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

Aprotic lattice inclusions involving bulky cyclopropano hosts. Crystal structures of inclusion compounds with nitromethane and toluene

Ingeborg Csöregh[a]; Olga Gallardo[a]; Edwin Weber[b]; Manfred Hecker[b]; Andreas Wierig[b]
[a] Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, Stockholm, Sweden [b] Institute für Organische Chemie der Technischen Universität Bergakademie Freiberg, Freiberg/Sachs., Germany

To cite this Article Csöregh, Ingeborg , Gallardo, Olga , Weber, Edwin , Hecker, Manfred and Wierig, Andreas(1994) 'Aprotic lattice inclusions involving bulky cyclopropano hosts. Crystal structures of inclusion compounds with nitromethane and toluene', Supramolecular Chemistry, 3: 4, 319 — 325

To link to this Article: DOI: 10.1080/10610279408034931

URL: http://dx.doi.org/10.1080/10610279408034931

SUPRAMOLECULAR CHEMISTRY, Vol. 3, pp. 319-325
Reprints available directly from the publisher
Photocopying permitted by license only

Aprotic lattice inclusions involving bulky cyclopropano hosts.[#] Crystal structures of inclusion compounds with nitromethane and toluene

INGEBORG CSÖREGH*, OLGA GALLARDO, EDWIN WEBER*†, MANFRED HECKER† and ANDREAS WIERIG†

Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden and †Institute für Organische Chemie der Technischen Universität Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachs., Germany

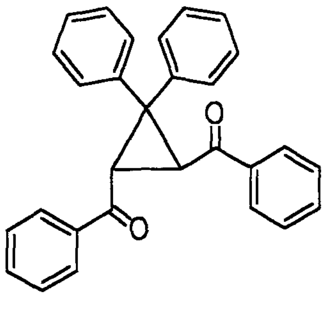
(Received November 1, 1993)

The crystal structures of the inclusion compounds between *trans*-2,3-dibenzoyl-1,1-diphenylcyclopropane (1) and nitromethane, $1 \cdot MeNO_2$ (1:1) (1a), and between *trans*-2,3-dibenzoylspiro[cyclopropane-1,9′-fluorene] (2) and toluene, 2·toluene (1:1) (2a), have been studied by X-ray diffraction. Crystals of 1a show monoclinic symmetry ($P2_1/n$) with $a = 12.9074(8)$, $b = 11.0327(6)$, $c = 17.6178(10)$ Å, $\beta = 98.739(8)°$, $Z = 4$ and $D_c = 1.2416(1)\ \mathrm{g\,cm^{-3}}$; final $R = 0.050$ for 3121 reflections collected at $T = 291(1)$ K. Crystals of 2a are monoclinic ($A2/c$) with $a = 17.3805(7)$, $b = 8.4322(3)$, $c = 18.8641(7)$ Å, $\beta = 95.596(3)°$, $Z = 4$ and $D_c = 1.1892(1)\ \mathrm{g\,cm^{-3}}$; final $R = 0.057$ for 1895 observations collected at $T = 173(1)$ K. In the absence of hydrogen bonds, the molecular packing is governed by rather weak electrostatic intermolecular forces in both crystals, but in different ways. The co-crystals of 1a are held together by dipole-dipole and C(H)...O interactions involving the polar groups of both host and guest, whereas in 2a only the host molecules are joined by C(H)...O interactions. The non-polar toluene guests are trapped in the voids of the host matrix by packing forces only, thus yielding a true lattice type clathrate structure for that compound.

INTRODUCTION

Molecules comprising a three-membered central ring with various substituents are a new family of crystalline hosts.[1] The substituents attached can be nonpolar and bulky (aryl) as well as polar groups capable of forming H bonds.[2] They involve specific interactions and orientations of guest molecules in particular aggregate patterns.[3] In the case of carboxylic groups and alcohol guests, H-bonded helices or closed loops are formed depending on the geometric parameters,[1,4] whereas dimethyl sulphoxide, which is a polar aprotic guest, yields a distinct H-bonded complex.[5] On the other hand, cyclopropano hosts lacking a proton donor function proved to be efficient clathrate formers with aprotic and apolar guests.[1,2] A previous X-ray study,[1] involving the acetonitrile inclusion of a p-methyl-substituted analogue of host compound **1**, revealed a true lattice type clathrate.[6]

In order to learn more about the microstructure of aprotic inclusions of this host type, we determined the crystal structures of **1a** and **2a**, which are 1:1 nitromethane and toluene inclusions of **1** and **2**, respectively. Host **1** is the basic diketone type of cyclopropano host,[1] and **2** is a bridged derivative that has a different geometry of the aromatic nuclei directly attached to the central ring. Selection of these two inclusion species was also prompted by the guest compounds involved. They are very useful solvents,[7]

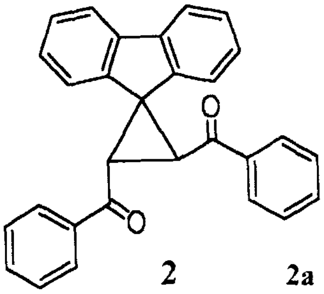


1

1a = **1** · $MeNO_2$ (1 : 1)

[#] Small-Ring Inclusion Hosts. Part 6. For Part 5 of this series see Ref. 4.

