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Versatility in Complexation of Six-Membered Heterocyclic Guests by Singly Bridged Triarylmethanol Hosts.#
X-Ray Crystal Structures and Thermal Stabilities of Inclusion Compounds with Piperidine, Thioxane/Dioxane, and Morpholine

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9-Phenylfluoren-9-ol (**1**), 2,7-dibromo-9-phenylfluoren-9-ol (**2**), and 9-phenylethynylfluoren-9-ol (**3**) enclathrate different six-membered heterocyclic guests involving piperidine, thioxane, dioxane, and morpholine. X-Ray crystal structure determinations of corresponding inclusion compounds [**1**·piperidine (1:1), **1**·thioxane·dioxane (2:2:1), **2**·morpholine (1:2), and **3**·morpholine (1:1)] are reported, showing remarkable variety in the packing relations. Host compound **1** forms H-bonded 1:1 host:guest units with both piperidine and thioxane, but in the latter case additional dioxane guests are incorporated in the crystal, thus yielding a ternary complex. Host compound **3** is capable of forming closed loops of hydrogen bonds with full hydrogen bond saturation in its inclusion compound with morpholine, whereas in the related morpholine complex of **2** H-bonded 1:2 associates are created without maximal saturation of the hydrogen bonds, and with different binding modes for the two guests of the stoichiometric unit. In the crystals, the various H-bonded host-guest units are linked together by Van der Waals' forces, occasionally supported by weak electrostatic interactions. The stabilities of the four different inclusion compounds were studied by thermal analysis indicating complex decomposition modes.

Designed crystalline inclusion compounds and supramolecular complexes[2] composed of host and guest components have aroused considerable interest in the past few years due to the potential uses for analytical problems[3] and in materials science[4] including sensor technology.[5] A family of singly bridged triarylmethanols[6] are particularly promising in this respect. They have proved to be efficient hosts in crystalline inclusion formation with organic guests of different compound classes.[6,7] Systematic studies of crystalline inclusion structures involving dioxane a well as DMF, acetone, and alcohol guests have been done previously,[1,8,9] suggesting characteristic modes of supramolecular recognition. The dioxane inclusions[8] showed specific two-fold hydrogen bond acceptorship of dioxane and single hydrogen bond donorship of the hosts, although dioxane in the single hydrogen acceptor state and dioxane free of hydrogen bonds is also encountered in compounds involving host species with rather bulky substituents.

In order to learn more about the effect of substitution of oxygens in dioxane by other atoms on host–guest interactions and, in view of a rational inclusion design,[10] we have studied the crystalline inclusion compounds of singly bridged triarylmethanol hosts **1**—**3** with piperidine, thioxane (in addition to dioxane) and morpholine, namely the inclusion compounds **4**—**7** (Chart 1). The saturated heterocyclic guests are analogues of dioxane, of similar ring size but with carbon, nitrogen, or sulfur as replacement atoms, thus exhibiting different proton donor/acceptor abilities. Accordingly, sulfur in thioxane is a much weaker H bond acceptor than oxygen in dioxane; NH in piperidine and morpholine is both an H bond donor and acceptor, whereas CH_2 in piperidine is neither H bond acceptor nor donor. How does this influence the packing of supramolecular structures

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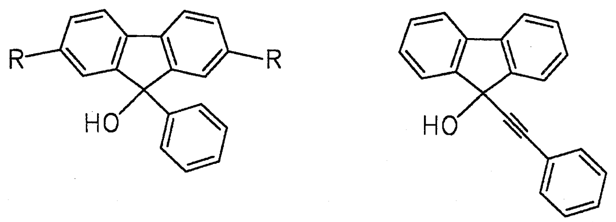
#Triarylmethanol Hosts and Analogues. Part 11. For part 10 of this series see Ref. 1.



1 R = H
2 R = Br

3

4 = **1** · piperidine (1 : 1)
5 = **1** · thioxane · dioxane (2 : 2 : 1)
6 = **2** · morpholine (1 : 2)
7 = **3** · morpholine (1 : 1)

Chart 1.

relative to the dioxane inclusions?

We report herewith synthesis, X-ray crystal structure determinations and thermal stability studies of the respective inclusion compounds **4**—**7** and discuss interaction modes in view of the problems mentioned before.

Experimental

Sample Preparation. The host compounds **1**—**3**, synthesized as described previously,[6)] were dissolved in a minimum amount of the respective guest solvent, or of the mixture of guest solvents. Crystals, suitable for X-ray analysis, were grown by slow evaporation. The selected single crystals were coated with epoxy glue in order to prevent possible solvent evaporation during the X-ray data collection.

X-Ray Data Collection and Processing. Crystal data and details of the data reduction and structure refinement calculations are shown in Table 1. Intensity data were collected on an automatic STOE/AED2 diffractometer, equipped with graphite monochromator, with either Mo $K\alpha$ (λ=0.71069 Å) or Cu $K\alpha$ radiation (λ=1.54183 Å), using the ω–2θ scan technique. The net intensities were corrected for decay, Lorentz and polarization effects, and in the case of compounds **5** and **6** also for absorption effects. The empirical absorption correction, applied to the data from compound **5** was based on ψ scans of eight reflections within the range $75<\chi<87°$ and $21<2\theta<82°$. The transmission factors varied between 0.535 and 0.638. The correction for the bromine-containing complex **6** was carried out with the numerical absorption correction programme of the SHELX[11)] system. The minimum and maximum values of the transmission factors in this latter case were 0.264 and 0.453, respectively.

Structure Analysis and Refinement. A preliminary structural model for **6** was derived by a combination of Patterson synthesis and direct methods,[12)] whereas the remaining three structures were solved by application of direct methods.[12)] Conventional Fourier syntheses and full-matrix least-squares calculations, based on $|F|$ (SHELX),[11,13)] were used for the refinement of the structural models. The oxygen- and nitrogen-bonded H atoms in each structure and all hydrogens in **6** were located from difference electron density ($\Delta\rho$) maps and were held riding on their parent atoms during the subsequent calculations. The carbon-bonded H atoms in **4**, **5**, and **7**, however, were either located from $\Delta\rho$ maps and were treated as mentioned above, or were assumed to be in geometrically idealized positions with C–H=1.00 Å (**4** and **7**) or with C–H=1.08 Å (**5**), which were recalculated after each cycle of the refinements, using geometric evidence.

