(1S*,2S*,4R*,5R*)-Cyclohexane-1,2,4,5-tetracarboxylic acid

Akira Uchida,[a]* Masatoshi Hasegawa,[b] Shinya Yamaguchi,[c] Eiichiro Takezawa,[c] Atsushi Ishikawa[c] and Takashi Kagayama[c]

[a]Department of Biomolecular Science, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan, [b]Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan, and [c]Department of Research and Development, Gas Chemical Division, Iwatani Industrial Gases Corporation Ltd., 10 Otakasu-cho, Amagasaki, Hyogo 660-0842, Japan

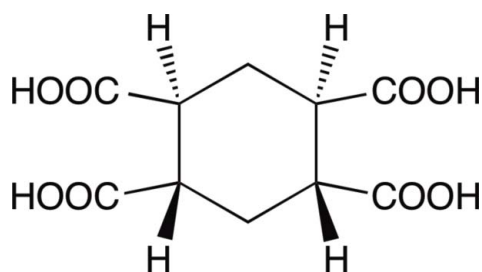Correspondence e-mail: auchida@biomol.sci.toho-u.ac.jp

The title compound, $C_{10}H_{12}O_8$, a prospective raw material for colourless polyimides which are applied to electronic and microelectronic devices, lies about an inversion centre and the cyclohexane ring adopts a chair conformation. Two crystallographically independent carboxylic acid groups on adjacent C atoms are in equatorial positions, resulting in a mutually *trans* conformation. In the crystal, O—H···O hydrogen bonds around an inversion centre and a threefold rotoinversion axis, respectively, form an inversion dimer with an $R_2^2(8)$ motif and a trimer with an $R_3^3(12)$ motif.

Related literature

For background to polyimides, see: Ando *et al.* (2010); Hasegawa *et al.* (2007, 2013); Hasegawa & Horie (2001). For related structures, see: Uchida *et al.* (2003, 2012).

Experimental

Crystal data

$C_{10}H_{12}O_8$	$Z = 9$
$M_r = 260.20$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}$	$\mu = 0.13$ mm^{-1}
$a = 17.6970$ (6) Å	$T = 298$ K
$c = 9.5455$ (6) Å	$0.33 \times 0.26 \times 0.26$ mm
$V = 2589.0$ (2) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	6439 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1653 independent reflections
$T_{min} = 0.891$, $T_{max} = 0.966$	1388 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.119$	
$S = 1.06$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
1653 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
90 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H4···O1[i]	0.81 (3)	1.93 (3)	2.705 (2)	160 (3)
O4—H5···O3[ii]	0.94 (3)	1.70 (3)	2.632 (1)	176 (3)

Symmetry codes: (i) $-x + y + 1, -x + 1, z$; (ii) $-x + 1, -y, -z + 1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2013*.

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supplementary materials

(1*S**,2*S**,4*R**,5*R**)-Cyclohexane-1,2,4,5-tetracarboxylic acid

Akira Uchida, Masatoshi Hasegawa, Shinya Yamaguchi, Eiichiro Takezawa, Atsushi Ishikawa and Takashi Kagayama

1. Comment

Aromatic polyimides (PI) are one of the most important heat-resistant polymeric materials in various electronic applications for their reliable combined properties: considerably high glass transition temperatures (T_g), non-flammability, and good dielectric and mechanical properties (Ando *et al.*, 2010). However, intensive coloration of conventional PI films, which arises from charge-transfer (CT) interactions (Hasegawa & Horie, 2001), often disturbs their applications as optical materials. A recent strong demand is to replace inorganic glass substrates in flat panel displays (300–700 μm thick) by plastic substrates (< 100 μm thick), thereby the displays become drastically light and flexible. However, it is difficult to obtain the substrate materials simultaneously possessing excellent combined properties, *i.e.*, optical transparency, heat resistance, dimensional stability against thermal cycles undergoing in the device fabrication process, flexibility, and processability. The most effective strategy for completely erasing the coloration is to inhibit the CT interactions by using non-aromatic (cycloaliphatic) monomers either in tetracarboxylic dianhydride or diamine components. For this purpose, we previously investigated the steric structures of hydrogenated pyromellitic dianhydride isomers, *i.e.*, 1*S*,2*R*,4*S*,5*R*-cyclohexanetetracarboxylic dianhydride (H-PMDA) (Uchida *et al.*, 2003) and 1*R*,2*S*,4*S*,5*R*-cyclohexanetetracarboxylic dianhydride (H"-PMDA) (Uchida *et al.*, 2012). H"-PMDA showed much higher reactivity with diamines than H-PMDA and provided highly flexible colourless PI films with significantly improved solution-processability while keeping very high T_gs (Hasegawa *et al.*, 2007, 2013). The results are based on a peculiar steric structure of H"-PMDA. Unfortunately, neither H-PMDA nor H"-PMDA led to PI films with low coefficients of thermal expansion (CTE) required for the excellent dimensional stability, probably owing to their non-linear/non-planar steric structures. An additional H-PMDA isomer, *i.e.*, 1*S*,2*S*,4*R*,5*R*-cyclohexanetetracarboxylic dianhydride (H′-PMDA) can be expected to derive a novel low-CTE colourless PI system. The present work reports a crystal structure of a hydrolyzed compound of H′-PMDA.