* To whom correspondence should be addressed.



2 2a = 2 · Toluene (1 : 1)

but give rise to storage and handling problems,[8] where enclathration may help. Moreover, there is great demand for chemical sensor developments aimed at the detection of organic solvents.[9] Sorptive clathrate formation is very promising in this respect.[10]

EXPERIMENTAL

Sample preparation

The host compounds **1** and **2**, and inclusion compounds **1a** and **2a** were prepared as previously described.[1] Crystals of **1a** and **2a**, suitable for single crystal diffraction studies, were grown by slow evaporation of solutions of the host in the guest solvent. The selected single crystal of **1a**, **1**·nitromethane (1:1), was put in a glass capillary, and that of **2a**, **2**·toluene (1:1), was covered by epoxy glue in order to prevent possible solvent evaporation during the data collection.

X-Ray data collection and processing

Intensity data were collected on a STOE/AED2 diffractometer, equipped with graphite monochromator, using the ω-2θ scan technique. Five and four standard reflections were monitored once every hour for **1a** and **2a**, respectively, for control of the crystal alignment. No systematic variation of intensity was observed for **1a**, whereas the intensities decreased by about 4% during the data collection for **2a**. The collected observed intensities were corrected for background, decay, Lorentz and polarization effects, but the rather low absorption effects (*cf.* Table 1) were ignored. The unit cell dimensions were refined against θ values of 69 ($17 < 2\theta < 38°$) and 63 ($31 < 2\theta < 45°$) carefully

Table 1 Crystal data and selected details of the data reduction and structure refinement calculations

Compound	*1a*	*2a*
Formula	$C_{29}H_{22}O_2{\cdot}CH_3NO_2$	$C_{29}H_{20}O_2{\cdot}C_7H_8$
Formula weight	463.53	492.62
Space group	$P2_1/n$	$A2/n$[a]
Cell dimensions		
a, Å	12.9074(8)	17.3805(7)
b, Å	11.0327(6)	8.4322(3)
c, Å	17.6178(10)	18.8641(7)
α, deg.	90.0	90.0
β, deg.	98.739(8)	95.596(3)
γ, deg.	90.0	90.0
V_c, Å^3	2479.7(3)	2751.5(2)
Z	4	4
$F(000)$	976	1040
D_c, g cm^{-3}	1.2416(1)	1.1892(1)
Radiation/λ, Å	Mo$K\alpha$/0.71069	Mo$K\alpha$/0.71069
μ, cm^{-1}	0.77	0.67
Temperature, K	291(1)	173(1)
Approximate crystal size, mm	0.55 × 0.49 × 0.70	0.30 × 0.53 × 0.49
No. of collected reflections	9714	4028
θ limit, deg.	32.5	30
Range of h, k, l	$0 \Rightarrow 19, 0 \Rightarrow 16, -26 \Rightarrow 26$	$-24 \Rightarrow 24, 0 \Rightarrow 11, 0 \Rightarrow 26$
No. of unique non-zero reflections	7214	3455
No. of significantly observed reflections	3121	1895
Criterion of significance	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$
No. of refined variables	341	196
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.050	0.057
$wR = [\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.065	0.072
wR_{tot}	0.070	0.075
Final $\Delta\rho_{max}/\Delta\rho_{min}$, e$^-$Å^{-3}	0.28/−0.24	0.48/−0.69
Weighting: $w = [\sigma^2(F) + \mathbf{g}{\cdot}F^2]^{-1}$		
with $\mathbf{g} =$	0.00020	0.00027

[a] $A2/n$ is the same space group as $C2/c$ but with a different choice of unit cell.

centred reflections for **1a** and **2a**, respectively. Crystal data and further experimental details are given in Table 1.

