

# Conformation of *cis,trans*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid derivatives: crystal structures and semiempirical molecular orbital calculations



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The conformation of three derivatives of the *cis,trans* epimer of Kemp's triacid with *cis*-carboxy groups, namely the 4-*tert*-butylbenzyl ester (**1**), the phenethyl ester (**2**) and the phenethyl amide (**3**) was investigated. The determination of crystal structures showed that, while **1** and **2** are in the *boat* conformation, previously unobserved in this family of compounds, **3** is in the *chair* conformation, all of them with axial carboxy groups. In the first two cases, dimers are formed by hydrogen bonding between carboxy groups of adjacent molecules whereas in the third case, the presence of other hydrogen bonds involving the amide groups gives rise to the formation of layers. The conformations observed were compared with that assumed by **1** in its uranyl complex previously reported. Semiempirical molecular orbital calculations have shown that the *chair* and *boat* forms have intrinsically similar conformational stabilities. We also investigated by X-ray diffraction and differential scanning calorimetry the phase transition presented by **1**.

*cis,cis*-1,3,5-Trimethylcyclohexane-1,3,5-tricarboxylic acid, usually called Kemp's triacid,<sup>1</sup> together with its *cis,trans* epimer and their various derivatives (including Rebek's diacids<sup>2</sup>) constitute a family of compounds of interest for molecular recognition<sup>2</sup> or selective cation complexation and transport.<sup>3,4</sup> Because of their great impact on recognition properties, the conformations of some simple members of this family have been investigated by solution NMR spectrometry and single-crystal X-ray diffraction. Apparently, in solution<sup>1,2a,5,6</sup> as well as in the solid state,<sup>2a,5-7</sup> the *chair* conformation of Kemp's triacid predominates, with the three acid groups in axial positions. The trianion is an exception, with its acid groups in equatorial positions due to electrostatic repulsion.<sup>1,6</sup> However, NMR experiments and molecular dynamics calculations have shown that Mg<sup>2+</sup> complexation could convert the trianionic form from a *chair* into a *half-chair* conformation.<sup>8</sup> In the absence of methyl groups, the three acid groups are in equatorial positions.<sup>1,5</sup> The same trend holds true when the carboxy groups are replaced by methoxycarbonyl ones<sup>1,2a,5</sup> and when methyl substituents are replaced by more bulky ones such as benzyl.<sup>5</sup> It ensues that there is a general tendency for such molecules to adopt the *chair* conformation with the substituents in equatorial position, with a preference for alkyl over carboxy groups which is due to the axial crowding (1,3-diaxial repulsions), more important with the former than with the latter. However, when the *cis,trans* epimer is considered, all methyl groups cannot be in equatorial positions, hence conformational trends become more difficult to predict. However, NMR spectroscopy indicates that the *cis,trans* epimer of Kemp's triacid in its tri-, di- or mono-protonated form is in the *chair* conformation with the two *cis*-carboxy groups in axial positions, which is in agreement with the preceding 'rule of thumb', whereas in the trianionic form, the two *cis*-carboxy groups are equatorial.<sup>6</sup>

We have reported recently the synthesis and crystal structure of a nanometer-sized supramolecule made from the self-assembling of eight UO<sub>2</sub><sup>2+</sup> (uranyl) ions, four peroxo O<sub>2</sub><sup>2-</sup> ions

and eight deprotonated molecules of the diacid monoester *trans*-5-(4-*tert*-butylbenzyloxycarbonyl)-1,3,5-trimethylcyclohexane-*cis*-1,3-dicarboxylic acid (**1**).<sup>9</sup> In this assembly, each molecule of **1**, in the *chair* conformation, bridges two uranyl ions by its bidentate acid groups, which are in equatorial positions. This conformation may not be the most stable one because the two methyl groups geminal to the acid functions are in unfavourable axial positions. To make this point clearer, we determined the crystal structure of the free ligand **1**, which appeared to present a temperature-driven phase transition (**1a**↔**1b**) unrelated with the *chair/boat* conformations. This phase transition was further probed by Differential Scanning Calorimetry (DSC). The structure of two related ligands, the diacid monoester *trans*-5-(2-phenethyloxycarbonyl)-1,3,5-trimethylcyclohexane-*cis*-1,3-dicarboxylic acid (**2**) and the diacid monoamide *trans*-5-(*N*-phenethylcarbamoyl)-1,3,5-trimethylcyclohexane-*cis*-1,3-dicarboxylic acid (**3**) were also determined and compared with the structure of **1**. We also performed some semiempirical molecular orbital calculations to obtain insight into the relative energies of the different possible conformations.