The crystallographic asymmetric unit of **5** contains one host alcohol, one thioxane molecule and a half of the dioxane guest. Both the thioxane and the dioxane rings occur in two major conformations, but they are disordered in different ways [cf. Figs. 2(a) and 2(b)]. In the thioxane molecule all four carbon atoms are disordered, whereas in the dioxane ring only tow atoms, C(D2) and its centrosymmetrically related equivalent, are flipping between two partially occupied positions. In the thioxane molecule, the four carbon disorder sites, belonging to the same conformer and all labelled either 'a' or 'b', and also their hydrogens, were assumed to have the same site occupation factor (sof), and the sum of the sof of each 'a'–'b'-pair in both molecules was set equal to 1.0. Accordingly, in the thioxane ring the sof of the 'a' and 'b' positions refined to 0.54(1) and 0.46(1), respectively, whereas refinement of the probability of the disorder sites in the dioxane molecule yielded a sof of 0.65(2) for C(D2a), and only 0.35(2) for C(D2b). In the least-squares calculations, the disordered carbon atoms (with partial site occupancies) had to be held riding on their S and O atoms in order to yield acceptable geometry.

In the last stage of the refinements, the non-hydrogen atoms were allowed to vibrate anisotropically, whereas common isotropic displacement parameters were refined for the hydrogen positions. The final refinement of **5** included also an empirical isotropic extinction correction factor x $[F'=F(1-0.0001\cdot x\cdot F^2/\sin\theta)]$,[11,13)] which refined to 0.0188(1). Moreover, three reflections were omitted for potential systematic errors. On the other hand, one and two reflections with considerably lower F_{obsd} than F_{calcd}, most likely depending on extinction effects, have been excluded from the last refinement calculation of **6** and **7**, respectively. The final reliability indices, R, wR and wR_{tot}, are shown in Table 1. The wR_{tot} values were calculated for the final structural models using all unique non-zero reflections. It is noteworthy that only a small fraction of the unique, non-zero reflections were significantly observed for compounds **4** (43%) and **6** (35%), (cf. Table 1), indicating a rather poor scattering ability of those crystals. The refined fractional atomic coordinates of the non-hydrogen atoms and those of the oxygen- and nitrogen-bonded H atoms are listed in Table 2.

Thermal Analysis. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Perkin–Elmer PC7 Series System. Crystals were removed from their mother liquor, blotted dry on filter and crushed before analysis. Sample weights were between 3 and 5 mg. The temperature ranged from ambient to approx. 50 °C beyond the melting point of the host at a heating rate of 20 °C min^{-1}, except where otherwise indicated.

Results and Discussion

The stoichiometric units with atomic numbering of compounds **4**—**7** are depicted in Figs. 1(a)—(d), respectively. Figure 2 shows the disorder models of thioxane (a) and dioxane (b) in the ternary compound **5** with

Table 1. Crystal Data and Selected Details of the Data Reduction and Structure Refinement Calculations (esd's, where given, in parentheses)

Compound	**4** **1**·piperidine (1 : 1)	**5** **1**·thioxane·dioxane (2 : 2 : 1)	**6** **2**·morpholine (1 : 2)	**7** **3**·morpholine (1 : 1)
Formula unit	$C_{19}H_{14}O\cdot$ $C_5H_{11}N$	$C_{19}H_{14}O\cdot$ $2C_4H_8OS\cdot C_4H_8O_2$	$C_{19}H_{12}OBr_2\cdot$ $2C_4H_9NO$	$C_{21}H_{14}O\cdot$ C_4H_9NO
Formula weight	343.47	406.54	590.35	369.46
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	Pc	$P2_1/a$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions				
a/Å	8.773(1)	16.336(1)	12.1075(1)	9.344(1)
b/Å	8.710(1)	8.631(1)	15.1378(1)	9.859(1)
c/Å	12.890(1)	16.357(2)	13.9873(3)	12.272(1)
α/°	90.0	90.0	90.0	110.916(5)
β/°	103.18(1)	105.98(1)	98.924(3)	99.146(4)
γ/°	90.0	90.0	90.0	104.210(2)
V_c/Å^3	959.0(2)	2217.2(3)	2532.6(4)	985.0(2)
Refinement of the unit cell dimensions:				
No. of reflections used	35	40	76	36
2θ-range/°	20—37	33—52	25—41	30—40
Z	2	4	4	2
D_c/g cm^{-3}	1.1894(2)	1.2179(2)	1.5483(1)	1.2457(2)
F(000)	368	864	1200	392
T/K	173(1)	291(1)	193(1)	173(1)
Radiation	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ/cm^{-1}	0.67	14.30	31.99	0.73
Range of 2θ/°	3—60	3—140	3—60	3—60
No. of collected reflections	2975	5057	7909	5744
No. of standard reflections	5	5	4	5
Time interval between the standard/min	90	90	90	90
Intensity instability	<1%	<3%	<1%	<1%
No. of unique non-zero reflections	2332	3439	5683	5175
No. of significantly observed reflections	996	1874	1967	3422
Criterion of significance	$I/\sigma(I)>2$	$I/\sigma(I)>3$	$I/\sigma(I)>3$	$I/\sigma(I)>3$
No. of refined parameters	234	282	313	276
Final agreement factors				
$R[=\sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.039	0.063	0.033	0.040
$wR[=(\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_o\rvert^2)^{\frac{1}{2}}$	0.038	0.087	0.038	0.050
wR_{tot}	0.051	0.107	0.073	0.054
Weighting: $w=[\sigma^2(F)+\boldsymbol{g}\cdot F^2]^{-1}$ with $\boldsymbol{g}=$	0.00050	0.00025	0.00051	0.00017
Final $\Delta\rho_{max}/\Delta\rho_{min}$ [e$^-$ Å^{-3}]	0.15/−0.17	0.25/−0.12	0.64/−0.44	0.25/−0.21

the disorder sites labelled as in the text. Table 3 lists the distances and angles in hydrogen bonds and in possible C–H···O interactions. The molecular packings in crystals **4**—**7** are illustrated in Figs. 3(a)—(d), and the TG and DSC traces for compounds **4**—**7** are shown in Figs. 4(a)—(d), respectively.[15)]