Structure analysis and refinement

The structures were solved by application of direct methods,[11] and refined by full-matrix least-squares calculations based on $|F|$.[12] The crystallographic asymmetric unit of the toluene inclusion compound, **2a**, contains one half of the host and one half of the guest molecule. The host molecule exhibits C_2 molecular symmetry, which perfectly coincides with the crystallographic two-fold rotor. The toluene guest, on the other hand, is located around the centre of symmetry, but possesses no inversion symmetry. Nevertheless, the E-map, based on the direct method calculation,[11] yielded five peaks [labelled as C(T1)... C(T5), *cf.* Fig 2*b*], which together with their inversion related equivalents formed an approximate skeleton of two centrosymmetrically related toluene molecules, partly overlapping each other [Fig 2*b*]. Accordingly, the toluene guest has two major disorder locations, related by the centre of symmetry, each having 50% site occupancy due to the space group symmetry requirements. The hydrogen atoms in both structures, except those belonging to the disorder sites of the toluene guest in **2a**, were located from difference electron density ($\Delta\rho$) maps and were held riding on their 'mother' atoms during the subsequent calculations.

In the final stage of the refinements, the non-hydrogen atom positions were refined together with their anisotropic displacement parameters, whereas isotropic vibrational parameters were refined for the hydrogens. No toluene H atoms were taken into account in the structure factor calculation, and the model of the disordered toluene guest had to be subjected to constrained refinement in order to retain acceptable geometry. Furthermore, seven low-θ reflections with considerably higher F_{calc} than F_{obs}, in all probability due to extinction effects, were excluded from the last refinement calculation for the nitromethane inclusion compound, **1a**. The final R values are shown in Table 1. The wR_{tot} values were calculated for the refined structural models, using all unique non-zero reflections. The atomic scattering factors were taken from the literature.[13] Final fractional atomic coordinates of the non-hydrogen atoms are listed in Table 2. The geometric features were calculated using the PARST program,[14] and the illustrations were drawn with the program PLUTO.[15]

RESULTS AND DISCUSSION

A perspective view of the stoichiometric unit of **1a** is shown in Fig 1, whereas the host **2** and the disorder

Table 2 Fractional atomic coordinates and equivalent isotropic displacement parameters,[a] B_{eq} (Å^2), for the non-hydrogen atoms of **1a** and **2a**

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
1a [**1**·nitromethane (1:1)]				
C(1)	0.3336(2)	0.3338(2)	0.0737(1)	3.64(6)
C(2)	0.4052(2)	0.3324(2)	0.1509(1)	3.88(6)
C(3)	0.3797(2)	0.4510(2)	0.1100(1)	3.82(6)
C(4)	0.3741(2)	0.2855(2)	0.0039(1)	3.78(6)
C(5)	0.3859(2)	0.3595(2)	−0.0580(1)	4.46(6)
C(6)	0.4183(2)	0.3113(3)	−0.1233(1)	5.35(8)
C(7)	0.4382(2)	0.1886(3)	−0.1275(2)	6.19(9)
C(8)	0.4264(2)	0.1141(3)	−0.0659(2)	6.30(9)
C(9)	0.3952(2)	0.1631(2)	−0.0004(2)	5.14(8)
C(10)	0.2185(2)	0.3081(2)	0.0726(1)	3.95(6)
C(11)	0.1847(2)	0.2198(2)	0.1190(2)	5.29(7)
C(12)	0.0786(2)	0.1938(3)	0.1150(2)	6.79(10)
C(13)	0.0064(2)	0.2548(3)	0.0639(2)	6.87(11)
C(14)	0.0381(2)	0.3428(3)	0.0172(2)	6.43(9)
C(15)	0.1450(2)	0.3697(2)	0.0220(2)	5.41(8)
C(16)	0.5145(2)	0.2834(2)	0.1576(1)	4.19(6)
O(16)	0.5781(1)	0.3291(2)	0.1219(1)	5.62(5)
C(17)	0.5427(2)	0.1779(2)	0.2096(1)	4.11(6)
C(18)	0.6481(2)	0.1442(3)	0.2262(1)	5.13(7)
C(19)	0.6770(2)	0.0490(3)	0.2764(2)	5.99(9)
C(20)	0.6035(2)	−0.0134(3)	0.3091(2)	5.83(8)
C(21)	0.4998(2)	0.0174(3)	0.2924(2)	5.78(9)
C(22)	0.4692(2)	0.1124(2)	0.2429(1)	4.86(7)
C(23)	0.3125(2)	0.5382(2)	0.1458(1)	4.22(7)
O(23)	0.2735(2)	0.5086(2)	0.2021(1)	5.93(5)
C(24)	0.2936(2)	0.6598(2)	0.1116(1)	4.13(6)
C(25)	0.3117(2)	0.6881(2)	0.0382(1)	4.61(7)
C(26)	0.2884(2)	0.8026(3)	0.0078(2)	5.35(8)
C(27)	0.2490(2)	0.8895(3)	0.0511(2)	5.72(9)
C(28)	0.2339(3)	0.8649(3)	0.1247(2)	6.96(11)
C(29)	0.2553(2)	0.7504(2)	0.1548(2)	5.99(9)
C(N)	0.8755(5)	0.8500(4)	0.1134(3)	12.08(21)
N	0.8960(2)	0.9608(3)	0.1601(2)	6.53(9)
O(N1)	0.9579(3)	0.9624(3)	0.2156(2)	11.53(11)
O(N2)	0.8437(2)	1.0486(3)	0.1387(2)	11.22(12)
2a [**2**·toluene (1:1)]				
C(1)	0.25	−0.2043(4)	0.75	2.27(8)
C(2)	0.2516(1)	−0.0444(3)	0.7106(1)	2.32(5)
C(3)	0.3238(1)	0.0094(3)	0.6805(1)	2.39(5)
O(3)	0.3803(1)	0.0520(2)	0.7192(1)	2.90(4)
C(4)	0.3239(1)	0.0112(3)	0.6015(1)	2.62(6)
C(5)	0.3826(2)	0.0940(4)	0.5722(1)	3.50(7)
C(6)	0.3851(2)	0.0990(4)	0.4989(2)	4.61(9)
C(7)	0.3296(2)	0.0209(4)	0.4552(2)	4.76(9)
C(8)	0.2710(2)	−0.0613(4)	0.4838(2)	4.66(10)
C(9)	0.2681(2)	−0.0662(3)	0.5567(1)	3.64(8)
C(10)	0.3181(1)	−0.3124(3)	0.7654(1)	2.51(5)
C(11)	0.2917(2)	−0.4700(3)	0.7589(1)	2.87(6)
C(12)	0.3446(2)	−0.5947(3)	0.7702(1)	3.75(8)
C(13)	0.4210(2)	−0.5624(4)	0.7889(2)	4.15(8)
C(14)	0.4463(2)	−0.4077(4)	0.7985(2)	3.75(8)
C(15)	0.3948(1)	−0.2806(3)	0.7871(1)	2.95(6)
C(T1)	0.4548(4)	0.0774(8)	0.9600(6)	13.8(4)
C(T2)	0.4937(7)	0.0335(13)	0.9018(5)	9.7(5)
C(T3)	0.5584(6)	−0.0668(10)	0.9118(5)	13.6(4)
C(T4)	0.5795(11)	−0.1319(22)	0.9785(9)	43(3)
C(T5)	0.5216(6)	−0.0181(12)	0.9684(4)	38(1)