## Experimental

### Synthesis

The synthesis of compounds **1**, **2** and **3** was reported previously.<sup>4e</sup> Elemental analyses were performed at the Materials Analysis Research Center of the National Institute of Materials and Chemical Research (Tsukuba, Japan). **1**, calc. for C<sub>23</sub>H<sub>32</sub>O<sub>6</sub>: C, 68.29; H, 7.97; found: C, 68.30; H, 8.03%. **2**, calc. for C<sub>20</sub>H<sub>26</sub>O<sub>6</sub>: C, 66.28; H, 7.23; found: C, 66.21; H, 7.35%. **3**, calc. for C<sub>20</sub>H<sub>27</sub>NO<sub>5</sub>: C, 66.46; H, 7.53; N, 3.88; found: C, 66.63; H, 7.55; N, 3.79%. Colourless single crystals suitable for X-ray crystallography were obtained from slow evaporation of (1 : 1) CH<sub>3</sub>OH–CHCl<sub>3</sub> (**1**), (1 : 1) CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>CN (**2**) and CH<sub>3</sub>OH (**3**) solutions.

**Table 1** Crystal data and structure refinement details

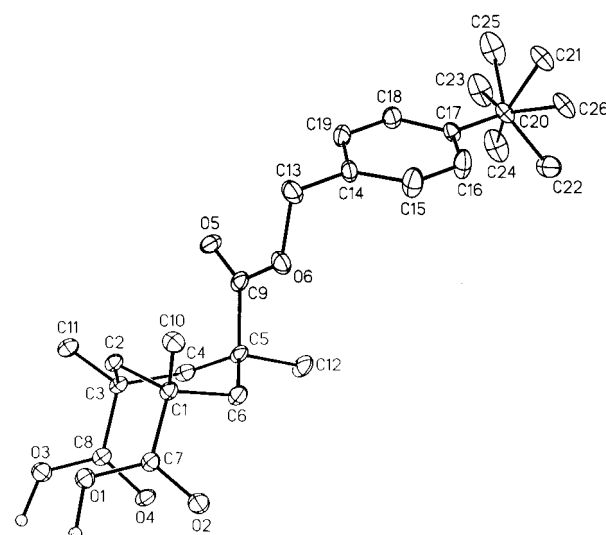
	<b>1a</b>	<b>1b</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>23</sub> H <sub>32</sub> O <sub>6</sub>	C <sub>23</sub> H <sub>32</sub> O <sub>6</sub>	C <sub>20</sub> H <sub>26</sub> O <sub>6</sub>	C <sub>20</sub> H <sub>27</sub> NO <sub>5</sub>
<i>M</i> /g mol <sup>-1</sup>	404.49	404.49	362.41	361.43
<i>T</i> /K	293(2)	123(2)	123(2)	123(2)
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pbcn</i>
Crystal size/mm <sup>3</sup>	0.60 × 0.30 × 0.15	0.60 × 0.30 × 0.15	0.40 × 0.35 × 0.30	0.40 × 0.40 × 0.40
<i>a</i> /Å	18.3529(12)	12.6745(7)	12.3657(7)	24.3829(15)
<i>b</i> /Å	6.4184(5)	18.0319(11)	13.0496(5)	9.8960(6)
<i>c</i> /Å	19.1454(13)	19.9940(11)	13.4977(7)	15.7266(5)
<i>a</i> (°)	90.	84.929(3)	61.992(3)	90.
<i>β</i> (°)	93.695(3)	72.592(3)	76.774(2)	90.
<i>γ</i> (°)	90.	89.799(3)	88.767(3)	90.
<i>V</i> /Å <sup>3</sup>	2251(3)	4342(2)	1863(2)	3795(2)
<i>Z</i>	4	8	4	8
$\mu$ /mm <sup>-1</sup>	0.085	0.088	0.095	0.090
Reflections collected	20567	32811	14083	25229
Independent reflections	3863	16960	7221	3527
<i>R</i> <sub>int</sub>	0.036	0.082	0.039	0.059
<i>R</i> <sub>1</sub>	0.078	0.113	0.046	0.063
<i>wR</i> <sub>2</sub>	0.199	0.259	0.118	0.158