2. Experimental

The title compound, (I), was synthesized as follows. Pyromellitic dianhydride was first hydrolyzed with a NaOH aqueous solution. The pyromellitic acid tetrasodium salt formed was hydrogenated in a high-pressure hydrogen atmosphere at 160 °C in the presence of a ruthenium catalyst. After hydrogenation was completed, the solution was additionally heated at a precisely controlled temperature for several hours, and cooled to room temperature. The solution was neutralized by slowly adding conc. HCl. The white precipitate formed was collected by filtration, recrystallized from water, and dried in vacuum at 80 °C for 5 h to obtain crystals of (I) suitable for X-ray analysis.

3. Refinement

All H atoms were observable in a difference Fourier map. H atoms on O atoms were refined freely [O—H = 0.81 (3) and 0.94 (3) Å]. Other H atoms were placed in calculated positions with C—H = 0.97–0.98 Å, and allowed to ride on their carrier atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008).
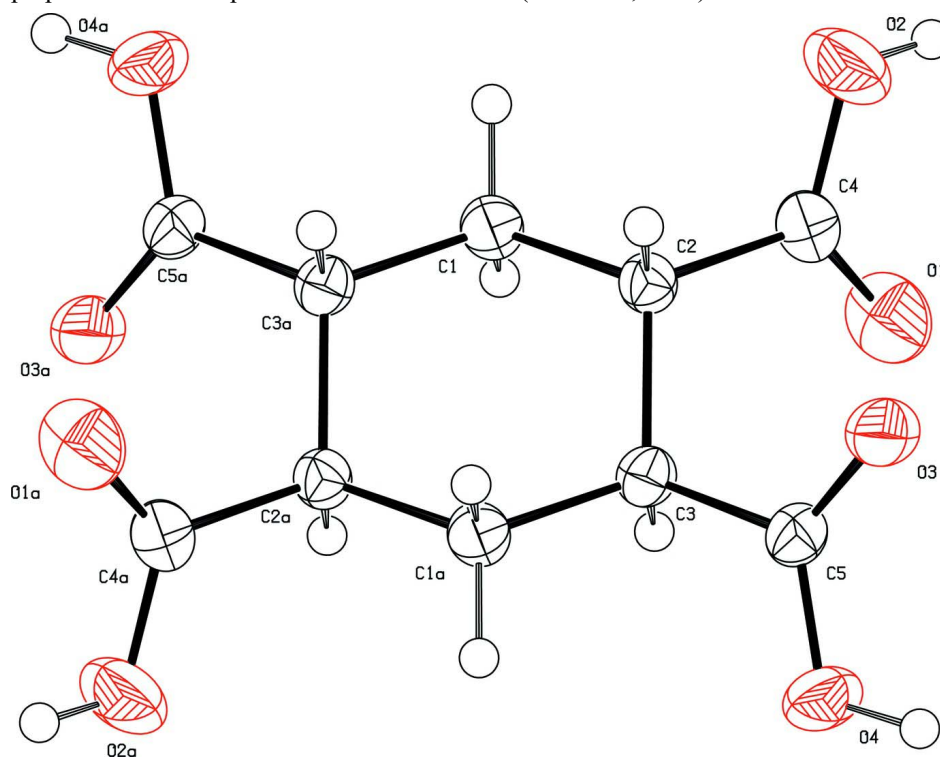

