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Acta Cryst. (1997). C**53**, 1892–1895

Solid Inclusion Compounds of Chiral Roof-Shaped Diamide Hosts

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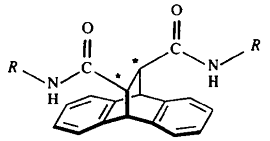
(*Received 11 March 1997; accepted 21 August 1997*)

Abstract

The hydrogen-bond-directed inclusion properties of two related enantiomerically pure diamide-type hosts have been investigated. The (11*S*,12*S*)-*trans-N,N'*-dicyclohexyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide host, $C_{30}H_{36}N_2O_2$, (I), formed a quaternary compound when crystallized from a dimethylformamide solution and also includes cyclohexylamine and HCl as guests [(I).DMF.cyclohexylamine.HCl 1:1:1:1], $C_{30}H_{36}N_2O_2.C_6H_{14}N^+.C_3H_7NO.Cl^-$, (I*a*). Three-component crystals were grown from a dimethyl sulphoxide solution of the (11*S*,12*S*)-*trans-N,N'*-di-*tert*-butyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide host, $C_{26}H_{32}N_2O_2$, (II), also containing H_2O as a guest [(II).DMSO.H_2O 1:2:1], $C_{26}H_{32}N_2O_2.2C_2H_6OS.H_2O$, (II*b*). Infinite supramolecular frameworks in both compounds are created involving host and guest molecules in a way that not only host–guest, but guest–guest hydrogen-bonding interactions are observed. However, no direct host–host hydrogen bonds were formed between the chiral diamide molecules (I) or (II).

Comment

Amide molecules usually use their self-complementary hydrogen-bonding functionality to form cyclic dimers or endless chains in crystals (Etter, 1990; MacDonald & Whitesides, 1994). Indeed, hydrogen-bond interactions were observed between closely related racemic diamide hosts (Csöregh, Finge & Weber, 1991) also in the presence of guests with pronounced proton donor and acceptor abilities (*e.g.* methanol and propionic acid).



(I) *R* = cyclohexyl (11*S*,12*S*)
(II) *R* = *tert*-butyl (11*S*,12*S*)
(I*a*) = (I).Cyclohexylamine.DMF.HCl (1:1:1:1)
(II*b*) = (II).DMSO.H_2O (1:2:1)

Contrary to related racemic hosts, the resolved (11*S*,12*S*) chiral diamide hosts (I) and (II) do not form direct host–host hydrogen-bond interactions in the present inclusion compound. Instead, the host functionalities are hydrogen bonded to complementary groups belonging to the guest molecules. Thus, the amide –NH functions of different host molecules in (I*a*) are linked *via* the chloride anion, yielding N(H)···Cl···(H)N interactions, whereas the C═O groups are involved in hydrogen bonding with the cyclohexylamine guest, forming O···(H)N(H)···O connections. The crystal packing is further stabilized by an inter-guest hydrogen bond from the positively charged cyclohexylamine N atom to the Cl^- anion. The infinite supramolecular network thus created (Fig. 3) can be seen to be a result of the tendency to incorporate as many acceptor sites as possible into the hydrogen-bonding scheme (Etter, 1982). The crystalline architecture of (I*a*) is in the form of parallel strings extending along the *a* axis and involving three components of the quaternary compound (Table 1). The fourth component, DMF, though known to be a good proton acceptor (Weber, 1989), is outside the hydrogen-bonding scheme. The proton-acceptor sites are in excess in (I*a*), and in such circumstances the best donor and the best acceptor preferentially form hydrogen bonds to one another (Etter, 1991). Thus, the DMF guest, competing with the host amide C═O groups and the Cl^- ion in (I*a*), is not able to participate in a hydrogen-bonding interaction. The DMF molecules are even found not to be involved in the weak C—H···O interactions and are retained in the voids of the crystal structure only by weak lattice forces, exhibiting rather high mobility [mean $U_{\rm iso}$ of the non-H atoms is 0.22 (2) Å^2]. The hydrogen-bonding pattern in this inclusion compound consists of two 11-membered rings. This corresponds to graph set $R^2_3(11)R^2_3(11)$ (Bernstein *et al.*, 1995).