### Crystallography

The data were collected on a Nonius Kappa-CCD area detector diffractometer using graphite monochromated Mo-*K* $\alpha$  radiation (0.71073 Å). The crystals were introduced in Lindemann glass capillaries. The lattice parameters were determined from ten images recorded with 1°  $\phi$ -scans and later refined on all data. A 180°  $\phi$ -range was scanned with 2° steps during data recording.<sup>10</sup> The crystal-to-detector distance was fixed (between 28 and 33 mm). The data were processed with the HKL package.<sup>11</sup> The structures were solved by direct methods with SHELXS-86<sup>12</sup> and subsequent Fourier difference synthesis and refined by full-matrix least-squares on *F*<sup>2</sup> with SHELXL-93.<sup>13</sup> No absorption correction was made. The *tert*-butyl group was disordered in **1a** and molecule A of **1b** (which comprises four crystallographically independent molecules). These groups have been modelled with two sets of three carbon atoms with refined occupation factors constrained to sum up to unity. All non-hydrogen atoms were refined anisotropically, with the exception of disordered ones in **1b**. The carboxy protons were located from the Fourier difference map and introduced as riding atoms with a displacement parameter equal to 1.2 times that of the attached oxygen atom. All the other hydrogen atoms were introduced (unless in the disordered parts) as riding atoms with a displacement parameter equal to 1.2 (NH, CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the attached carbon atom. The *R* factors for compound **1** are rather large due to low crystal quality; in particular, in the case of **1b**, some further deterioration of the crystal occurred upon phase transition. Analytical scattering factors for neutral atoms were corrected for the anomalous dispersion terms  $\Delta f'$  and  $\Delta f''$ . Crystal data and structure refinement parameters are given in Table 1.  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , calculated on 'observed' [ $I > 2\sigma(I)$ ] reflections;  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}$  with  $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$  where  $P = (F_o^2 + 2F_c^2)/3$  and *x* and *y* are refined values. The bond distances and angles lie in the usual range. The molecular drawings were done with SHELXTL.<sup>14</sup> All calculations were performed on a Silicon Graphics R5000 workstation at the CEA/Saclay. CCDC 188/184. See <http://www.rsc.org/suppdata/p2/1999/2077> for crystallographic data in .cif format.

### Calorimetric measurements

The thermal behaviour of **1** in single crystal form was investigated by differential scanning calorimetry (DSC) using a MAC Science DSC3100S at Saitama University. The heating and cooling rates were 10 °C min<sup>-1</sup>.



**Fig. 1** Molecular unit of **1a** with atomic numbering scheme. Carboxy hydrogen atoms only are represented for clarity.

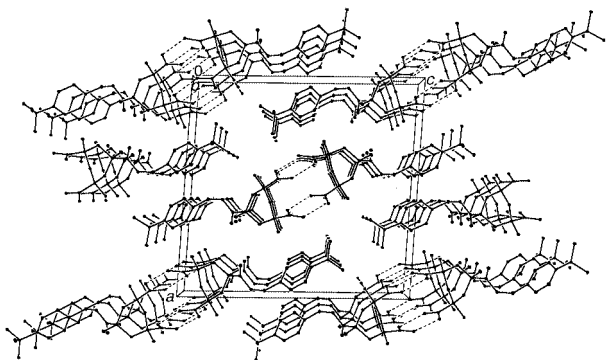
### Calculations

Simulation of the molecular structures of **1**, **2** and **3** by semi-empirical molecular orbital calculations was performed using MOPAC (PM3) on a SGI Power ONYX Computer in the Information Processing Center of Saitama University.

