LETTER

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Conglomerate and racemate formation of 2,3-bis-fluoren-9-ylidenesuccinic acid by inclusion complexation with achiral guest molecules

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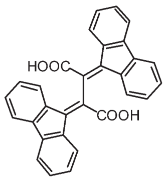
The title new host compound (1) forms conglomerates or racemates by inclusion complexation with achiral guest compounds, although 1 itself forms only a racemate.

Racemic organic compounds form either homochiral or heterochiral crystals. The homochiral crystals (conglomerates) contain pure *R* or *S* enantiomers, while the heterochiral crystals (racemates) contain equal numbers of *R* and *S* enantiomers. Generally, racemate formation is more frequent than conglomerate formation.[1] The problem of homochiral and heterochiral aggregation in crystals has received considerable attention in recent years not only due to its application to the simplest resolution method[2] but also due to the prebiotic origin of chirality.[3] Homochiral crystals are also promising for use in optoelectronics and other future technologies based on materials' properties. Earlier, we reported conglomerate and racemate formation of *rac*-7-bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]octa-2,4,7-trien-6-one by inclusion complexation with achiral guest compounds[2c] and, more recently, chiral inclusion crystallization of achiral tetra(*p*-bromophenyl)ethylene under gas–solid reaction conditions.[4] Here, we report a new example of guest-dependent conglomerate and racemate formation of a novel host compound (±)-**1**, which exists in the chiral forms *P*-**1** and *M*-**1** due to restricted rotation around the central C–C bond.



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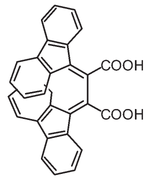
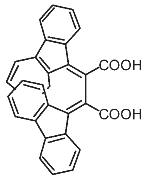


P-**1**



M-**1**

Compound **1** was prepared by condensation of fluorenone and succinic acid according to the method reported by Goldschmidt *et. al.*[5] Compound **1** was found to form stable inclusion complex crystals with a wide variety of guest compounds (Table 1), although Goldschmidt *et. al.* mentioned nothing about the inclusion ability of **1** in their paper. The inclusion crystals were prepared by recrystallization of **1** from neat guest solvents and characterized by thermogravimetric analysis (TGA) to determine the host-guest ratios. The host **1** showed high inclusion abilities for a wide variety of guest compounds containing functional groups such as alcohol, ketone, ester, ether, amide and sulfoxide, as shown in Table 1. The color of the crystals changes from red (guest-free) to pale yellow or yellow upon complexation with guest compounds. (Fig. 1) Interestingly, **1** was found to form chiral inclusion crystals (conglomerate) with some guest compounds. For example, **1** was recrystallized from acetone to give chiral 1:1 inclusion crystals. The chirality of the crystal was easily detected by measurement of the CD spectrum as its Nujol mull. For example, one piece of the 1:1 acetone inclusion crystals (10 mm × 4 mm × 2 mm) showed a (+)-Cotton effect and the other piece of crystal showed a (−)-Cotton effect. Thus, the optical resolution of **1** was achieved by the manual sorting of enantiomorph crystals or seeding the chiral crystal during the crystallization. Goldschmidt *et al.*[5] also reported a negative result for the attempted optical resolution of **1** by salt formation with brucine, due to its easy racemization in solution. Thus, this is the first example of the isolation of a pure enantiomer of **1** by conglomerate formation with acetone.

Table 1 Inclusion complexes of **1**

Guest	H:G[a]	Color	Crystal
None	1:0	Red	Racemate
Ethanol	1:1	Pale yellow	Racemate
Acetone	1:1	Pale yellow	Conglomerate
2-Butanone	1:1	Pale yellow	Racemate
Cyclopentanone	1:2	Yellow	Conglomerate
Cyclohexanone	1:1	Yellow	Racemate
Ethyl acetate	1:1	Pale yellow	Racemate
Tetrahydrofuran	1:2	Pale yellow	Racemate
Tetrahydropyran	1:1	Pale yellow	Conglomerate
Dioxane	1:1	Pale yellow	Racemate
DMF	1:1	Pale yellow	Racemate
DMSO	1:1	Pale yellow	Racemate

[a] Host:guest ratios were determined by TGA.

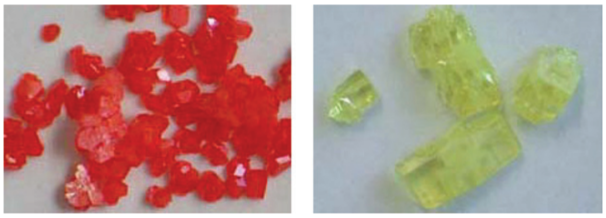


Fig. 1 Photographs of racemate crystals of free host **1** (left) and conglomerate crystals of the 1:1 inclusion complex of **1** with acetone (right).

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Similarly, **1** formed a conglomerate with cyclopentanone and tetrahydropyran, although **1** formed a racemate with EtOH, AcOEt, cyclohexanone, DMSO, and DMF.