In (II*b*), on the other hand, each host–NH group is involved in an N(H)···O(═S) interaction with a DMSO guest, known to be an eminent proton accep-

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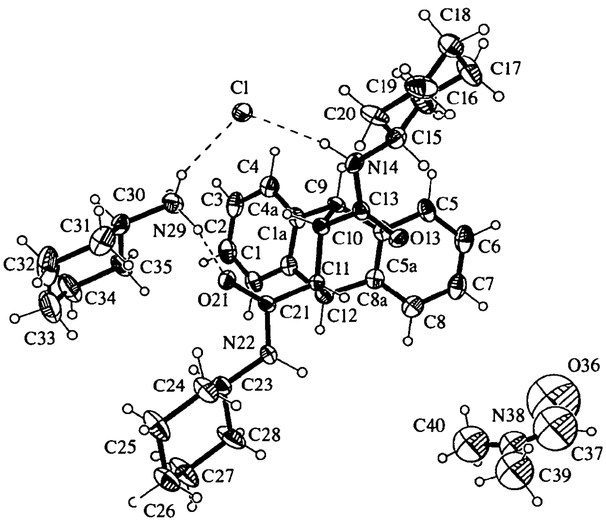

Fig 1. Perspective view of (I*a*) [(I).cyclohexylamine.HCl.DMF (1:1:1:1)] showing 30% probability displacement ellipsoids for the non-H atoms. H atoms are drawn as spheres of arbitrary diameter. Hydrogen bonds are shown as dashed lines.

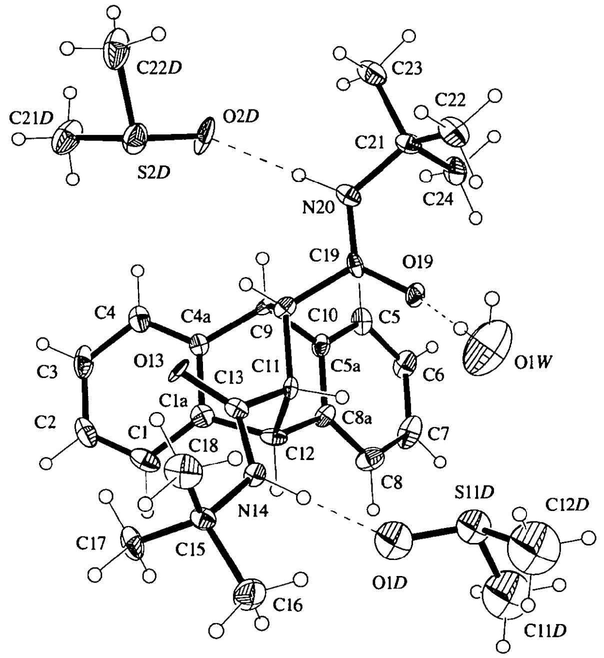

Fig. 2. Perspective view of (II*b*) [(II).DMSO.H_2O (1:2:1)] showing 30% probability displacement ellipsoids for the non-H atoms. H atoms are drawn as spheres of arbitrary diameter. For DMSO(1), only the disorder sites with the higher site occupancy are presented. The hydrogen bonds are shown as dashed lines.

tor (Csöregh *et al.*, 1990). Moreover, water-mediated O···(H)O*W*(H)···O hydrogen bonds connect one of the host C=O groups, C19=O19, to one of the sulphoxides [DMSO(2)]. These latter interactions link the hydrogen-bonded (II).DMSO (1:2) host–guest associates so forming infinite chains running parallel to the **a** direction (Fig. 4). The proton-acceptor sites are also in excess in this structure, ousting another host C=O group, C13=O13, from the hydrogen-bonding scheme, despite one of the DMSO guests [DMSO(2); Fig. 4] being the acceptor in two hydrogen bonds. In these circumstances, the C13=O13 group of host (II) seems to be involved in a weak C—H···O interaction (Taylor & Kennard, 1982; Desiraju, 1991; Jefferey, 1995) involving one of methyl groups of a neighbouring host molecule. Details of the hydrogen-bond connections for (II*b*) are given in Table 2. The hydrogen-bonding pattern ···O=C—N—H···O(=S)···H—O—H··· in this inclusion compound corresponds to graph set $C^3_3(8)$ (Bernstein *et al.*, 1995).