[a] $B_{eq} = \frac{1}{3}\sum a_i^* a_j^* B_{ij} a_i \cdot a_j$

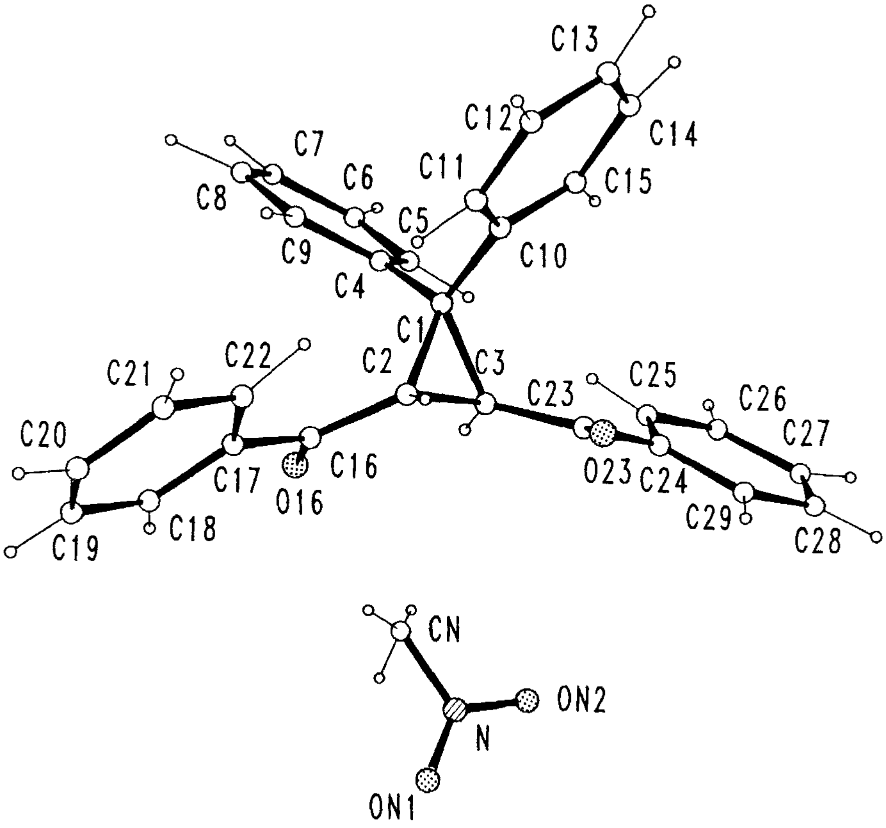


Figure 1 Perspective view of the asymmetric unit of **1a** [**1**·nitro-methane (1:1)], with crystallographic labelling of the atoms. O atoms are dotted, N atom is hatched.

