atoms were allowed to vibrate anisotropically, and isotropic displacement parameters were assumed for the hydrogens. The carbon-bonded H atom positions in **4** were given an augmented B_{iso} of their parent atoms $[B_{\mathrm{iso(H)}} = B_{\mathrm{iso(C)}} + 1{\cdot}0]$. Moreover, in the last refinement of **3**, nine low-θ reflections with F_o considerably less than F_c, probably owing to extinction effects, were excluded. At the same time the final refinements of **1** and **2** included also an empirical isotropic extinction correction factor (χ) according to Sheldrick[13] $[F' = F(1 - 0{\cdot}0001\chi F^2/\sin\theta)]$, which refined to 0·042(3) and 0·024(1), respectively. The calculations for **1**, **2** and **3** were carried out with the programs of Sheldrick,[13,14] whereas SDP-PLUS computer software[15] was used for compound **4**. Crystal data and some details of the refinement calculations together with the final R values are given in Table 1. The molecular geometries were calculated using the PARST program,[16] and the illustrations were drawn with the program PLUTO.[17]

Supplementary data. Lists of fractional atomic coordinates and equivalent isotropic/isotropic temperature factors of the non-hydrogen atoms and of the alcoholic hydrogens in **1**–**4** (Table 4), bond lengths and bond angles involving the non-hydrogen atoms (Tables 5 and 6), fractional atomic coordinates and isotropic vibrational parameters of the H atoms (Table 7) and covalent bond distances and bond angles involving the H atoms (Tables 8 and 9) have been deposited as supplementary data at the Cambridge Crystallographic Data Centre. List of the anisotropic displacement parameters of the non-hydrogen atoms (Table 10) and of the observed and calculated structure factors are available directly from the authors.

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