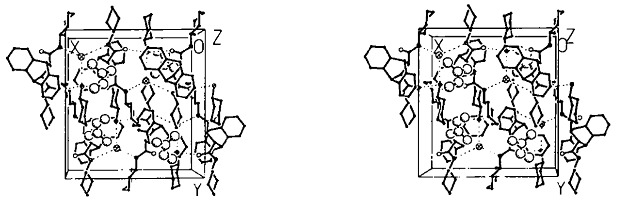

Fig. 3. Stereopacking diagram of (I*a*) [(I).cyclohexylamine.HCl.DMF (1:1:1:1)]. Host (I) together with the cyclohexylamine and HCl guests are shown in ball-and-stick style. The DMF guest is shown as a space-filling model. The O and N atoms, and the Cl^- anions are shown as circles with larger diameter having dotted, hatched or cross-hatched patterns, respectively. The H atoms have been omitted for clarity. The hydrogen bonds are shown as dashed lines.

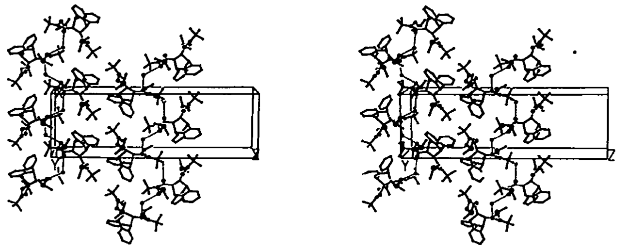

Fig. 4. Stereopacking diagram of (II*b*) [(II).DMSO.H_2O (1:2:1)]. The O, S and N atoms are shown as circles with larger diameter having dotted, cross-hatched or hatched patterns, respectively. The H atoms have been omitted for clarity. The hydrogen bonds are shown as dashed lines.

Experimental

The optically resolved (11*S*,12*S*)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxamide hosts, carrying *N*,*N*′-dicyclohexyl, (I), or *N*,*N*′-di-*tert*-butyl substituents, (II), were synthesized as described for the racemic analogues of (I) and (II) (Weber *et al.*, 1988) using optically resolved (11*S*,12*S*)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (Csöregh *et al.*, 1992). The inclusion behaviour of both compounds (I) and (II) was tested upon recrystallization from two different slowly cooled solvents, DMF or (undried) DMSO. (I) contained trace amounts of cyclohexylammonium chloride as a by-product of the synthesis, crystals were grown only from a DMF solution, not from DMSO. For (II), on the other hand, crystals were obtained only from a DMSO solution, not from

DMF, and also included H_2O as a guest. Though the composition of the crystals formed by both host compounds is not as expected, because host (I) and the DMSO solution used were not pure, the formation of four- and three-component crystals by (I) and (II), respectively, shows the ability of these host compounds to form multi-component systems in the solid state and gives interesting information on competition between different functional groups in hydrogen-bond formation which could otherwise have been missed.

Compound (I*a*)

Crystal data

$C_6H_{14}N^+.Cl^-.C_3H_7NO.C_{30}H_{36}N_2O_2$
$M_r = 665.357$
Orthorhombic
$P2_12_12_1$
$a = 14.341\ (1)$ Å
$b = 15.206\ (1)$ Å
$c = 17.716\ (2)$ Å
$V = 3863.3\ (6)$ Å^3
$Z = 4$
$D_x = 1.144$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 56 reflections
$\theta = 10.3–18.0°$
$\mu = 0.14$ mm^{-1}
$T = 213$ K
Irregular
$0.42 \times 0.40 \times 0.40$ mm
Colourless