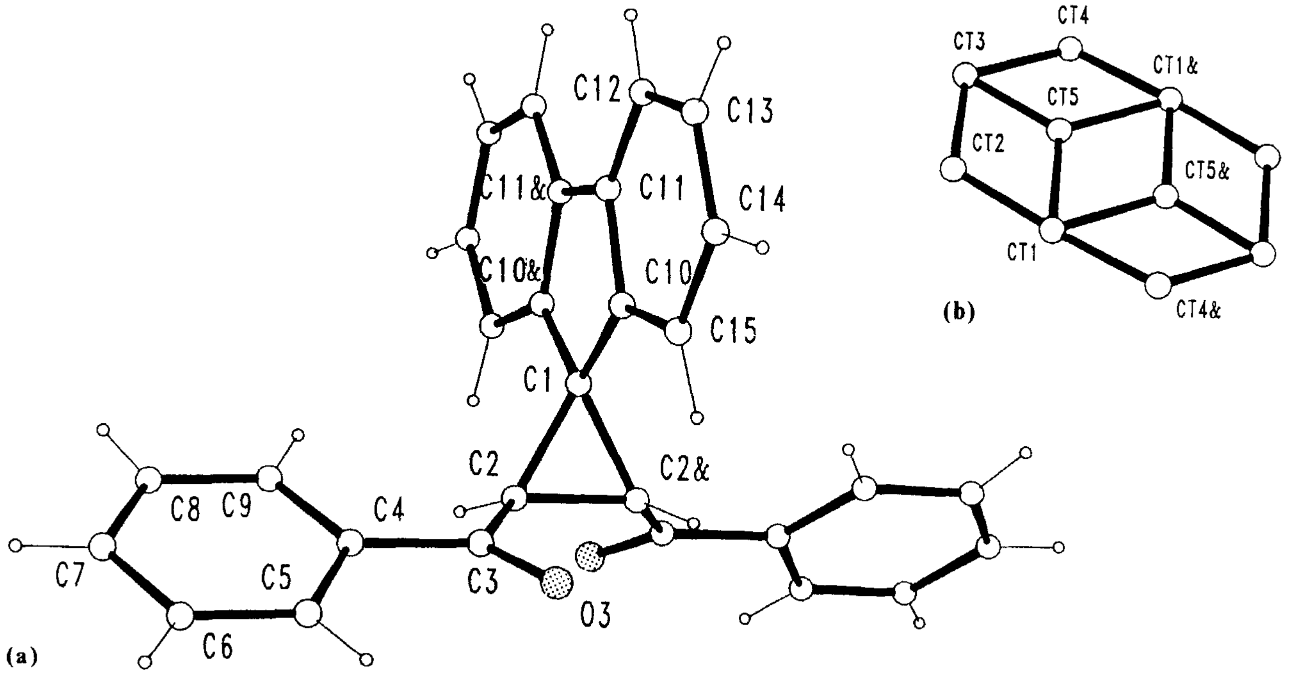


Figure 2 Perspective view of the host **2** (a) and of the disorder model of the toluene guest (b) in **2a** [**2**·toluene (1:1)], with crystallographic labelling of the atoms. O atoms are dotted.

del of the toluene guest in **2a** are depicted in Figs and *b*, respectively. Selected geometric features of host molecules are shown in Table 3 and possible —H...O interactions are listed in Table 4. The stal structures are illustrated in the stereo Figs 3 d 4.

ble 3 Selected conformational features[a] calculated for the host lecules **1** and **2**