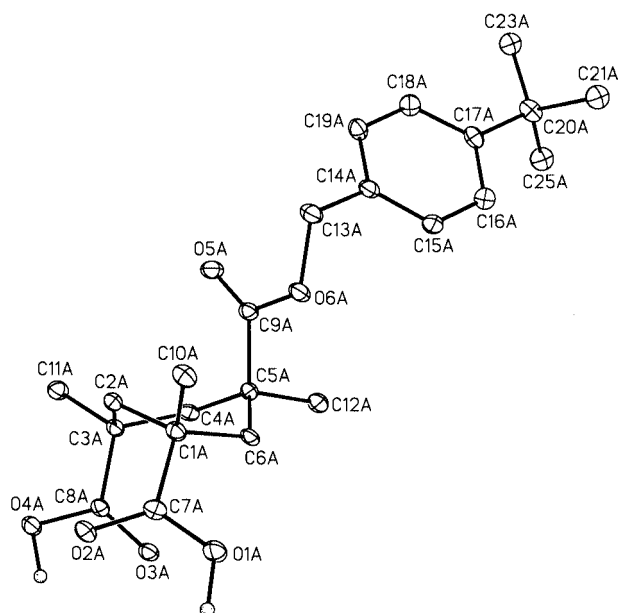
## Results and discussion

### Crystal structures and calorimetric measurements

The molecular unit of **1a**, determined at 293(2) K, is represented in Fig. 1. This molecule does not possess any symmetry element. It appears to be in a *skew boat* conformation, which, to the best of our knowledge, is the first evidence for the occurrence of this molecular shape in this family of compounds. The twist with respect to an ideal *boat* form can be estimated by the deviations of atoms C(1), C(3), C(4) and C(6) from their mean plane, which are within  $\pm 0.092(3)$  Å. Not surprisingly, the two *cis*-carboxy groups are in axial positions; however, in contrast to the *cis,cis* epimers, it ensues that the ester group is also axial, hence the three methyl groups are in the most stable equatorial position. The *tert*-butyl group is disordered over two positions, with refined occupations 0.83(1) and 0.17(1). The two carboxy groups make hydrogen bonds with the carboxy group pair of a



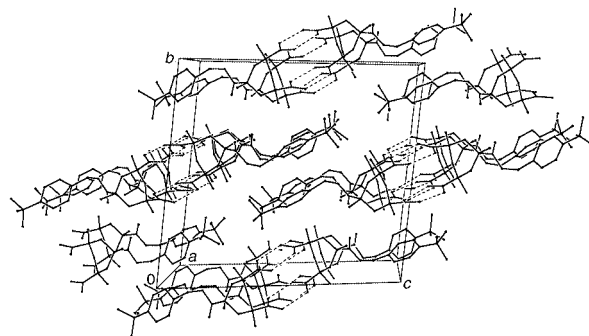
**Fig. 2** Crystal packing in **1a**. Hydrogen bonds in dashed lines. Hydrogen atoms omitted for clarity. Only one of the two positions of the *tert*-butyl groups is represented.



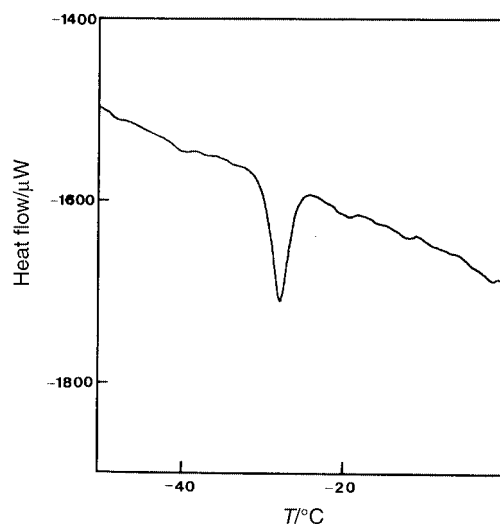
**Fig. 3** Molecular unit of **1b** (molecule A) with atomic numbering scheme. Carboxy hydrogen atoms only are represented for clarity. Minor components of disordered parts omitted.

neighbouring molecule [ $O \cdots O$  2.62(1) and 2.65(1) Å,  $O-H$  1.101 and 1.075 Å,  $H \cdots O$  1.52(1) and 1.61(1) Å,  $O-H \cdots O$  170(1) and 160(1)°], giving rise to the formation of dimers, as is apparent in the crystal packing represented on Fig. 2. The ester group is stretched away from the cyclohexane ring, presumably due to stacking interactions in the solid state.