Molecular Structures. Corresponding parameter values concerning the geometry and conformation of the phenyl- or phenyletynyl-substituted fluoren-9-ol moieties of the present host molecules (**1**—**3**) are comparable with each other and are generally within the range of our previous observations in related host molecules.[1,6—9,16)] Accordingly, the thirteen ring atoms forming the fluorene moiety are co-planar within 0.073 (host **1** in compound **4**), 0.117 (**1** in **5**), 0.100 (**2**), and 0.092 Å (**3**), and the dihedral angle[14)] between the least-squares (LS) planes of the bridged phenyl rings of the fluorene moiety are 2.8(2) and 4.0(2) in **1** (in com-

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic[a)]/Isotropic Displacement Parameters. $U_{\mathrm{eq}}/U_{\mathrm{iso}}$ (Å^2), for the Non-Hydrogen Atoms and for the N- and O-Bonded H Atoms of Compounds **4**—**7** (esd's, where given,[b)] are in parentheses)

Atoms	x/a	y/b	z/c	$U_{\mathrm{eq}}/U_{\mathrm{iso}}$
4[**1**·piperidine (1 : 1)]				
C(1a)	0.8446(6)	0.1856(5)	0.5145(4)	0.030(2)
C(1)	0.7869(6)	0.0392(6)	0.5237(4)	0.039(2)
C(2)	0.7307(7)	0.0022(7)	0.6133(5)	0.047(2)
C(3)	0.7332(7)	0.1102(8)	0.6925(5)	0.050(2)
C(4)	0.7896(7)	0.2574(8)	0.6838(4)	0.046(2)
C(4a)	0.8465(6)	0.2960(6)	0.5940(4)	0.036(2)
C(5a)	0.9139(6)	0.4376(6)	0.5626(4)	0.033(2)
C(5)	0.9368(7)	0.5820(7)	0.6106(4)	0.045(2)
C(6)	1.0049(8)	0.6964(6)	0.5630(5)	0.049(2)
C(7)	1.0501(7)	0.6704(6)	0.4676(5)	0.045(2)
C(8)	1.0273(7)	0.5267(6)	0.4191(4)	0.036(2)
C(8a)	0.9588(6)	0.4131(6)	0.4668(4)	0.029(2)
C(9)	0.9186(6)	0.2480(5)	0.4281(4)	0.028(2)
O(9)	0.8160	0.2444(4)	0.3243	0.032(1)
H(O9)	0.7095	0.2664	0.3285	0.055(3)
C(10)	1.0665(6)	0.1572(5)	0.4228(4)	0.027(2)
C(11)	1.0829(6)	0.0826(6)	0.3313(4)	0.032(2)
C(12)	1.2182(7)	−0.0009(6)	0.3307(5)	0.042(2)
C(13)	1.3364(7)	−0.0097(7)	0.4215(5)	0.047(2)
C(14)	1.3207(6)	0.0648(6)	0.5131(5)	0.045(2)
C(15)	1.1871(6)	0.1480(6)	0.5137(4)	0.040(2)
N(P1)	0.5113(5)	0.3060(5)	0.3373(4)	0.041(2)
H(N)	0.4868	0.1955(5)	0.3669(4)	0.055(3)
C(P2)	0.4839(7)	0.4221(7)	0.4124(5)	0.054(2)
C(P3)	0.5170(8)	0.5789(7)	0.3761(5)	0.060(2)
C(P4)	0.4142(8)	0.6124(7)	0.2655(5)	0.062(3)
C(P5)	0.4329(8)	0.4836(8)	0.1885(5)	0.061(3)
C(P6)	0.4055(7)	0.3270(7)	0.2323(5)	0.057(2)
5[**1**·thioxane·dioxane (2 : 2 : 1)]				
C(1a)	0.3551(3)	0.0895(6)	0.7291(3)	0.049(2)
C(1)	0.3299(3)	0.2239(6)	0.6836(3)	0.065(2)
C(2)	0.3068(4)	0.2138(8)	0.5952(4)	0.078(3)
C(3)	0.3096(4)	0.0750(9)	0.5548(3)	0.083(3)
C(4)	0.3344(4)	−0.0604(8)	0.6008(3)	0.074(3)
C(4a)	0.3582(3)	−0.0512(6)	0.6892(3)	0.056(2)
C(5a)	0.3899(3)	−0.1706(6)	0.7545(3)	0.054(2)
C(5)	0.4048(4)	−0.3272(7)	0.7472(4)	0.072(3)
C(6)	0.4385(4)	−0.4119(7)	0.8210(5)	0.079(3)
C(7)	0.4577(4)	−0.3407(7)	0.8996(5)	0.081(3)
C(8)	0.4414(3)	−0.1810(7)	0.9077(4)	0.066(2)
C(8a)	0.4073(3)	−0.0998(6)	0.8339(3)	0.050(2)
C(9)	0.3837(3)	0.0717(5)	0.8253(3)	0.049(2)
O(9)	0.4544(2)	0.1694(4)	0.8641(2)	0.061(1)
H(O9)	0.4935	0.1377	0.8354	0.11(2)
C(10)	0.3126(3)	0.1064(6)	0.8659(3)	0.058(2)
C(11)	0.3240(4)	0.1995(7)	0.9360(4)	0.082(3)
C(12)	0.2544(7)	0.2216(10)	0.9705(5)	0.114(4)
C(13)	0.1770(6)	0.1549(12)	0.9344(6)	0.122(5)
C(14)	0.1665(5)	0.0638(10)	0.8648(6)	0.111(4)
C(15)	0.2328(4)	0.0396(8)	0.8300(4)	0.084(3)
