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5,7-*syn*-Bis(trimethylsilyl)-5-norbornene-2,3-*endo*-dicarboxylic acid: a rare co-existence of dimeric and catemeric synthons

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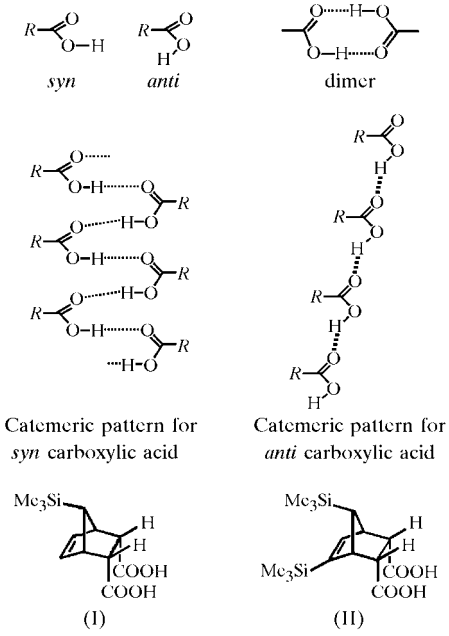
The crystal and molecular structure of the title compound, $C_{15}H_{26}O_4Si_2$, reveals a self-assembly facilitated *via* the rare co-existence of dimeric and catemeric patterns, which is attributed to the influence of the trimethylsilyl groups. The structure is dicussed in the context of a database search and subsequent analysis of structures of *cis*-1,2-dicarboxylic acids.

Comment

Carboxylic acid groups have been shown to self-assemble *via* dimeric and catemeric arrangements (Duchamp & Marsh, 1969; Leiserowitz, 1976; Ermer, 1988; Holy *et al.*, 1999). The latter may be formed in different ways (see scheme) (Duchamp & Marsh, 1969; Das & Desiraju, 2006). An analysis of entries in the Cambridge Structural Database (CSD, Version 5.29; Allen, 2002) reveals that the centrosymmetric dimer pattern is found in more than 90% and the catemeric pattern in less than 5% of the structures analysed (Das & Desiraju, 2006; Kolotuchin *et al.*, 1995).

In recent investigations on cyclic *cis*-1,2-dicarboxylic acids, we observed that a hydrophobic moiety such as the trimethylsilyl (TMS) group at position 7 in *syn*-7-trimethylsilyl-5-norbornene-*endo*-2,3-dicarboxylic acid, (I), induces helicity (Begum *et al.*, 2004). This and the novel self-assembly observed in the analogous cyclic *cis*-1,2-diols (Begum *et al.*, 2005) led us to explore the consequences of introducing an additional TMS group, which led to the present work on the title compound, (II). We report here the co-existence of dimeric and catemeric assemblies in the crystal structure of (II). From the structure of (II), in conjunction with analyses of the structures of *cis*-1,2-dicarboxylic acids reported in the CSD, it appears that both steric factors and the hydrophobic nature of the TMS group are responsible for the rare occurrence of the catemeric pattern together with the centrosymmetric dimer motif.

The geometry of the two carboxyl groups in (II) is found to be *syn* (Fig. 1). In the vicinal dicarboxylic acids, the carboxyl groups are *anti* with respect to each other, *i.e.* the two carbonyl



O atoms and the hydroxyl groups are oriented in opposite directions. Furthermore, the two carboxyl groups are not parallel, forming a dihedral angle of 58.2 (1)°. This presumably minimizes dipolar repulsions. Apart from this, there are no exceptional geometric features.

