Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

cis,cis,cis-1,2,4,5-Cyclohexanetetracarboxylic acid and its dianhydride

Akira Uchida,[a]* Masatoshi Hasegawa[b] and Hiroshi Manami[c]

[a]Department of Biomolecular Science, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi, Chiba 274-8510, Japan, [b]Department of Chemistry, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi, Chiba 274-8510, Japan, and [c]Research and Development Division, New Japan Chemical Company Ltd, 13 Yoshijima Yaguracho, Fushimi-ku, Kyoto 612-8224, Japan
Correspondence e-mail: auchida@biomol.sci.toho-u.ac.jp

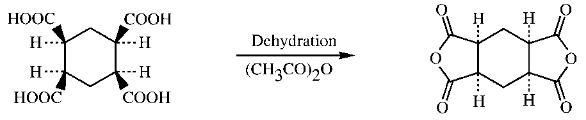
Received 1 May 2003
Accepted 16 June 2003
Online 12 July 2003

cis,*cis*,*cis*-1,2,4,5-Cyclohexanetetracarboxylic acid, $C_{10}H_{12}O_8$, (I), contains a mirror plane and the cyclohexane ring exhibits a chair conformation. Two crystallographically independent hydrogen bonds form $R_2^2(14)$, $R_2^2(16)$ and $R_4^4(16)$ ring motifs, and propagation of these two hydrogen bonds along the *c* and *b* axes generates $C_2^2(16)$ and $C_2^2(7)$ chains. *cis*,*cis*,*cis*-1,2:4,5-Cyclohexanetetracarboxylic dianhydride, $C_{10}H_8O_6$, (II), was prepared by the reaction of (I) with acetic anhydride. The cyclohexane ring of (II) exhibits a boat conformation and the dihedral angle between the two anhydro rings is 117.5 (1)°.

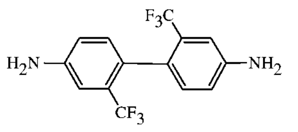
Comment

Over the past 15 years, considerable efforts have been made to obtain polyimide films possessing low linear thermal-expansion coefficients (CTEs) with the aim of reducing thermal stress (Numata *et al.*, 1986, 1987). Recently, polyimides with low dielectric constants (ε) have also been in demand in order to increase the signal-propagation rate in chips (Matsuura *et al.*, 1991; Sachdev *et al.*, 1999). We have attempted to develop polyimides with both low CTE and low ε values. According to the structure–property relationship, promising target materials include polyimides with stiff linear-chain structures for low CTEs and with low polarizability for low ε values (Hasegawa, 2001). We have highlighted the combination of cycloaliphatic 1,2:4,5-cyclohexanetetracarboxylic anhydride, (II), and rod-like 2,2′-bis(triflurometyl)benzidine, (III). The polyimide film (IV) resulted in low ε values, as expected, but did not show low CTE values (Hasegawa *et al.*, 2001). The present X-ray investigation was undertaken to obtain structural information about (II) and its intermediate, 1,2,4,5-cyclohexanetetracarboxylic acid, (I).

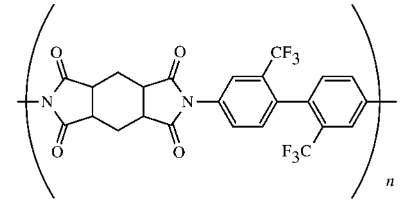
In (I), atoms C1 and C4 lie on a mirror plane (Fig. 1). The cyclohexane ring assumes a chair conformation, with the carboxyl group on atom C2 in an equatorial position and that on atom C3 in an axial position, resulting in the four carboxyl groups being in a mutually *cis* conformation, which is similar to that of tetramethyl *cis*,*cis*,*cis*-1,2,4,5-cyclohexanetetracarboxylate, (V) (Robinson *et al.*, 2000). Among the endocyclic angles, the C3—C4—C3^{i} angle [114.19 (18)°] of (I) (Table 1) and the corresponding angle [114.6 (3)°] of (V) are the largest as a result of the 1,3-diaxial repulsion, and the angles at atoms with axial substituents in both structures [110.67 (14)° in (I), and 108.9 (3) and 110.7 (3)° in (V)] are smaller [symmetry code: (i) $x, y, \frac{1}{2} - z$]. The two carbonyl groups of the carboxyl groups in (I) are synperiplanar with respect to an endocyclic bond [O1—C5—C2—C1 = −8.5 (2)° and O3—C6—C3—C2 = 3.0 (2)°], and all four carbonyl groups in (V) are also synperiplanar, with larger deviations from an eclipsed position [the corresponding torsion angles are −13.0 (6) and 21.4 (5)° for the equatorial carboxyl groups, and −19.8 (5) and −25.6 (5)° for the axial groups].