The X-ray structures of the host **1** and its inclusion complexes **1**·acetone and **1**·AcOEt were determined. The host crystallizes in a centrosymmetric space group and therefore contains both the *M*-**1** and *P*-**1** forms, with the space group also requiring each molecule to be located on a twofold axis (Fig. 2). In the crystal, each –COOH group is hydrogen-bonded to a –COOH group of a centrosymmetrically related molecule, forming a characteristic $R_2^2(8)$ ring system with the unique hydrogen bond O17–H···O16^i having an O···O separation of 2.741(1) Å and an angle subtended at H of 177(1)°. Polymeric columns of hydrogen-bonded molecules extend parallel to the crystal *c* axis. A view of the molecule parallel to the central C–C bond [1.505(2) Å] shows that the fluorenyl ring planes are nearly orthogonal and in this conformation the C15–C14–C14^{ii}–C15^{ii} torsion angle is 106.1(1)° ($ii = 1-x,\ y,\ \frac{1}{2}-z$).

Fig. 3 shows the asymmetric unit in **1**·acetone, which crystallizes in the chiral space group $P2_12_12_1$. The O17–H···O38 hydrogen bond [O···O 2.620(4) Å, angle subtended at H 168.2(2)°)] links host and guest. Host-guest units associate by hydrogen bonding in spiral arrays parallel to the crystal *a* axis *via* the unique O21–H···O16^i hydrogen bond [O···O 2.717(3) Å, angle at H 163.9(2)°, $i = 1/2+x,\ 3/2-y,\ 1-z$]. In this structure, the host molecule adopts a significantly different conformation from that in the pure host crystal, the C15–C14–C18–C19 torsion angle being 65.4(3)°. Comparison of the ring-stacking modes in the crystals of **1** and **1**·acetone reveals a similar extent of π-π interaction, namely one significantly short interaction in each case with ring centroid-centroid distances of 3.803 and 4.008 Å, respectively.

The asymmetric unit in **1**·AcOEt is shown in Fig. 4. The O21–H···O39 hydrogen bond [O···O 2.642(1) Å, angle subtended at H 166(2)°] links host and guest and the host conformation is similar to that in **1**·acetone, with a C15–C14–C18–C19 torsion angle of 77.1(1)° for the molecule shown. This crystal contains both *M*-**1** and *P*-**1** forms of the host molecule owing to the centrosymmetric space group. Host-guest units are linked *via* the screw axis parallel to *b* in an analogous fashion to those in **1**·acetone, the unique hydrogen bond being O17–H···O20^{ii} [O···O 2.709(1) Å, angle subtended at H 173(2)°, $ii = 1-x,\ -1/2+y,\ 3/2-z$]. The crystal structure of **1**·AcOEt is thus based on spiral arrays that are structurally analogous to those in the **1**·acetone, but the former crystal contains spirals constructed from host molecules *M*-**1** and spirals constructed from host molecules *P*-**1** in equal numbers, whereas the latter crystal contains homochiral spiral arrays. No π-π interactions with ring centroid-centroid distance of less than 4.5 Å were observed in **1**·AcOEt.

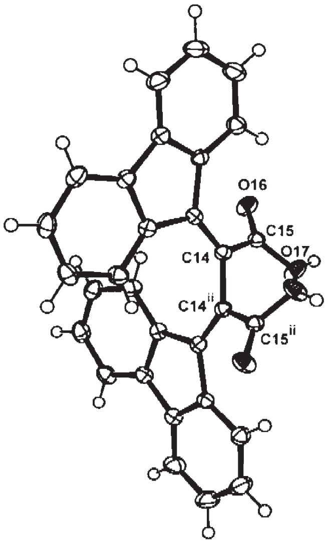

Fig. 2 Molecular conformation of the host **1**. Displacement ellipsoids are shown at 50% probability.

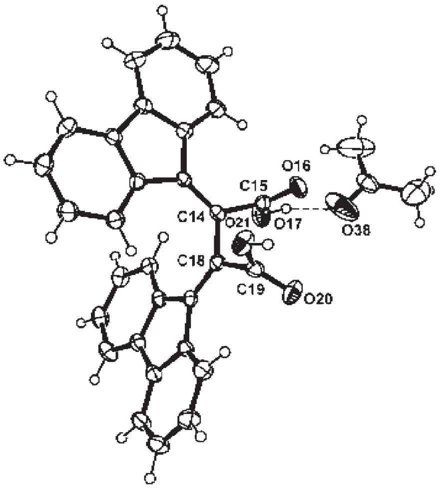

Fig. 3 The asymmetric unit in **1**·acetone showing the hydrogen bond between host and guest. Displacement ellipsoids are shown at 50% probability.