When the temperature is lowered to 123(2) K, another crystal form **1b** is observed, which is characterized by a lowering in crystal symmetry (from monoclinic to triclinic) and site multiplicity. Four independent molecules, noted A–D, are present in the asymmetric unit, which are all in the *boat* conformation. Only one of them (A) presents a *tert*-butyl group disordered over two positions with refined occupations 0.73(2) and 0.27(2). Two molecules, B and C, have the same geometry as the molecule in **1a**, whereas the two other ones, A and D, differ from the former ones by the position of the benzyl group. Whereas the benzyl rings were stacked parallel to each other, in a face-to-face manner, in **1a**, the rotation of these rings in molecules A and D of **1b** (Fig. 3) results in a tilt between successive rings along the *a*-axis, the stacking being intermediate between face-to-face and ‘herringbone’ (Fig. 4). An indicative sign of the benzyl ring rotation to come may be seen in the rather large components of the anisotropic displacement parameters of the lateral carbon atoms of the aromatic ring, perpendicular to its mean plane, in **1a**. Another difference with the room temperature form lies with the carboxy proton positions. The mole-



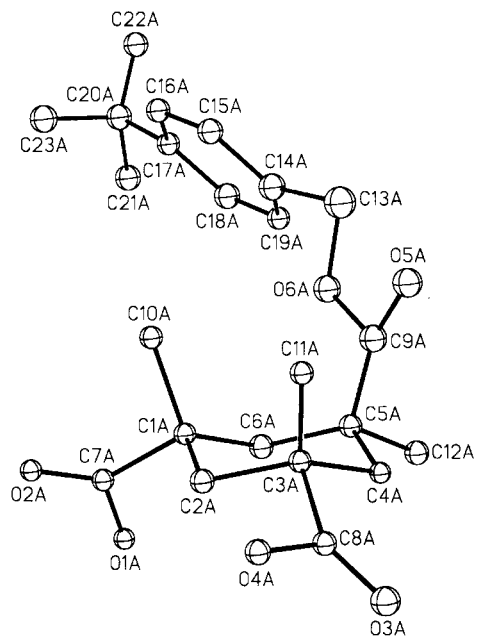
**Fig. 4** Crystal packing in **1b**. Hydrogen bonds in dashed lines. Hydrogen atoms omitted for clarity. Only one of the two positions of the *tert*-butyl groups of molecule A is represented.



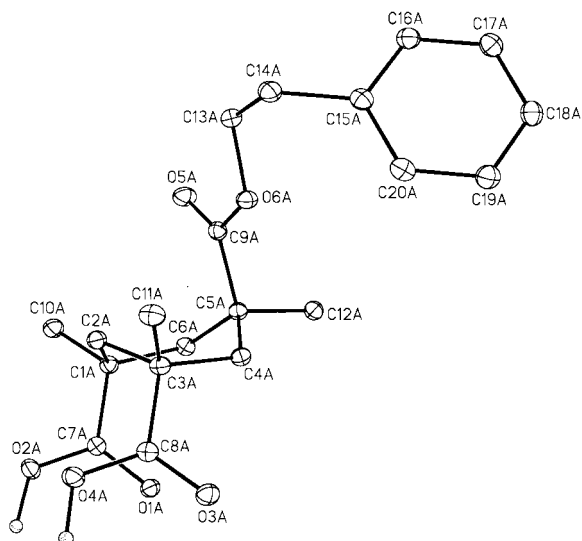
**Fig. 5** Differential scanning calorimetry measurement showing the thermal effect of the phase transition in **1**.

cules are arranged in dimers held by hydrogen bonds as in **1a**; the C–D dimerization is analogous to that in **1a**, whereas in the A–B dimer the acidic protons are not on the same side of the nearly parallel carboxy groups, as illustrated on Fig. 3 for molecule A. The deviations of atoms C(1), C(3), C(4) and C(6) from their mean plane are within  $\pm 0.104(3)$ ,  $0.080(4)$ ,  $0.074(4)$  and  $0.092(4)$  Å for molecules A–D, respectively; the mean value,  $\pm 0.087(13)$  is identical to the value in **1a**. The transition temperature has not been determined from diffraction experiments (intermediate transition states which do not correspond to either of the two extreme temperature unit cells seem to exist at 220, 250 and 270 K). The DSC measurement showed a well-defined endothermic peak corresponding to a solid–solid phase transition with a critical temperature of about 245 K and a transition heat of  $0.69 \text{ J g}^{-1}$  (Fig. 5). This heat flow was only observed in the heating process under the present experimental conditions.