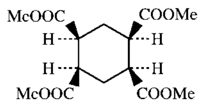
(I) (II)



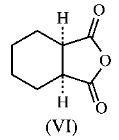
(III)



(IV)



(V)



(VI)

Two crystallographically independent hydrogen bonds (Table 2 and Fig. 2), *viz.* O2—H2···O3 and O4—H4···O1, form $R_2^2(14)$ rings about an inversion center, $R_2^2(16)$ rings along a 2_1 screw axis and $R_4^4(16)$ rigns about a twofold axis (Etter, 1990; Bernstein *et al.*, 1995). Propagation of these two hydrogen bonds along the *c* and *b* axes generates two chain motifs, *viz.* $C_2^2(16)$ and $C_2^2(7)$, resulting in a two-dimensional network perpendicular to the *a* axis.

In (II) (Fig. 3 and Table 3), the molecule possesses approximate C_{2v} symmetry. The displacement ellipsoids of atoms O3 and O4 are appreciably larger than those of the other atoms, which may be due to hydrolysis of the anhydro rings, and the hydrogen bonds associated with atoms O3 and O4 may promote the reaction (Table 4 and Fig. 4). Crystals kept at ambient temperature showed degradation of crystallinity after a few months.

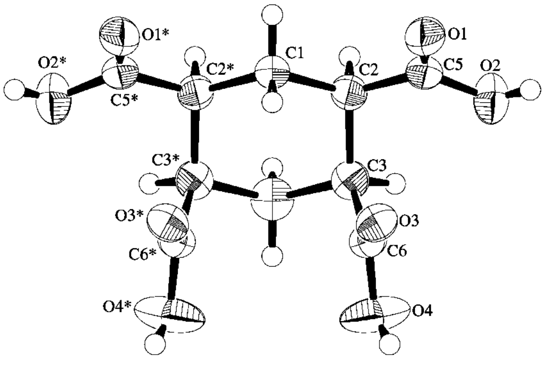


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level.

The cyclohexane ring of (II) assumes a boat conformation [Cremer & Pople (1975) puckering parameters are $Q = 0.749$ (2) Å, $\theta = 90.3$ (2)° and $\varphi = -61.8$ (2)°], while the cyclohexane ring of *cis*-1,2-cyclohexanedicarboxylic anhydride, (VI), adopts a chair conformation (Pawel *et al.*, 1982). The mean torsion angle of the cyclohexane ring of (I) is 52.2 (1)°, and the corresponding value in (VI) is 49 (4)°. The cyclohexane ring of (VI) is largely flattened at the anhydro side of the ring and puckered at the opposite side. Although the anhydro ring of (VI) adopts a slightly distorted envelope conformation, the anhydro rings of (II) assume a favorable planar conformation (maximum deviations are 0.03 Å for C1/C2/C8/O2/C7 and 0.01 Å for C4/C5/C10/O5/C9), as observed in succinic anhydride (Ehrenberg, 1965; Fodor *et al.*, 1984) and 5,6,11,12-tetrahydro-5,12;6,11-di-*o*-benzenodibenzo[*a*,*e*]cyclooctene-5,6-dicarboxylic anhydride (Cicogna *et al.*, 2002). For (VI), the strain induced on anhydro ring formation is relaxed by the deformations of the anhydro and cyclohexane rings, while for (II), the cyclohexane ring adopts a boat conformation, because the four carboxyl groups that are mutually *cis* form anhydro rings at either side of the cyclohexane ring.