S	0.6859(1)	−0.0940(3)	0.6809(1)	0.110(1)
C(T1a)	0.5802	−0.0048	0.6366	0.127(10)
C(T1b)	0.6196	0.0708	0.6484	0.102(8)
C(T2a)	0.5682	0.1282	0.6988	0.090(7)
C(T2b)	0.5466	0.0448	0.6796	0.104(9)
O(T1)	0.5723(2)	0.0730(4)	0.7782(2)	0.086(2)
C(T3a)	0.6500	0.0078	0.8246	0.094(7)
C(T3b)	0.6216	−0.0639	0.8137	0.082(7)
C(T4a)	0.6677	−0.1414	0.7796	0.099(7)
C(T4b)	0.7089	−0.0608	0.7953	0.076(6)
O(D)	0.4311(3)	0.6070(5)	0.5177(3)	0.097(2)
C(D1)	0.4184(3)	0.5012(5)	0.4494(3)	0.207(9)
C(D2a)	0.5048	0.5438	0.5799	0.170(11)
C(D2b)	0.5217	0.6459	0.5297	0.22(3)
6[**2**·morpholine (1 : 2)]				
C(1a)	0.0985(5)	0.2239(3)	0.4833(4)	0.017(2)
C(1)	0.1264(5)	0.2074(4)	0.3927(4)	0.021(2)
C(2)	0.0476(5)	0.2256(4)	0.3131(4)	0.023(2)
Br(2)	0.08035(6)	0.20092(5)	0.18700(4)	0.0359(2)
C(3)	−0.0566(5)	0.2610(4)	0.3206(4)	0.023(2)
C(4)	−0.0853(5)	0.2786(4)	0.4116(4)	0.024(2)
C(4a)	−0.0066(5)	0.2588(4)	0.4932(4)	0.020(2)
C(5a)	−0.0151(5)	0.2661(4)	0.5967(4)	0.019(2)
C(5)	−0.1008(5)	0.2955(4)	0.6436(4)	0.029(2)
C(6)	−0.0870(5)	0.2937(4)	0.7441(4)	0.034(2)
C(7)	0.0102(6)	0.2602(4)	0.7949(4)	0.030(2)
Br(7)	0.02434(7)	0.25378(5)	0.93253(5)	0.0480(3)
C(8)	0.0992(5)	0.2297(4)	0.7504(4)	0.024(2)
C(8a)	0.0841(5)	0.2345(4)	0.6498(4)	0.022(2)
C(9)	0.1669(4)	0.2052(4)	0.5830(4)	0.018(2)
O(9)	0.2683(3)	0.2542(3)	0.6003(3)	0.024(1)
H(O9)	0.2615	0.3153	0.5667	0.05(2)
C(10)	0.1953(5)	0.1073(4)	0.5946(4)	0.019(2)
C(11)	0.3046(5)	0.0774(4)	0.6086(4)	0.030(3)
C(12)	0.3284(6)	−0.0122(4)	0.6189(5)	0.036(3)
C(13)	0.2425(6)	−0.0728(4)	0.6146(4)	0.033(3)
C(14)	0.1315(5)	−0.0438(4)	0.6003(4)	0.027(2)
C(15)	0.1109(5)	0.0449(4)	0.5912(4)	0.025(2)
O(M11)	0.2248(4)	0.4012(3)	0.2864(3)	0.051(2)
C(M12)	0.3254(6)	0.4512(5)	0.2806(5)	0.049(3)
C(M13)	0.3358(6)	0.4718(5)	0.1777(6)	0.060(4)
N(14)	0.2394(5)	0.5199(4)	0.1320(4)	0.042(2)
H(N14)	0.2667	0.5184	0.0604	0.29(8)
C(M15)	0.1428(6)	0.4642(5)	0.1329(5)	0.059(3)
C(M16)	0.1284(6)	0.4477(5)	0.2369(5)	0.045(3)
O(M21)	0.2533(4)	0.5479(3)	0.6534(3)	0.042(2)
C(M22)	0.1551(6)	0.4949(5)	0.6258(5)	0.039(3)
C(M23)	0.1468(5)	0.4676(4)	0.5212(4)	0.034(3)
N(24)	0.2475(4)	0.4162(3)	0.5091(4)	0.029(2)
H(N24)	0.2433	0.4019	0.4449	0.04(2)
C(M25)	0.3478(5)	0.4705(4)	0.5381(5)	0.034(2)
C(M26)	0.3513(6)	0.4988(5)	0.6422(5)	0.041(3)
7[**3**·morpholine (1 : 1)]				
C(1a)	0.6405(2)	0.6635(2)	0.7317(1)	0.0216(5)
C(1)	0.7548(2)	0.6201(2)	0.7823(1)	0.0274(6)
C(2)	0.8652(2)	0.5909(2)	0.7212(2)	0.0329(7)
C(3)	0.8598(2)	0.6048(2)	0.6120(2)	0.0331(7)
C(4)	0.7466(2)	0.6507(2)	0.5622(1)	0.0285(6)
C(4a)	0.6368(2)	0.6808(2)	0.6229(1)	0.0223(5)
C(5a)	0.5049(2)	0.7298(2)	0.5929(1)	0.0232(5)
C(5)	0.4567(2)	0.7683(2)	0.4982(1)	0.0325(7)
C(6)	0.3272(2)	0.8135(2)	0.4927(2)	0.0388(8)
C(7)	0.2470(2)	0.8197(2)	0.5793(2)	0.0365(7)
C(8)	0.2944(2)	0.7801(2)	0.6740(2)	0.0295(6)
C(8a)	0.4239(2)	0.7364(2)	0.6802(1)	0.0221(5)
C(9)	0.5026(2)	0.6939(2)	0.7768(1)	0.0219(5)
O(9)	0.5440(1)	0.8100(1)	0.8967(1)	0.0262(4)
H(O9)	0.5783	0.9031	0.8958	0.063(7)
C(10)	0.4012(2)	0.5528(2)	0.7771(1)	0.0248(6)
C(11)	0.3187(2)	0.4391(2)	0.7773(1)	0.0269(6)
C(12)	0.2199(2)	0.3004(2)	0.7761(1)	0.0253(6)
C(13)	0.2557(2)	0.2562(2)	0.8704(2)	0.0309(6)
C(14)	0.1625(2)	0.1202(2)	0.8669(2)	0.0358(7)
C(15)	0.0340(2)	0.0279(2)	0.7705(2)	0.0341(7)
C(16)	−0.0037(2)	0.0718(2)	0.6776(2)	0.0354(7)