Molecule **1**, in its deprotonated state, has been used as a building block in the uranyl complex previously reported.<sup>9</sup> The eight ligand molecules in the complex are in the *chair* conformation with the carboxy groups equatorial. One of them is represented in Fig. 6 for comparison with **1a** and **1b**. This conformation, which brings only one methyl group into an equatorial position, may not be the most stable one in the uncomplexed protonated state, according to the ‘rule’ previously stated. However, it has been observed in the trianion of the *cis,trans* epimer of Kemp’s triacid<sup>6</sup> and it may be analogously stabilized in the uncomplexed dianion of **1**. This conformation enables **1** to bridge two uranyl ions, each of them bonded to one bidentate carboxy group, whereas the axial position of the two



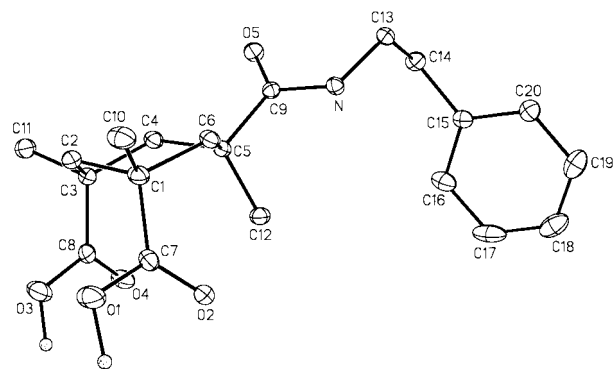
**Fig. 6** Molecular unit of **1** in its deprotonated form complexed to uranyl ions<sup>9</sup> with atomic numbering scheme. Ligand A only is represented. Uranyl ions omitted.



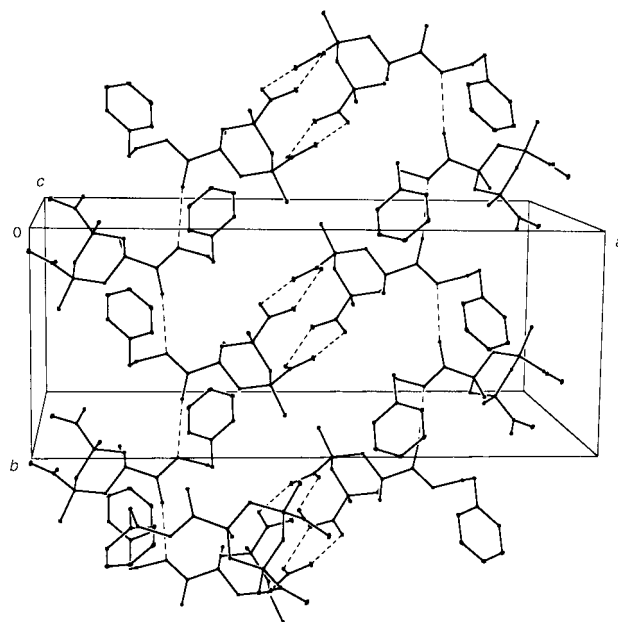
**Fig. 7** Molecular unit of **2** (molecule A) with atomic numbering scheme. Carboxy hydrogen atoms only are represented for clarity.

groups would bring them too close together and prevent this bonding mode. Furthermore, the two carboxy groups in equatorial positions make an angle close to 90°, which results in the formation of a ring comprising four uranyl ions and four bridging ligands, as discussed previously.<sup>9</sup> The range of deviations of atoms C(1), C(3), C(4) and C(6) from their mean plane is  $\pm 0.034$ – $0.084$  Å for the eight molecules; the mean value,  $\pm 0.03(2)$  Å, is lower than those in **1a** and **1b**, but the low accuracy of this structure determination prevents the drawing of any definitive conclusions from this difference. In this case, the free and complexed ligand conformations are quite different and no preorganization effect can be invoked. To the contrary, the flexibility of the ligand appears to play a key role in complexation.