The crystal packing (Fig. 2) includes two modes of self-assembly for the carboxyl groups. The first is a centrosymmetric head-to-head dimer motif formed between the carboxyl group at C14 (O4—H17···O3^{i}) and the equivalent group in the molecule at (1 − *x*, −*y*, 2 − *z*). The second is formed by molecules related by the 2_1 screw axis and hydrogen bonded in a *syn*-catemeric fashion, as shown schematically above. The chain is propagated by the 2_1 axis, with the molecule at (*x*, *y*, *z*) donating an O2—H16···O1^{ii} hydrogen bond to its neighbour

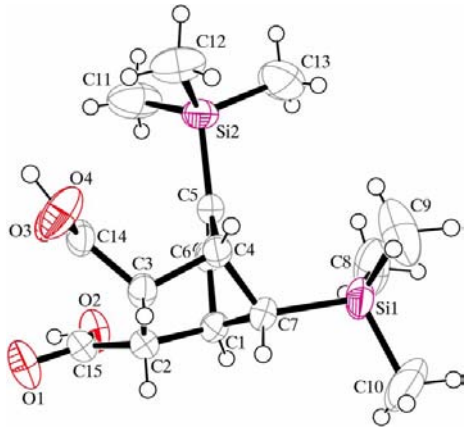


Figure 1
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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at $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, *viz*. (ii). The base molecule (x, y, z) accepts an equivalent hydrogen bond from its 2_1-related neighbour at $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$.

Given the rarity of the concurrence of the two aggregation patterns observed for (II), a search of the CSD was conducted to shed light on other factors that might play an important role. We retrieved 353 structures for 1,2-dicarboxylic acids. A total of 21 hits were distilled from the initial set for 1,2-*cis*-dicarboxylic acids, with subsequent elimination of cases for which the two carboxylic acids are geometrically *anti*, as well as those cases for which there is potential interference by interactions due to other functional groups present in the molecules. In Table 2 are shown the most relevant cases and the pattern of association observed for each; Fig. 3 defines each compound. As can be seen, the predominant pattern observed for 1,2-dicarboxylic acids, with the exception of 3,3-dimethylcyclopropane-1,2-dicarboxylic acid, is dimeric; to the best of our knowledge, the latter is the only example in addition to the diacid (II) of the present study in which the co-existence of both dimeric and catemeric motifs has been found.

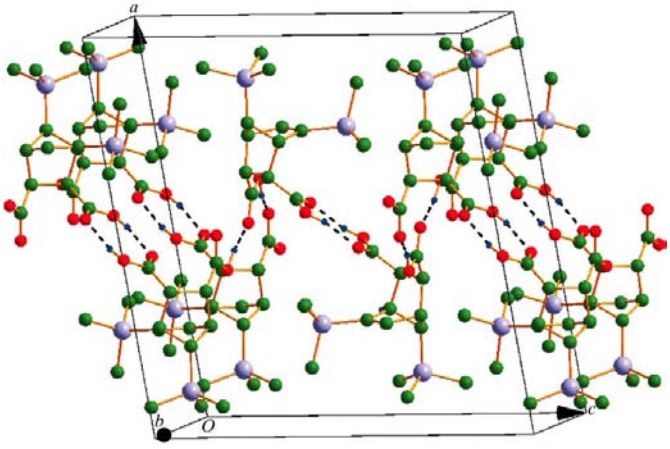

Figure 2
The two modes of self-assembly in (II), showing both dimeric and catemeric motifs.