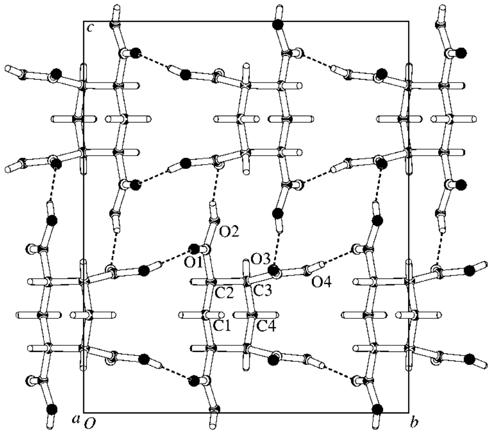


Figure 2
The crystal packing of (I), showing the hydrogen bonding.

The dihedral angle between the two anhydro rings is 117.5 (1)°. Hence, the polyimide chain containing (II) as an anhydride monomer is expected to be non-linear. We ascribe the high CTE of the polyimide film (IV) to the non-linearity of the polyimide chain.

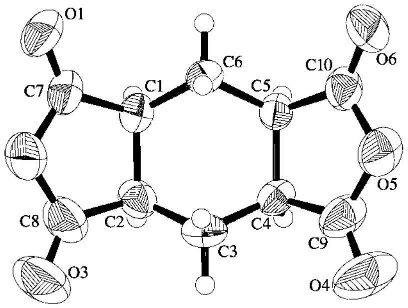


Figure 3
The molecular structure of (II), showing displacement ellipsoids at the 50% probability level.

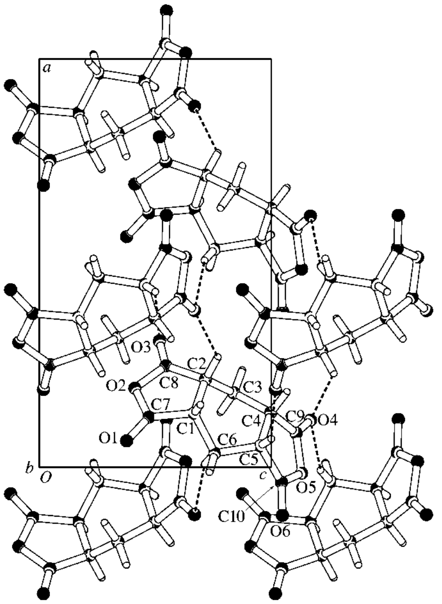


Figure 4
The crystal packing of (II), showing the hydrogen bonding.

Experimental

Compound (I) was prepared by esterifying 1,2:4,5-benzenetetracarboxylic dianhydride with methanol in the presence of $Ti(OBu)_4$ to give tetramethyl 1,2,4,5-benzenetetracarboxylate and then hydrogenating the latter at 423 K under 5 MPa hydrogen pressure in the presence of Ru on a carbon support (New Japan Chemical Company Ltd, 1996). Hydrolysis of the resulting ester in the presence of water and sulfuric acid gave (I). Compound (II) was prepared by the reaction of (I) with acetic anhydride. Crystals of (I) and (II) suitable for X-ray diffraction studies were obtained by slow evaporation of an aqueous solution and an acetic anhydride solution, respectively, at room temperature.

Compound (I)

Crystal data

$C_{10}H_{12}O_8$
$M_r = 260.20$
Orthorhombic, *Pbcm*
$a = 5.9425$ (18) Å
$b = 12.436$ (2) Å
$c = 14.999$ (2) Å
$V = 1108.5$ (4) Å^3
$Z = 4$
$D_x = 1.559$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 25.1$–$28.2°$
$\mu = 1.21$ mm^{-1}
$T = 298$ (2) K
Cubic, colorless
$0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku AFC-6*R* diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.774$, $T_{\max} = 0.786$
1188 measured reflections
1188 independent reflections
1038 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\max} = 74.9°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 19$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.041$
$wR(F^2) = 0.113$
$S = 1.11$
1188 reflections
88 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.3575P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0050 (7)

Table 1
Selected geometric parameters (Å, °) for (I).