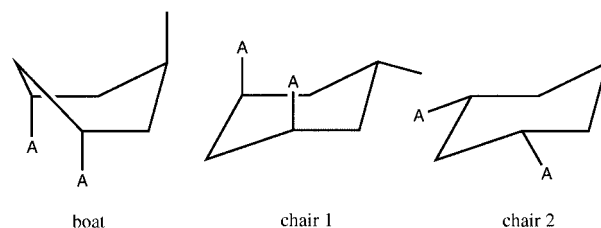
The diacid monoester **2** is also in the *boat* form, with features analogous to those of **1a** (Fig. 7). Two independent molecules are present in the asymmetric unit, which differ mainly by the positioning of carboxy protons, which are either on the same side or on opposite sides of the nearly parallel carboxy groups. Dimers are formed by hydrogen bonding, as in **1a** and **1b**



**Fig. 8** Molecular unit of **3** with atomic numbering scheme. Carboxy hydrogen atoms only are represented for clarity.



**Fig. 9** Crystal packing in **3** showing the formation of sheets parallel to the *ab* plane. Hydrogen bonds in dashed lines. Hydrogen atoms omitted for clarity.



**Fig. 10** Schematic representation of the three conformations observed. 'A' denotes carboxy groups. Methyl groups omitted.

[O $\cdots$ O 2.58(1)–2.66(1) Å, O–H 0.853–1.081 Å, H $\cdots$ O 1.56(1)–1.74(1) Å, O–H $\cdots$ O 165(1)–177(1)°]. The deviations of atoms C(1), C(3), C(4) and C(6) with respect to their mean plane, within  $\pm 0.049(3)$  and  $0.050(3)$  Å for molecules A and B, respectively, are lower than in **1a** and **1b**. The structure of the diacid monoamide **3** is more interesting. Only one molecule constitutes the asymmetric unit. As can be seen in Fig. 8, it assumes the *chair* conformation, but, at variance with the complexed form of **1**, the two carboxy groups are in axial positions, which places the two corresponding methyl groups in equatorial positions and also permits the formation of hydrogen-bonded dimers as in the preceding cases [O $\cdots$ O 2.75(1) and 2.61(1) Å, O–H 1.112 and 1.088 Å, H $\cdots$ O 1.65(1) and 1.54(1) Å, O–H $\cdots$ O 168(1) and 167(1)°]. Another hydro-

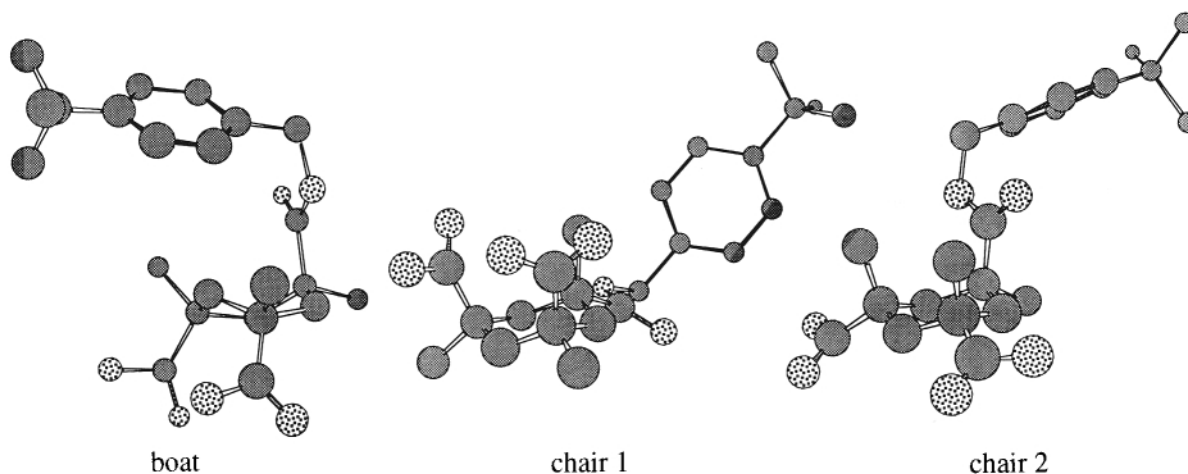


Fig. 11 Structure of **1** in *boat*, *chair 1* and *chair 2* forms, optimized with MOPAC (PM3). Hydrogen atoms omitted for clarity.