a) $U_{\mathrm{eq}}=\frac{1}{3}\sum_i\sum_j U_{ij}\,a_i^*\,a_j^*\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) The H atom positions in general, and the disorder sites in the **1**·thioxane·dioxane (2:2:1) structure (**5**) were not refined (cf. the text).

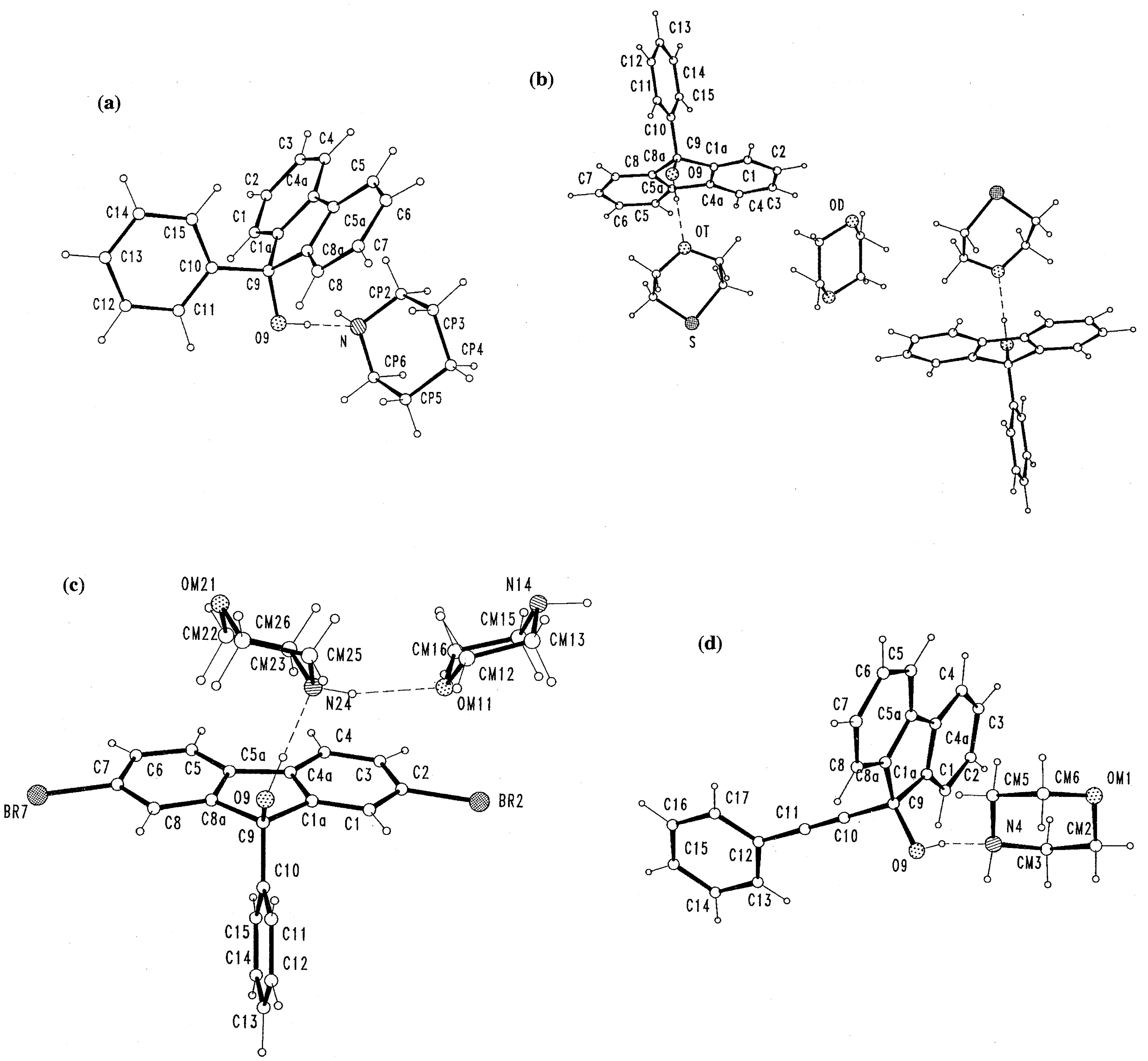


Fig. 1. Perspective views of the stoichiometric units with atomic numbering for compounds (a) **4** [**1**·piperidine (1 : 1)], (b) **5** [**1**·thioxane·dioxane (2 : 2 : 1)], (c) **6** [**2**·morpholine (1 : 2)], and (d) **7** [**3**·morpholine (1 : 1)]. Solid and dashed lines represent covalent and hydrogen bonds, respectively; O atoms are dotted, N atoms are hatched.

pounds **4** and **5**, respectively), 4.2(2) in **2** and 3.49(5)° in **3**. Furthermore, the 9-phenyl substitutent is nearly perpendicular to the fluorene group [the calculated dihedral angles are 91.4(1) and 86.9(2)° for **1** in **4** and **5**, respectively, and 87.9(1)° for **2** in compound **6**] whereas the dihedral angle between the LS planes through the fluorene moiety and the phenyl ring of the phenylethynyl substitutent is only 71.40°. The deviations of the bromine substituents from the fluorene plane in **2** [0.170(1) at C(2) and 0.173(1) Å at C(7)] are, however, slightly larger than those observed earlier in alcoholic or dioxane inclusion compounds of the same host.[8,9)]

The guests, such as piperidine, thioxane, dioxane, and morpholine, are saturated six-membered heterocyclic molecules, occuring in more or less distorted chair forms. The observed bond distances and bond angles generally conform to expected values. Nevertheless, in the case of the ternary **1**·thioxane·dioxane (2 : 2 : 1) complex (**5**) the X-ray analysis revealed both included heterocycles to be disordered at room temperature by flipping between two different chair conformations, independently of each other [cf. Figs. 2(a) and 2(b)]. In consequence of the disorder and of the relatively high thermal mobility (cf. the atomic displacement parameters in Table 9, Supplementary Data), the bond lengths and bond angles in the thioxane and dioxane molecules show wider scatter around the mean values and higher uncertainty than those of the other guests mentioned above. It must be stressed, however, that the structural model of piperidine in **4** and that of morpholine

Table 3. Distances (Å) and Angles (°) of Hydrogen Bonds and of Possible C–H···N/O Interactions in Compounds **4**—**7** (esd's, where given,[a] are in parentheses)

Atoms involved	Symmetry	Distances			Angle
		Donor···Acceptor	D–H	H···A	∠D–H··· A
4 [**1**·piperidine (1 : 1)]					
O(9)–H(O9)··· N	x, y, z	2.769(5)	0.97	1.80	179
5 [**1**·thioxane·dioxane (2 : 2 : 1)]					
O(9)–H(O9)··· O(T1)	x, y, z	2.804(6)	0.93	1.87	180
6 [**2**·morpholine (1 : 2)]					
O(9)–H(O9)··· N(24)	x, y, z	2.758(6)	1.04	1.72	179
N(24)–H(N24)··· O(M11)	x, y, z	3.092(7)	0.92	2.19	166
C(1)–H(1)··· N(14)	$0.5-x$, $-0.5+y$, $0.5-z$	3.315(8)	0.99	2.59	130
C(3)–H(3)··· O(9)	$-0.5+x$, $0.5-y$, $-0.5+z$	3.466(6)	1.00	2.50	163
C(4)–H(4)··· O(M21)	$-x$, $1-y$, $1-z$	3.359(7)	0.98	2.62	132
C(8)–H(8)··· O(M21)	$0.5-x$, $-0.5+y$, $1.5-z$	3.439(7)	1.04	2.63	135
7 [**3**·morpholine (1 : 1)]					
O(9)–H(O9)··· N(4)	x, y, z	2.679(2)	0.90	1.79	168
N(4)–H(N4)··· O(9)	$1-x$, $2-y$, $2-z$	3.017(2)	1.02	2.03	161
C(1)–H(1)··· O(M1)	x, $-1+y$, z	3.411(3)	1.02	2.78	120
C(14)–H(14)··· O(9)	$1-x$, $1-y$, $2-z$	3.395(2)	1.00	2.63	134
C(M2)–H(M21)··· O(M1)	$2-x$, $3-y$, $2-z$	3.370(2)	1.00	2.64	130

a) The H atom positions were not refined (cf. the text).