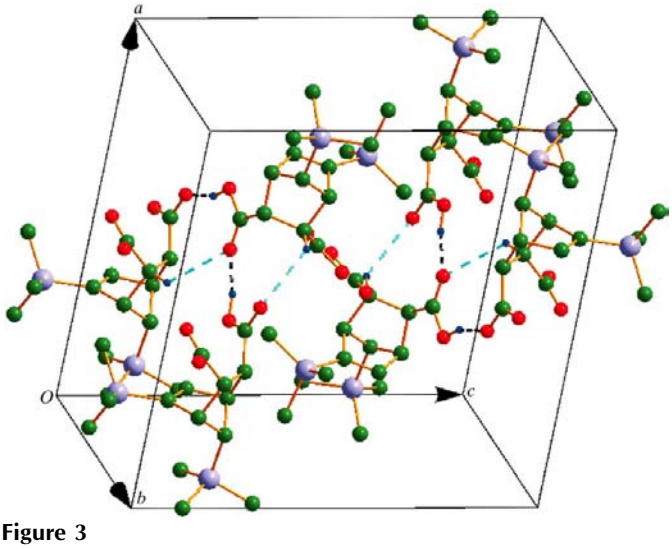

Figure 3
The catemeric associations of the diacid (II). Note that auxiliary C—H···O hydrogen bonds compliment the strongly directional O—H···O hydrogen bonds.

In (II), the O—H···O hydrogen-bonded catemeric assembly is supported by very weak C—H···O contacts (Fig. 3), in this case involving atom C3 and the C15 carboxyl O atom, C3—H3···O1^{iii} [symmetry code: (iii) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$]. It has been proposed that the catemeric motif arises due to auxiliary/supporting weak interactions such as C—H···O hydrogen bonds (Duchamp & Marsh, 1969; Das & Desiraju, 2006; Kuduva *et al.*, 1999). Evidently, an increase in hydrophobicity through further TMS substitution in (II) compared with diacid (I) (Begum *et al.*, 2004), as well as weak C—H···O hydrogen bonds, lead to the appearance of a catemeric motif in diacid (II), a motif not present in (I) or in the other simple *cis*-norbornene-1,2-carboxylic acids (Table 2). That the hydrophobic factor itself does appear to play a role in the generation of the catemeric motif can be clearly inferred from the comparison of the crystal packings of *cis*-cyclopropane-1,2-dicarboxylic acid (CSD refcode FOJRAX) and its 3,3-dimethyl analogue (KOJZEO; Table 2). While the dimeric motif is common to both carboxylic acids, it is the dimethyl substitution in *cis*-cyclopropane-1,2-dicarboxylic acid that causes the co-existence of two patterns. The tendency for increased hydrophobic aggregation in the crystal structures appears to have a decisive effect in the overall crystal packing, leading to the observation of the co-existence of the two patterns in (II).

The co-existence of dimeric and catemeric motifs observed for the title compound, for which we found just one precedent in the CSD, thus appears to be directed by the hydrophobic aggregation of the TMS groups. Though not uncommon, this aggregation influences the usual dimeric motif in favour of the further formation of the chain. This is another instance of how weak interactions may potentially influence the molecular association based on strongly directional supramolecular synthons/motifs.

Experimental

To a suspension of small pieces (1 mm) of sodium (6.1 g, 0.265 mol) in dry tetrahydrofuran (100 ml) in a 500 ml three-necked round-bottomed flask fitted with a mechanical stirrer, a dropping funnel and a condenser, under a nitrogen atmosphere, was added freshly distilled 1,3-cyclopentadiene (16.5 g, 0.25 mol) over a period of 45 min. The dark-red reaction mixture was stirred for 2 h at room temperature. Chlorotrimethylsilane (27.25 g, 0.25 mol) was then added dropwise over a period of 1 h, during which time the mixture became warm and changed colour from dark-red to blue to white with copious precipitation of NaCl. Stirring was continued for another 3 h, and then the mixture was filtered through glass wool and the precipitate washed with tetrahydrofuran (2 × 10 ml). The combined filtrates were cooled in an ice–water bath and carefully treated with water (75 ml). The layers were then separated. The aqueous layer was washed with ether (3 × 50 ml), and the organic layers were combined, washed with water (3 × 75 ml), dried (Na_2SO_4) and concentrated. The residue was distilled under vacuum on a spinning band column. The fraction

collected at 341–344 K and 20 Torr (1 Torr = 133.322 Pa) was 99.9% pure (by gas chromatography) 2,5-bis(trimethylsilyl)cyclopentadiene.