gen bond between the amide nitrogen atom and the amide oxygen atom of a neighbouring molecule [ $N \cdots O$  2.84(1) Å,  $N-H$  0.86 Å,  $H \cdots O$  2.03(1) Å,  $N-H \cdots O$  155(1) $^\circ$ ] further extends the hydrogen bonded network, which results in the formation of layers parallel to the *ab* plane (Fig. 9). By contrast with the preceding cases, the atoms C(1), C(3), C(4) and C(6) are close to their mean plane, with deviations within  $\pm 0.019(1)$  Å only. The conformation of **3** is in agreement with the analogous conformation of the *cis,trans* epimer of Kemp's triacid deduced from NMR experiments in solution.<sup>6</sup>

The present solid state investigation shows the occurrence of three different conformations, which are illustrated in Fig. 10. The most frequent is the *skew boat* conformation (**1a**, **1b**, **2**), observed for the first time, which may be particularly stable since, in the case of *cis,trans* epimers, it permits an equatorial positioning of the three methyl groups. Two *chair* forms can be obtained. The first one (*chair 1*), with two axial *cis*-carboxy groups, and subsequently two equatorial methyl groups, is observed in the uncomplexed molecule **3**, whereas the second one (*chair 2*), with two equatorial *cis*-carboxy groups, and only one equatorial methyl group, is observed in the deprotonated complexed form of molecule **1**. In all cases, specific constraints contribute to the final conformation in the solid state, namely the formation of dimers by hydrogen bonding in the conformations with two axial *cis*-carboxy groups (*boat*, *chair 1*) and of course the strong geometric constraint induced by macrocyclic complexation in the case of *chair 2*. A quantitative comparison of those conformations requires molecular calculations.

#### Semiempirical calculations

The structural simulation was performed for **1**, **2** and **3** by a semiempirical method using MOPAC (PM3).<sup>15</sup> However, the calculation on molecule **1** did not converge from an arbitrary starting structure in our normal calculation time period. It was evident that molecular flexibility and the *cis,trans* relationship between three methyl groups allowed many conformations with small differences in energy. Therefore we used the structure determined from the X-ray diffraction experiment as the input structure and the molecular dynamics calculations were performed to obtain local minima structures. The PM3 molecular orbital calculations were then applied to the structures with the option 'PRECISE' in order to increase the criteria by 100 times from the default. Even with this concession, many conformations are obtained as stable ones with a small difference in heat of formation. The *boat*, *chair 1* and *chair 2* forms obtained during these calculations resulted in the forms represented in Fig. 11. Their heats of formation ( $-281$ ,  $-279$  and  $-281$  kcal mol<sup>-1</sup>, respectively) can be considered as equal considering the accuracy of the present calculation (the heat of formation of the *boat* form with the methyl groups in 1,3-positions axial is

$-282$  kcal mol<sup>-1</sup>, identical to the one of the *boat* form in which they are equatorial), which prevents determination of the most stable form. Interestingly, more *boat* forms were observed as local minima with a variety of different side chain conformations.

The situation is similar for the cases of **2** and **3**. However, a disparity existed for **3** between the calculated *boat* conformation and the *chair* form observed in the crystal structure. In this case, we considered a single molecule without any accompanying species in the calculations, which is a situation quite different from that observed in the solid state. The hydrogen bonds involving the amide nitrogen atoms in the latter case could in some way stabilize the *chair* conformation. As a result it can be concluded that the *chair* and *boat* forms of both monoester and monoamide derivatives of *cis,trans*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid have intrinsically similar conformational stabilities. This result is in agreement with the observation of the two forms in the solid state structures here reported, in which the prediction of the final conformation, which results from the factors cited above (hydrogen bonds, complexation), is not as straightforward as the usual 'rules' may indicate.

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