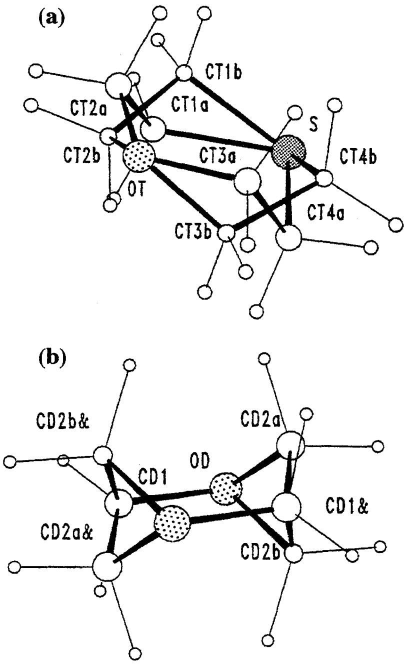


Fig. 2. Perspective views of the disorder models of (a) thioxane, and (b) dioxane guests in the crystal structure of the ternary **1**·thioxane·dioxane (2 : 2 : 1) complex **5**, with the disorder sites labelled as in the text. The 'a' disorder sites have the same atom radii as those with full site occupancy, whereas the 'b' sites, with the slightly lower site occupation factors, are drawn with somewhat reduced radii.

in **6** and **7** were based on data collected at lower temperatures (cf. Table 1).

Packing Relations and Host–Guest Interactions. The present host molecules are all alcohols with somewhat different sizes and shapes. The guests, on the other hand, differ with respect to hetero atoms and, as a consequence of that, also in proton donor/acceptor properties. Despite the resemblance of the host molecules, and the similar shape of the guests, the packing relations in the present crystal structures show a remarkable variety.

Although the piperidine guest, like its alcoholic host, possesses both proton donor and acceptor ability, in the **1**·piperidine complex (**4**) there is only a one-way O–H···N hydrogen bond from the host to the guest, thus yielding a 1 : 1 host–guest associate. These associates are then linked together by ordinary Van der Waals' forces in the crystal so as to form a channel-like arrangement [Fig. 3(a)] in which the aryl parts of the hosts construct the channel around the H-bonded piperidine guests.

The thioxane guest has approximately the same shape and size as piperidine and it is H-bonded to the host alcohol **1** in **5** in the same way. Nevertheless, in the crystal the H-bonded 1 : 1 host–thioxane units include additional guests with only weak Van der Waals' interactions. The additional guests here are not thioxane but dioxane molecules, thus giving rise to a ternary complex with 2 : 2 : 1 host : thioxane : dioxane stoichiometry. It seems likely that the hydrogen bonded 1 : 1 host : thioxane associates create a host framework with cages suitable for the dioxane guests [Fig. 3(b)]. In comparison, host **1** also yields an inclusion compound with dioxane alone,[6] which contains H-bonded 2 : 1 host : guest associates, corresponding to the two-fold H-bond acceptorship of dioxane.[10] In the crystal, similarly to the former