Data collection

Siemens–Stoe AED-2 four-circle diffractometer
$\omega–2\theta$ scans
Absorption correction: none
6220 measured reflections
6220 independent reflections
2420 reflections with $I > 1.5\sigma(I)$
$\theta_{\max} = 30°$

$h = 0 \rightarrow 20$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 24$
5 standard reflections
frequency: 90 min
intensity decay: 2%

Refinement

Refinement on F
$R = 0.084$
$wR = 0.095$
$S = 1.690$
2420 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.0019F^2]$
$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.558$ e Å^{-3}
$\Delta\rho_{\min} = -0.360$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Rogers (1981)
Rogers parameter = 0.4 (4)

Table 1. *Hydrogen-bonding geometry (Å, °) for (Ia)*

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N14—H14$\cdots$Cl	1.00	2.27	3.264 (7)	180
N22—H22$\cdots$Cl^{i}	1.03	2.32	3.330 (6)	168
N29—H29*A*$\cdots$Cl	0.97	2.53	3.270 (6)	133
N29—H29*C*$\cdots$O13^{ii}	1.02	1.74	2.725 (9)	162
N29—H29*B*$\cdots$O21	1.04	1.98	2.760 (8)	130

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

Compound (II*b*)

Crystal data

$C_{26}H_{32}N_2O_2.2C_2H_6OS.H_2O$
$M_r = 578.824$
Orthorhombic
$P2_12_12_1$
$a = 10.004\ (3)$ Å
$b = 9.966\ (3)$ Å
$c = 32.06\ (1)$ Å
$V = 3196\ (2)$ Å^3
$Z = 4$
$D_x = 1.203$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 4.7–11.0°$
$\mu = 0.21$ mm^{-1}
$T = 298$ K
Irregular
$0.20 \times 0.15 \times 0.11$ mm
Colourless

Data collection

Siemens–*P4/RA* single-crystal diffractometer
$\omega–2\theta$ scans
Absorption correction: none
6520 measured reflections
6195 independent reflections
2692 reflections with $I > 3.0\sigma(I)$
$R_{\rm int} = 0.035$

$\theta_{\max} = 30°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 14$
$l = -1 \rightarrow 45$
3 standard reflections
every 200 reflections
intensity decay: 4%

Refinement

Refinement on F
$R = 0.088$
$wR = 0.108$
$S = 2.193$
2692 reflections
318 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.00105F^2]$
$(\Delta/\sigma)_{\max} = 0.005$

$\Delta\rho_{\max} = 0.960$ e Å^{-3}
$\Delta\rho_{\min} = -0.886$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Rogers (1981)
Rogers parameter = 1.0 (6)

Table 2. *Hydrogen-bonding geometry (Å, °) for (IIb)*

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N14—H14$\cdots$O1*D*	1.00	1.88	2.881 (10)	180
N20—H20$\cdots$O2*D*	1.00	1.94	2.935 (9)	180
O1*W*—H31*A*$\cdots$O2*D*^{i}	1.00	2.05	3.051 (13)	180
O1*W*—H31*B*$\cdots$O19	1.00	1.84	2.838 (11)	180
C23—H23*A*$\cdots$O13^{ii}	1.00	2.73	3.70 (1)	162

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$.