The color change of the crystals from red for **1** to pale yellow upon inclusion complexation with acetone and ethyl acetate reflect its conformation in the crystals. The torsion angles about the central =C–C= bonds are 106.1(1)° in guest-free **1**, 65.4(3)° in **1**·acetone and 77.1(1)° in **1**·AcOEt, respectively. The degree of electron delocalization is thus expected to be smaller in **1**·acetone and **1**·AcOEt than in guest-free **1**. This is a simple method for determining whether or not inclusion complexation occurred and can be applied to sensor materials, relying on its color change upon host-guest complexation.

In conclusion, we have found guest-dependent conglomerate and racemate formation of 2,3-bisfluoren-9-ylidenesuccinic acid (**1**) by inclusion crystallization with achiral guest compounds. The design of a variety of similar systems is under investigation.

Experimental

The guest-free crystal of **1** was prepared by recrystallization of (±)-**1**[4] from an MeCN solution. The host-guest inclusion

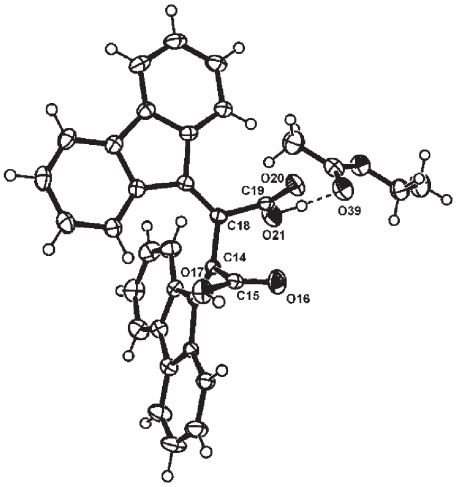

Fig. 4 The asymmetric unit in **1**·AcOEt showing the hydrogen bond between host and guest. Displacement ellipsoids are shown at 50% probability.

crystals were prepared by recrystallization of host compound **1** from the neat guest (solvent) solution and the host-guest ratios were determined by thermogravimetric analysis (TGA).

X-Ray structures

Intensity data were collected on a Nonius Kappa CCD diffractometer[6] using Mo-Kα radiation ($\lambda = 0.71073$ Å) with the crystals cooled to $T = -70\,°C$ in a stream of nitrogen vapor. Cell refinement and data reduction were performed with DENZO-SMN.6[7] Structures were solved with SHELXS-86[8] and refined on F^2 with SHELXL-97.[9]†

Crystal data for 1. $C_{30}H_{18}O_4$, crystal size $0.20 \times 0.20 \times 0.30$ mm^3, $M = 442.47$, orthorhombic, space group $Pbcn$, $a = 15.8893(3)$, $b = 9.7361(2)$, $c = 13.3280(2)$ Å, $U = 2061.84(7)$ Å^3, $Z = 4$, $D_c = 1.425$ g cm^{-3}, μ(Mo-Kα) = 0.094 mm^{-1}. Of 14 383 integrated reflections, 2435 were unique ($R_{int} = 0.030$) and were used in all calculations. Final $wR_2 = 0.0949$ (all data), R_1 [$F^2 > 2\sigma(F^2)$] = 0.0376, and goodness-of-fit on F^2, $S = 1.043$ (CCDC 210132).

Crystal data for 1·acetone. $C_{30}H_{18}O_4{\cdot}C_3H_6O$, crystal size $0.12 \times 0.12 \times 0.20$ mm^3, $M = 500.55$, orthorhombic, space group $P2_12_12_1$, $a = 9.9117(2)$, $b = 14.1651(3)$, $c = 18.1568(5)$ Å, $U = 2549.2(1)$ Å^3, $Z = 4$, $D_c = 1.304$ g cm^{-3}, μ(Mo-Kα) = 0.087 mm^{-1}. Of 11 267 integrated reflections, 5507 were unique ($R_{int} = 0.040$) and were used in all calculations. Final $wR_2 = 0.1392$ (all data), R_1 [$F^2 > 2\sigma(F^2)$] = 0.0545, and goodness-of-fit on F^2, $S = 1.030$ (CCDC 210133).

Crystal data for 1·AcOEt. $C_{30}H_{18}O_4{\cdot}C_4H_8O_2$, crystal size $0.20 \times 0.20 \times 0.20$ mm^3, $M = 530.55$, monoclinic, space group $P2_1/c$, $a = 12.1730(1)$, $b = 12.3379(2)$, $c = 17.7792(2)$ Å, $\beta = 94.282(1)°$, $U = 2662.79(6)$ Å^3, $Z = 4$, $D_c = 1.323$ g cm^{-3}, μ(Mo-Kα) = 0.090 mm^{-1}. Of 12 170 integrated reflections, 6306 were unique ($R_{int} = 0.022$) and were used in all calculations. Final $wR_2 = 0.0978$ (all data), R_1 [$F^2 > 2\sigma(F^2)$] = 0.0390, and goodness-of-fit on F^2, $S = 1.037$ (CCDC 212455).

Acknowledgements

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† CCDC reference numbers 210132, 210133 and 212455. See http://www.rsc.org/suppdata/nj/b3/b314192f/ for crystallographic data in .cif or other electronic format.