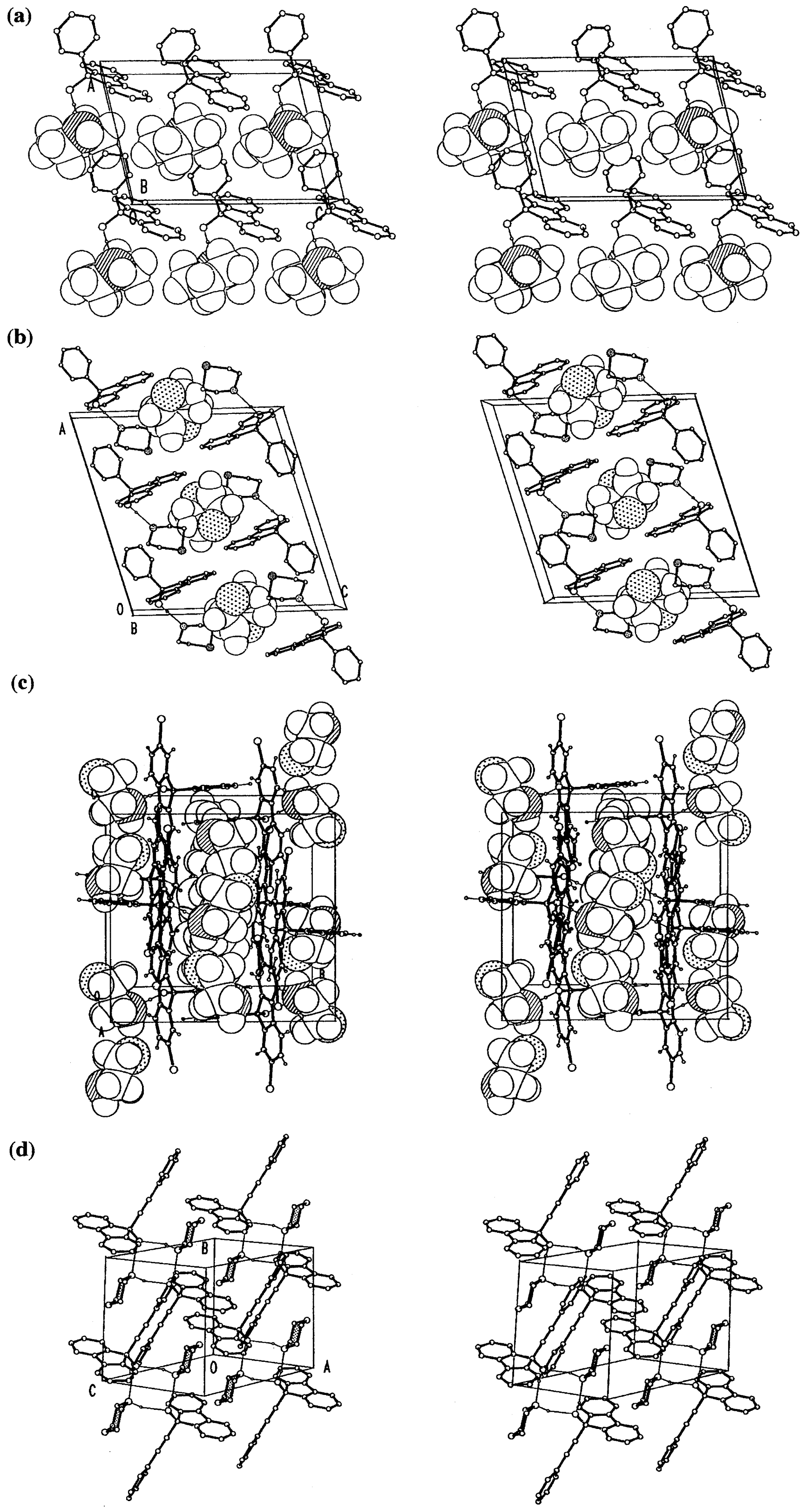


Fig. 3. Stereo packing illustrations of the inclusion compounds (a) **4** [**1**·piperidine (1:1)], (b) **5** [**1**·thioxane·dioxane (2:2:1)], (c) **6** [**2**·morpholine (1:2)], and (d) **7** [**3**·morpholine (1:1)]. The piperidine guests in (a), the dioxane molecules in (b), and the morpholine guests in (c) are represented by space filling models, whereas the host molecules in all illustrations together with the thioxane molecules in (b) and the morpholine guests in (d) are drawn as ball-and-stick models. The carbon-bonded H atoms of the ball-and-stick models are omitted for clarity. Thin lines represent hydrogen bonds.

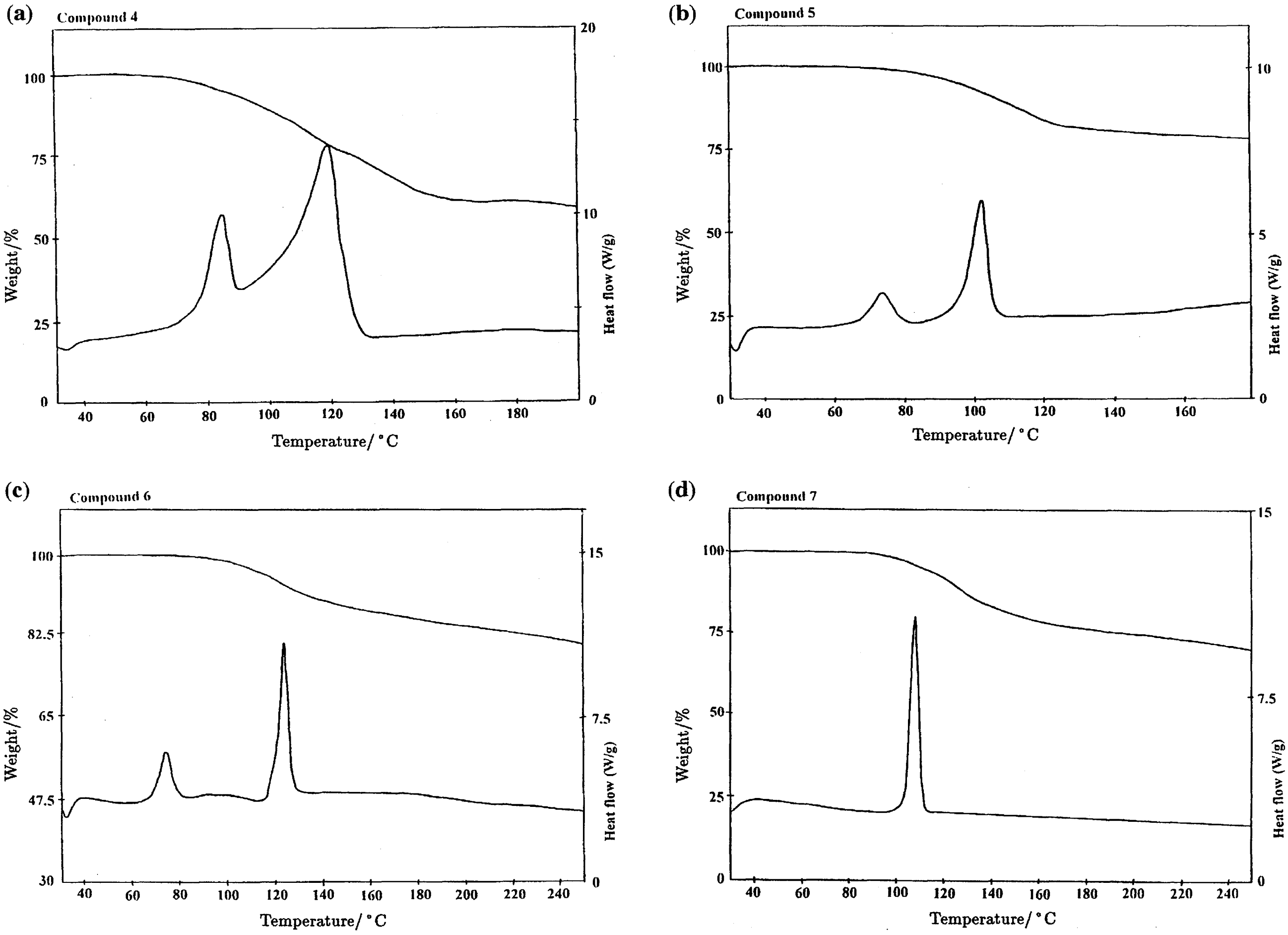


Fig. 4. TG and DSC traces for compounds **4** [**1**•piperidine (1 : 1)] (a), **5** [**1**•thioxane:dioxane (2 : 2 : 1)] (b), **6** [**2**•morpholine (1 : 2)] (c), and **7** [**3**•morpholine (1 : 1)] (d). All traces were measured at a heating rate of 20 °C min^{-1} except Fig. 4(a) TG, which was measured at 40 °C min^{-1}.

case, further dioxane molecules are included, which fill up the voids between the 2 : 1 complexes, thus resulting in 4 : 3 stoichiometry for that compound. At the same time, the molecular packing and mode of complexation in **5** shows pronounced similarity to that of the dioxane inclusion in the 9-phenylxanthen-9-ol host.[8] The H-bonded 1 : 1 host : guest associates in the latter case pack almost analogously with those of the **1**•thioxane (1 : 1) aggregates, thus forming cages around the inversion centres, in which additional dioxane guests are incorporated by weak Van der Waals' forces.