st molecule 1	
hedral angle (deg) between the LS planes[b] of	
cyclopropane/$C_4 - C_9$ ring (phenyl-1)	53.6(1)
cyclopropane/$C_{10} - C_{15}$ ring (phenyl-2)	124.6(1)
phenyl-1/phenyl-2	77.5(1)
cyclopropane/$C_{17} - C_{22}$ ring (phenyl-3)	115.6(1)
cyclopropane/$C_{24} - C_{29}$ ring (phenyl-4)	54.4(1)
phenyl-3/phenyl-4	62.8(1)
lected torsion angles (deg)	
C(1)-C(2)-C(16)-O(16)	60.8(3)
C(3)-C(2)-C(16)-O(16)	−10.0(3)
C(1)-C(3)-C(23)-O(23)	64.0(3)
C(2)-C(3)-C(23)-O(23)	−6.1(3)
ost molecule 2	
ihedral angle (deg) between the LS planes[b] of	
cyclopropane/$C_{10} - C_{15}$ ring (phenyl-1)	81.9(1)
cyclopropane/$C_4 - C_9$ ring (phenyl-2)	124.3(1)
phenyl-1/phenyl-2	94.9(1)
cyclopropane/fluorene moiety	82.9(1)
fluorene moiety/$C_4 - C_9$ ring (phenyl-2)	95.5(1)
the two phenyl rings of the fluorene moiety	2.7(1)
elected torsion angles (deg)	
C(1)-C(2)-C(3)-O(3)	−71.0(3)
C(2)[&]-C(2)-C(3)-O(3)	0.6(3)

he calculations were carried out according to Nardelli.[14]
etails of the LS plane calculations are given in Table 10 (supplementary material).
Symmetry related atomic position. Symmetry code: *0.5 − x, y, 1.5 − z*.

Molecular structures

No anomalous values have been observed for the covalent bond distances and bond angles in the host molecules **1** and **2**. Some characteristic mean bond lengths (with the dispersion around the arithmetic average given in angular brackets, when averaged over more than two values) for host **1** are: $C^3_{sp} - C^3_{sp} = 1.518[9]$, $C_{sp^2} - C_{sp^2} = 1.383[9]$, $C_{sp^3} - C_{sp^2} = 1.496[11]$, C=O = 1.220(2) Å; and for host **2**: $C_{sp^3} - C_{sp^3} = 1.518(24)$, $C_{sp^2} - C_{sp^2} = 1.387[11]$, $C_{sp^3} - {}_{sp^2} = 1.496[5]$, C=O = 1.219(3) Å. The observed geometries of the guests show larger uncertainty than those of the hosts, however. At the same time, inspection of the atomic displacement parameters indicates more intense thermal motion for the atoms of the guests than for those of the hosts in both structures. Thus, the wider scatter of the observed bond lengths and bond angles in the nitromethane and the toluene molecules might depend on the lively thermal motion of these guest molecules. Nevertheless, the difference between the two N—O distances in the nitromethane guest [N—O(N1) = 1.165(4), N—O(N2) = 1.208(4) Å] can probably also depend on different crystallographic environments for these atoms (*cf.* discussion of intermolecular interactions). The mean value of the C—C distances in the structural model of the toluene guest is 1.40[3] Å, and the average deviation of the bond angles from 120° is 1[1]°.

The geometry of the semi-rigid host **1** resembles, at least partly, that of the 1,1-diphenylcyclopropane-2,3-*trans*-dicarboxylic acid hosts previously studied by us.[1,5] Accordingly, the dihedral angles between the least-sqaures (LS) planes of the cyclopropane ring and

able 4 Distances (Å) and angles (deg) in possible (C-)H...O(=C/N) interactions. The eds's, where given,[a] are in parentheses

		Distances			*Angles*	
toms involved	*Symmetry*	*C—H*	*C...O*	*H..O*	*<C—H..O*	*<H..O = C/N*
nitromethane (1:1)						
(25)-H(25)..O(16)	*1 − x, 1 − y, −z*	0.99	3.351(3)	2.70	123	155
(26)-H(26)..O(16)	*1 − x, 1 − y, −z*	1.04	3.391(3)	2.73	121	119
(21)-H(21)..O(23)	*0.5 − x, −0.5 + y, 0.5 − z*	1.06	3.545(4)	2.74	132	117
(28)-H(28)..O(23)	*0.5 − x, 0.5 + y, 0.5 − z*	1.00	3.453(4)	2.65	137	150
(12)-H(12)..O(N1)	*−1 + x, −1 + y, z*	1.09	3.596(5)	2.53	163	89
(12)-H(12)..O(N2)	*−1 + x, −1 + y, z*	1.09	3.510(4)	2.81	121	75
(13)-H(13)..O(N2)	*1 − x, 1 − y, z*	1.04	3.487(5)	2.77	126	120
(18)-H(18)..O(N2)	*x, −1 + y, z*	1.07	3.244(4)	2.79	111	137
(19)-H(19)..O(N2)	*x, −1 + y, z*	1.03	3.478(5)	2.98	110	86
(26)-H(26)..O(N2)	*1 − x, 2 − y, −z*	1.04	3.305(4)	2.68	119	158
(27)-H(27)..O(N2)	*1 − x, 2 − y, −z*	1.08	3.444(4)	2.86	114	109
·toluene (1:1)						
(15)-H(15)..O(3)	*x, y, z*	1.01	3.084(3)	2.41	124	106
(12)-H(12)..O(3)	*x, −1 + y, z*	0.96	3.210(3)	2.51	130	98
(14)-H(14)..O(3)	*1 − x, −0.5 − y, 1.5 − z*	1.00	3.298(3)	2.62	125	107

The hydrogen positions are taken from $\Delta\rho$ maps and are not refined.