To finely powdered maleic anhydride (2.44 g, 0.025 mol) in a 25 ml conical flask was added 2,5-bis(trimethylsilyl)cyclopentadiene (5.16 g, 0.025 mol) dropwise over a period of 15 min with shaking and occasional cooling in water. The mixture was allowed to stand for 3 h and then stirred with CH_2Cl_2 (20 ml). The solution was filtered and the filtrate concentrated to obtain 2,7-*anti*-bis(trimethylsilyl)bicyclo-[2.2.1]hept-2-ene-5,6-*endo*-dicarboxylic acid anhydride (m.p. 360–361 K). A portion of this (1.0 g) was stirred in water (10 ml) for 3 h and then filtered off, and the title dicarboxylic acid was recrystallized from chloroform (m.p. 399 K).

Crystal data

$C_{15}H_{26}O_4Si_2$
M_r = 326.54
Monoclinic, $P2_1/c$
a = 16.9370 (4) Å
b = 6.8184 (16) Å
c = 16.5770 (4) Å
β = 97.667 (4)°
V = 1897.3 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 293 (2) K
0.3 × 0.2 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
17324 measured reflections
3338 independent reflections
2641 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.182
S = 1.12
3338 reflections
228 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 1
Hydrogen-bond and short-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H17···O3^{i}	0.88 (4)	1.79 (4)	2.666 (4)	167 (4)
O2—H16···O1^{ii}	0.95 (3)	1.69 (3)	2.622 (3)	161 (3)
C3—H3···O1^{iii}	0.95 (2)	2.66 (2)	3.299 (3)	124 (2)

Symmetry codes: (i) $-x+1, -y, -z+2$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Methyl H atoms were treated using a riding model, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). The remaining H atoms were refined freely [C—H = 0.89 (3)–0.96 (3) Å; O—H = 0.89 (4) and 0.96 (4) Å].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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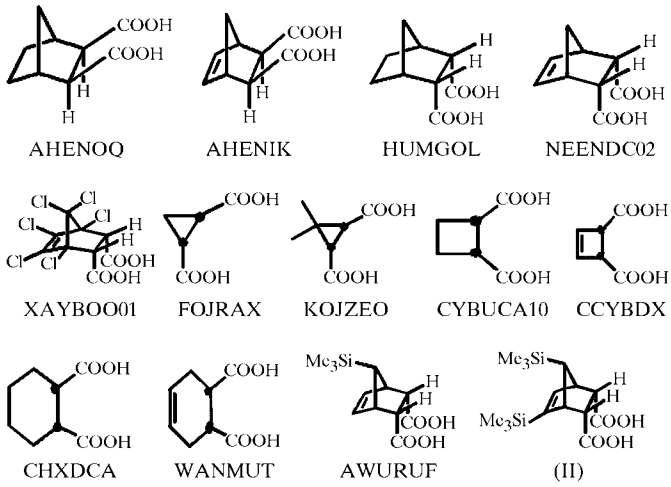
Table 2
The reported structures and corresponding patterns of self-assembly of cyclic *cis*-dicarboxylic acids.



Data are for compounds retrieved from the Cambridge Structural Database (Allen, 2002).

Refcode	Space group	Pattern of self-assembly
AHENOQ	$C2_1/c$	Dimeric
AHENIK	$P\overline{1}$	Dimeric
HUMGOL	$P2_1/c$	Dimeric
NBENDC02	$P2_1/c$	Dimeric
XAYBOO01	$P2_1$	Dimeric
FOJRAX	$P2_1/n$	Catemeric
KOJZEO	$P2_1/c$	Dimeric + catemeric
CYBUCA10	$P2_1/c$	Dimeric
CCYBDX	$P2_1/n$	Dimeric
CHXDCA	$P\overline{1}$	Dimeric
WANMUT	$P\overline{1}$	Dimeric
AWURUF	$Pna2_1$	Helical
(II)	$P2_1/c$	Dimeric + catemeric

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3150). Services for accessing these data are described at the back of the journal.

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