Morpholine possesses two-fold proton acceptorship and a single H-bond donorship through its two heteroatoms. In the 1 : 2 morpholine inclusion of **2** (dibromo derivative of host **1**) (**6**), both guest molecules (M1 and M2) of the crystallographic asymmetric unit are H-bonded, but in different ways. Guest M1 is H-bonded by guest M2 [N(24)H···O(M11)], which in turn is H-bonded also to the host [O(9)H···N(24), Fig. 1(c)]. In this way 1 : 2 host–guest associates are formed. The N(14) in M1 and the O(M21) in M2, however, take no advantage of ordinary H-bonds, only of weak C–H···N/O interactions (cf. Table 3). In the crystal [Fig. 3(c)], the H-bonded 1 : 2 host–guest units are arranged so as to form a layer structure: Layers consisting of flat dibromofluorene moieties alternate with layers of morpholines, the latter ones are regularly interspersed by the 9-phenyl substituents of the hosts. It is seen in the packing illustration [Fig. 3(c)] that the N(14)–H group of morpholine M1 points just in the direction of the center of the adjacent 9-phenyl ring of a host, suggesting a possible interaction of H-bond type from the NH group to the π-electron cloud of the aromatic ring. The observed distances [N(14)···centroid=3.691 and H(N14)···centroid=2.720 Å] are, however, significantly longer than those previously published for this type of interaction.[16—18] Consequently, the probability of considerable attraction between the N(H) group and the π-electron system of the adjacent phenyl ring seems to be non-existent in the present case.

On the contrary, in **7**, the morpholine inclusion of the related 9-phenylethynylfluoren-9-ol molecule (**3**), the host and also the guest act as both H-bond donator and acceptor, yielding closed loops of hydrogen bonds with full H-bond saturation [Fig. 3(d)]. The eight-membered (including the hydrogens) 'pseudo' ring involves two host –OH and two guest $\rangle$NH groups, located around the center of symmetry. Similar H-bond topology, however, with the rings formed by four –OH groups, has recently been found in the crystal structures of several alcoholic inclusions of related singly bridged triarylmethanols,[9] as well as in the solvent free crystal of 9-methylfluoren-9-ol host[16] and in the benzene inclusion of **1**.[6] The occurrence of closed rings of hydrogen bonds in the two latter cases can be regarded as a result of self-association of the 9-substituted fluorenol hosts.[16] This pattern of forming loops via H-bonds also characterizes the recognition of various alcoholic and carboxylic guests, and sometimes also of dimethylformamide (DMF), by numerous carboxylic acidic hosts.[19] It must be remarked, though, that in the case of DMF guest the loop, closed via both $O(H)\cdots O$ and $C(H)\cdots O$ bonds, is weaker due to the reduced proton donor ability of that guest, as compared with alcohols or carboxylic acids.

Accordingly, numerous observations[6,9,16,19, and references therein] support the view that the tendency towards formation of coupled systems of hydrogen bonds with full saturation, such as closed loops, seems to be a common characteristic feature for packing relations involving molecules with strong or relatively strong H-donor/H-acceptorship.[20] It must be stressed, however, that packing in organic crystal structures is always a result of simultaneous satisfaction of the tendency towards maximum formation of hydrogen bonds and the requirement of close packing. Consequently, if the hydrogen bonded complexes are not able to pack with enough density, some of the expected H-bonds will not be formed, and the crystal will be built up of smaller units, linked together by weaker interactions. This seems to be the case in the morpholine inclusion of the dibromofluorenol host **2** (see above), and in the propan-2-ol inclusion of the same host,[9] as well as, e.g., in the guest free crystals of 9-phenyl-, 9-naphthyl-, and 9-biphenylylfluoren-9-ol hosts.[16]

Thermal Analysis. The TG curve for **4** [Fig. 4(a)] showed a continuous decomposition over the range 50—120 °C. Repeating the experiment at 40 °C min^{-1} resolved a step in the weight loss curve at 40.3%. This indicates a host : guest ratio of 1 : 2 which is not observed in the crystal structure. Microanalysis of this compound did not resolve the host : guest ratio. The DSC curve [Fig. 4(a)] shows two peaks, one immediately after the other, with onset temperatures of 78 and 104 °C. The first peak is owing to the release of the piperidine guest, which is immediately followed by the melting of the host. The second endotherm is caused by the boiling of piperidine. This analysis was conformed by visual observation of the decomposition on a Linkam TH600 hot stage set on a Nikon SMZ-10 stereo microscope.

The DSC trace of compound **5**, given in Fig. 4(b), shows two endotherms with onset temperatures of 69 and 98 °C, respectively. We suggest that the first endotherm is caused by the loss of the guest and the second by melting of the remaining host compound (mp 91—94 °C). However, the TG curve [Fig. 4(b)] shows a mass loss of only 21.1%. The C,H,N analysis indicated that the compound had decomposed to 1 : 1 (host : dioxane) with a trace of thioxane (%S=1.8). The TG weight loss expected in this case is 25.4%.

The weight losses observed in the TG curves of compounds **6** and **7** are 28.5 and 25.9%, which correspond well with the expected values of 29.5 and 23.6%, respectively. These curves are shown in Figs. 4(c) and 4(d). The DSC curve of **6** [Fig. 4(c)] shows two endotherms with onset temperatures of 69 (release of guest) and 121 °C. The latter temperature is too low to be attributed to the host's melting (mp of **2** is 163—164 °C), and instead is believed to be the dissolution of the host compound in the high boiling (bp 129 °C) morpholine guest. A similar effect is seen in the DSC curve of **7** [Fig. 4(d)], which has only one endotherm at 105 °C, caused by the release of guest with immediate dissolution of the host. The DSC experiments were repeated at both faster (40 °C min^{-1}) and slower (5 °C min^{-1}) heating rates, but neither helped to resolve the various processes. We have seen similar effects with compounds were the guest is released below its boiling point.[8]

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