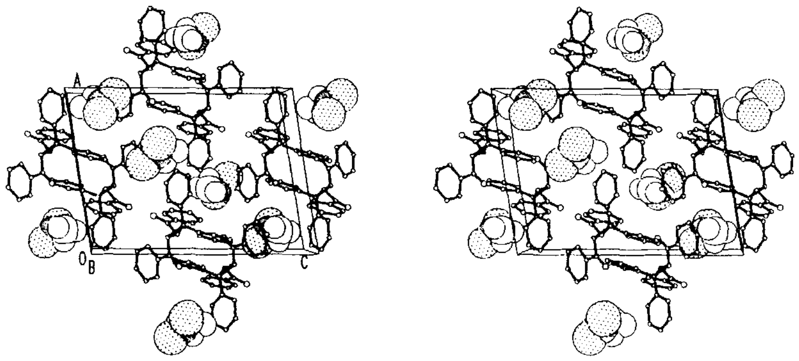


Figure 3 Stereo packing diagram of **1a** [**1**·nitromethane (1:1)]. The hosts were drawn in ball-and-stick style whereas the atoms of the guest are represented with van der Waals' radii. The H atoms of the host are omitted for clarity. O atoms of the nitromethane guests are dotted, N atoms are hatched.

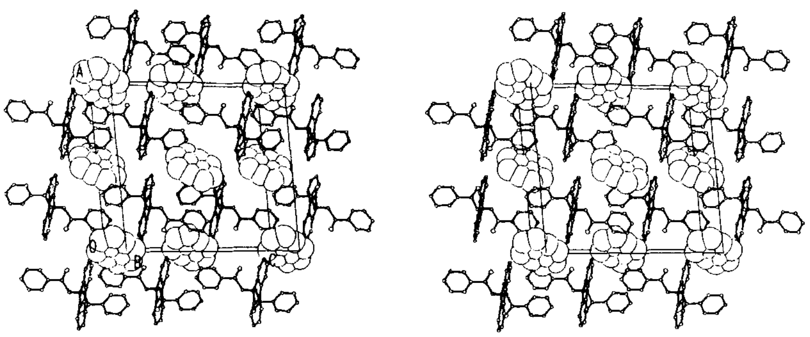


Figure 4 Stereo packing diagram of **2a** [**2**·toluene (1:1)]. The disorder model of the carbon skeleton of the toluene guest is drawn with van der Waals' radii, whereas the host molecules, excluding the H atoms, are represented in ball-and-stick style.

its phenyl substituents as well as between the two phenyl planes (Table 3) are in the range of the corresponding ones observed in the related dicarboxylic acid hosts.[5] Molecule **2** is more rigid than **1** because of the bridge between the two phenyl substituents of the cyclopropane ring. The 13 atoms of the fluorene moiety make up a plane, within 0.092 Å, which forms a nearly right angle with the cyclopropane plane. This conformation is possibly stabilized by an intramolecular C—H...O interaction between the carbonyl O(3) atom and the nearest C—H group [C(15)—H(15)] in both halves of the molecule (*cf.* Table 4). The conformations of the remaining parts of these two hosts, including the linkage of two carboxybenzyl groups to the cyclopropane ring, are comparable to each other, although host **2** possesses perfect C_2 molecular symmetry, whereas **1** does not.

Packing relations and host-guest interactions

In **1a**, **1**·nitromethane (1:1), both the host and the guest contain polar groups but have no pronounced proton donor ability. The shortest intermolecular approach between non-hydrogen atoms was observed between the carbonyl C(16) atom of the host and the nitro oxygen O(N1) of the guest [$C(16)..O(N1)_{1.5-x,-0.5+y,0.5-z} = 2.962(4)$ Å] indicating a dipole-dipole interaction of the type discussed by Bolton[16,17] and by Silverman *et al.*,[18] which usually occurs in organic crystals containing a number of carbonyl groups.[17-19] This interaction also leads to a relatively short non-bonded contact between C(2) and O(N1) [$C(2)..O(N1)_{1.5-x,-0.5+y,0.5-z} = 3.074(4)$ Å]. The other host carbonyl group [C(23) = O] and the second nitro oxygen [O(N2)] of the guest, however, take no advantage of this type of interaction. Nevertheless, inspection of the intermolecular distances indicates several possible C—H... O contacts involving all four oxygens of the structure. The C—H...O contact, like the 'ordinary' O(H)...O and N(H)...O hydrogen bonds, is a largely electrostatic, attractive interaction with long-range character.[20] The length of the bond is variable but depends on the acid character of the C—H group.[20] Thus, the C—H... O interactions, listed in Table 4, suggest only weak attraction forces because of the low acidicity of the phenyl H atoms. Accordingly, besides the dipole-dipole interaction mentioned above, the packing in the **1a** inclusion crystal seems to be stabilized by numerous weak intermolecular interactions of an electrostatic nature, involving both the host and the guest molecules.