C1—C2	1.5267 (19)	C3—C4	1.533 (2)
C2—C3	1.543 (2)		
C2$^{\rm i}$—C1—C2	112.13 (19)	C4—C3—C2	110.67 (14)
C1—C2—C3	113.18 (13)	C3$^{\rm i}$—C4—C3	114.19 (18)
C1—C2—C5—O1	−8.5 (2)	C2—C3—C6—O3	3.0 (2)

Symmetry code: (i) $x, y, \frac{1}{2} - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3$^{\rm ii}$	0.82	1.89	2.699 (2)	167
O4—H4···O1$^{\rm iii}$	0.82	1.83	2.653 (2)	176

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

Compound (II)

Crystal data

$C_{10}H_8O_6$
$M_r = 224.16$
Orthorhombic, $Pna2_1$
$a = 13.591$ (2) Å
$b = 9.306$ (2) Å
$c = 7.711$ (3) Å
$V = 975.2$ (5) Å^3
$Z = 4$
$D_x = 1.527$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 26.6$–$28.4°$
$\mu = 1.12$ mm^{-1}
$T = 298$ (2) K
Rod, colorless
$0.25 \times 0.25 \times 0.20$ mm

Data collection

Rigaku AFC-6*R* diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.723$, $T_{\max} = 0.799$
1074 measured reflections
1074 independent reflections
984 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.017$
$\theta_{\max} = 74.9°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 9$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.110$
$S = 1.07$
1074 reflections
146 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.1313P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.053 (11)

Table 3
Selected geometric parameters (Å, °) for (II).

O2—C7	1.371 (4)	C1—C2	1.531 (4)
O2—C8	1.382 (5)	C2—C3	1.512 (4)
O5—C9	1.384 (4)	C3—C4	1.532 (4)
O5—C10	1.397 (4)	C4—C5	1.531 (3)
C1—C6	1.525 (4)	C5—C6	1.535 (4)
C7—O2—C8	111.2 (3)	C2—C3—C4	108.74 (19)
C9—O5—C10	110.4 (2)	C5—C4—C3	113.9 (2)
C6—C1—C2	114.2 (2)	C4—C5—C6	112.8 (2)
C3—C2—C1	113.0 (2)	C1—C6—C5	108.8 (2)
C2—C1—C7—O1	174.0 (3)	C5—C4—C9—O4	177.5 (5)
C1—C2—C8—O3	−177.8 (6)	C4—C5—C10—O6	−179.3 (4)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O3$^{\rm iv}$	0.98	2.45	3.320 (5)	148
C2—H2···O4$^{\rm v}$	0.98	2.42	3.193 (4)	135
C6—H6*A*···O4$^{\rm vi}$	0.97	2.49	3.406 (4)	158

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

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation/Rigaku, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97, *PLATON* and *PARST* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1124). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacobazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Acta Cryst. (2003). C**59**, o435–o438 Akira Uchida *et al.* • $C_{10}H_{12}O_8$ and $C_{10}H_8O_6$ **o437**

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Cicogna, F., Ingrosso, G. & Marchetti, F. (2002). *Acta Cryst.* C**58**, o359–o361.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Ehrenberg, M. (1965). *Acta Cryst.* **19**, 698–703.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Fodor, G., Sussangkarn, K., Mathelier, H., Arnold, R., Karle, I. & George, C. (1984). *J. Org. Chem.* **49**, 5064–5069.

Hasegawa, M. (2001). *High Perform. Polym.* **13**, S93–106.

Hasegawa, M., Uchida, A. & Manami, H. (2001). *Polym. Prepr. Jpn*, **50**, 1767–1768.

Matsuura, T., Hasuda, Y., Nishi, S. & Yamada, N. (1991). *Macromolecules*, **24**, 5001–5005.

Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software.* Version 5.32. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation/Rigaku (2000). *TEXSAN.* Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

New Japan Chemical Company Ltd (1996). Patent No. JP1996–325196.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Numata, S., Fujisaki, K. & Kinjyo, N. (1987). *Polymer*, **28**, 2282–2288.

Numata, S., Oohara, S., Fujisaki, K., Imaizumi, K. & Kinjyo, N. (1986). *J. Appl. Polym. Sci.* **31**, 101–110.

Pawel, A., Woller, K.-H., Strumpel, M. & Luger, P. (1982). *Cryst. Struct. Commun.* **11**, 647–652.

Robinson, P. D., Hua, D. H., Fan, J., Liu, L., McGill, J. W., Arshid, M. & Meyers, C. Y. (2000). *Acta Cryst.* C**56**, 1471–1472.

Sachdev, H. S., Khojasteh, M. M. & Feger, C. (1999). Editors. In *Advances in Polyimides and Low Dielectric Polymers*. New York: Society of Plastic Engineers.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germary.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.