The crystals of both compounds proved to have rather modest X-ray scattering ability. Thus, at the resolution level 0.9–0.8 Å, only 133 out of 1272 theoretically possible reflections for (I*a*), and only 101 out of 1077 for (II*b*), collected with a Stoe AED-2 diffractometer ($T = 213$ K, Mo $K\alpha$ radiation, $q_{\max} = 30°$) had detectable intensities. A second data collection for (II*b*), using a Siemens *P4/RA* instrument, equipped with a rotating anode resulted in 453 reflections with observed intensities at the same resolution level and has been used in the analysis. Nevertheless, a considerable part of the collected data have large uncertainty due to the modest scattering ability of the crystals on the one hand and the technical limitation of the instruments used for intensity measurements on the other. In order to increase the observation-to-parameter ratios, the phenyl rings of the dihydroanthracene moieties of both host molecules, (I) and (II), were fitted to regular hexagons (C—C = 1.39 Å) and the C atoms of this moiety in host (I) were refined isotropically. As a result of the high mobility and/or disorder of the guest molecules, only the Cl^- in (I*a*), and the DMSO(2) and H_2O guests in (II*b*) could be refined anisotropically. The cyclohexylamine and the DMF molecules in (I*a*) and the DMSO(1) guest in (II*b*) had to be refined isotropically with bond-length constraints in order to yield acceptable geometry. Two major disorder sites were modelled for the S atom in DMSO(1). The refined site-occupation factors are 0.65 (1) and 0.35 (1) for S11*D* and S12*D*, respectively. Rather high residual electron density (0.960 e Å^{-3}) was observed in the proximity of the S atom in DMSO(2) indicating possible disorder. However, it could not be modelled in a chemically reasonable way. The H-atom positions were either calculated assuming ideal geometry with C—H = 1.00 Å (C-bonded atoms) or were derived from $\Delta\rho$ maps (N- or O-bonded atoms). They were held riding on their carrier atoms during subsequent calculations. Their $U_{\rm iso}$ values were either kept riding on the respective carrier atoms [DMF and C-bonded H atoms of cyclohexylamine guests in (I*a*); H_2O and DMSO(1) guests in (II*b*)] or were refined isotropically (all other H atoms). Since both compounds contain the respective host molecule in stereochemically pure form, the final refinement calculations were carried out twice assuming either *S*,*S* or *R*,*R* configuration for the chiral centres at C11 and C12, and the η parameter (Rogers, 1981) was refined. The *R* and *wR* values calculated for the 11*S*,12*S* and the 11*R*,12*R* models of (I*a*) are indistinguishable (R = 0.0839 and wR = 0.0950). For (II*b*), the final agreement factors for the 11*S*,12*S* configuration are slightly lower (R = 0.0880 and wR = 0.1076) than for the 11*R*,12*R* (R = 0.0887 and wR = 0.1094). Large e.s.d. values of the η parameter, which refined to 0.4 (4) for (I*a*) and 1.0 (6) for (II*b*), assuming the 11*S*,12*S* configuration, do not allow us to support the absolute configuration assignment based on chemical correlation *via* synthesis. The observed disorder, together with the modest data quality, might be the reason that the refinement of both inclusion compounds (I*a*) and (II*b*) ended with relatively high crystallographic *R* values.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*) for (I*a*); *XSCANS* (Siemens, 1994) for (II*b*). Cell refinement: *DIF*4 for (I*a*); *XSCANS* for (II*b*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*) for (I*a*); *XSCANS* for (II*b*). For both compounds, program(s) used to solve structures: *MULTAN*80 (Main *et al.*, 1980); program(s) used to refine structures: *SHELXTL/PC* (Sheldrick, 1990); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *PLATON* (Spek, 1990).

OH and IC thank Professor Rolf Norrestam (Stockholm University) for kind interest and helpful assistance. Financial support from the Swedish Natural Science Research Council (NFR) to IC, and from the Deutsche Forschungsgemeinschaft (GRK 208/1) and the Fonds der Chemischen Industrie to EW is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1479). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1895–1897

2′-Hydroxy-4-*N*-methylstilbazonium Iodide Methanol Solvate,† $C_{14}H_{14}NO^+.I^-.CH_3OH$

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(*Received 8 April 1997; accepted 21 July 1997*)

Abstract

The cation in the title compound has a planar structure [the maximum deviation from the best plane through the non-H atoms is 0.043 (3) Å]. The dihedral angle between the two rings is 0.9 (1)°. Cations are connected through I^- anions and weak O···H—O hydrogen bonds, and are packed in an anti-parallel fashion through $\pi\cdots\pi$ interactions along the *a* axis. Methanol molecules, which

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† Alternative name: 4-[2-(2-hydroxyphenyl)ethenyl]-*N*-methylpyridinium iodide methanol solvate.