In **2a**, **2**·toluene (1:1), only the host has polar groups. Therefore, the host molecules pack in a way which allows them to form C—H...O bonds besides the ordinary van der Waals' interactions (Table 4). The created host framework is stabilized by the toluene guest, which fills up the free space between the host molecules without any perceptible interaction with them. The void located around the centre of symmetry in the crystal is large enough to allow disorder for the loosely bounded guest molecule.

In summary, the presented investigations clearly demonstrate the importance of rather weak intermolecular interactions in co-crystalline structures. In the absence of 'ordinary' hydrogen bonds, weaker electrostatic forces govern the packing of the molecules *via* dipole-dipole and/or C—H...O interactions, and they thus determine the architecture of crystalline heteromolecular complexes.

ACKNOWLEDGEMENTS

Financial support from the Swedish Natural Science Research Council (NFR) to I.C., and the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie to E.W. is gratefully acknowledged.

REFERENCES

1 Weber, E.; Hecker, M.; Csöregh, I.; Czugler, M. *J. Am. Chem. Soc.* **1989**, *111*, 7866.
2 Weber, E.; Hecker, M.; Csöregh, I.; Czugler, M. *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 165.
3 Weber, E. *J. Mol. Graphics* **1989**, *7*, 12.
4 Csöregh, I.; Gallardo, O.; Weber, E.; Hecker, M.; Wierig, A. *J. Chem. Soc. Perkin Trans. 2* **1992**, 1939.
5 Csöregh, I.; Gallardo, O.; Weber, E.; Hecker, M.; Wierig, A. *J. Incl. Phenom.* **1992**, *14*, 131.
6 (a) Weber, E. in *Molecular Inclusion and Molecular Recognition—Clathrates I* (Weber, E., ed.), *Topics in Current Chemistry* **1987**, vol. 140, Springer-Verlag, Berlin-Heidelberg, p. 1. (b) Weber, E.; in *Inclusion Compounds* **1991**, *4*, (Key Organic Heat Systems), (Atwood, J.L., Davies, J.E.D. and MacNicol, D.D., eds.), Oxford University Press, Oxford-New York, p. 188.
7 Reichardt, C. *Solvent and Solvent Effects in Organic Chemistry* **1988**, 2nd edn., VCH Verlagsgesellschaft, Weinheim.
8 Koch, R. *Umweltchemikalien*, VCH Verlagsgesellschaft, Weinheim, **1989**.
9 Cammann, K.; Lemke, U.; Rohen, A.; Sander, J.; Wilken, H.; Winter, B. *Angew. Chem.* **1991**, *103*, 519; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 516.
10 (a) Ehlen, A.; Wimmer, C.; Weber, E.; Bargon, J. *Angew. Chem.* **1993**, *105*, 116; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 110. (b) Freestone, N.P.; *Chem. Ind. (London)* **1993**, 333.
11 Sheldrick, G.M. *Acta Crystallogr.* **1990**, *A46*, 467.
12 Sheldrick, G.M. *SHELX 76. Program for Crystal Structure Determination*, University of Cambridge, England, **1976**.
13 *International Tables for X-Ray Crystallography*, The Kynoch Press, Birmingham, England, **1974**, *IV*. [Distributed by Kluwer Academic Publishers, Dordrecht and Boston.]
14 Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.
15 Motherwell, S.; Clegg, B. *PLUTO, Program for Plotting Molecular and Crystal Structures*, University of Cambridge, England, **1978**.
16 Bolton, W. *Nature* **1964**, 987.
17 Bolton, W. *Acta Crystallogr.* **1964**, *17*, 147.
18 Silverman, J.; Krukonis, A.P.; Yannoni, F. *Cryst. Struc. Commun.* **1974**, *3*, 261.
19 Weber, E.; Finge, S.; Csöregh, I. *J. Org. Chem.* **1991**, *56*, 7281.
20 Desiraju, G.R. *Acc. Chem. Res.* **1991**, *24*, 290.