Figure 1

The molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level. H atoms are represented by circles of arbitrary size.
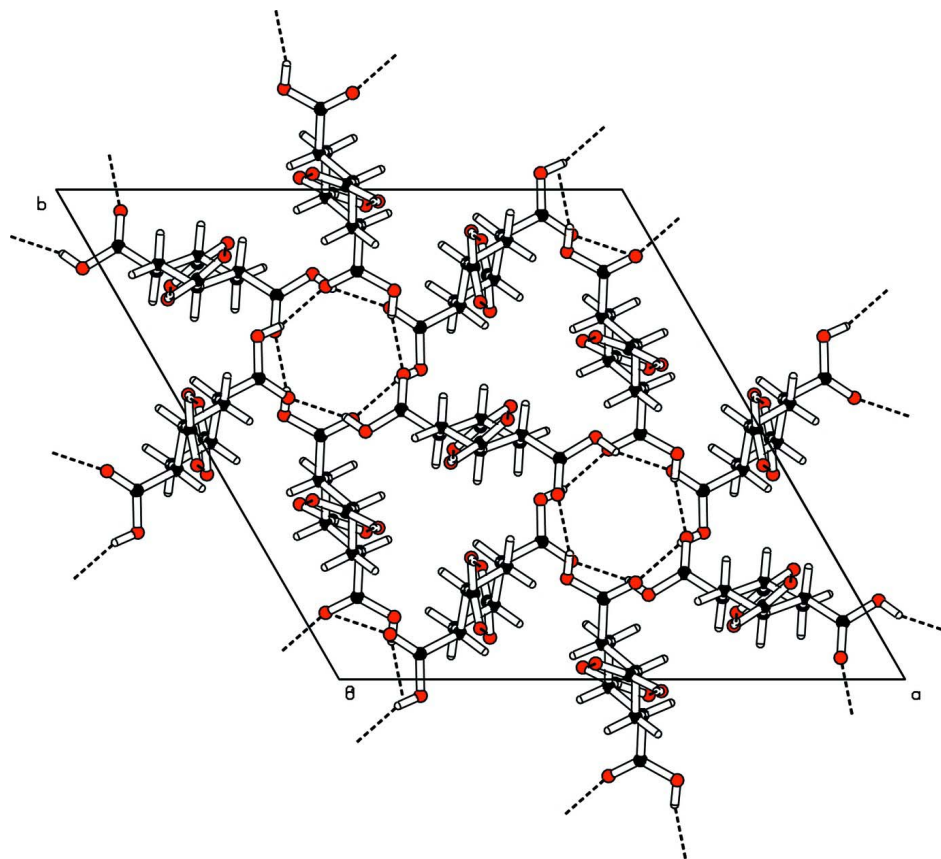
Figure 2

The packing of the title compound, viewed down the *c* axis,

(1*S**,2*S**,4*R**,5*R**)-Cyclohexane-1,2,4,5-tetracarboxylic acid

Crystal data

$C_{10}H_{12}O_8$	$D_x = 1.502$ Mg m^{-3}
$M_r = 260.20$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $R\overline{3}$	Cell parameters from 2340 reflections
$a = 17.6970$ (6) Å	$\theta = 2.3$–30.0°
$c = 9.5455$ (6) Å	$\mu = 0.13$ mm^{-1}
$V = 2589.0$ (2) Å^3	$T = 298$ K
$Z = 9$	Block, colourless
$F(000) = 1224$	$0.33 \times 0.26 \times 0.26$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	1653 independent reflections
Radiation source: fine-focus sealed tube	1388 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 30.0°$, $\theta_{min} = 2.3°$
$T_{min} = 0.891$, $T_{max} = 0.966$	$h = -24 \rightarrow 21$
6439 measured reflections	$k = -20 \rightarrow 24$
	$l = -13 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.041$	and constrained refinement
$wR(F^2) = 0.119$	$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 1.9122P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1653 reflections	$(\Delta/\sigma)_{max} < 0.001$
90 parameters	$\Delta\rho_{max} = 0.38$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.51496 (8)	0.07671 (7)	−0.08154 (11)	0.0279 (3)
H1A	0.4929	0.1116	−0.1242	0.034*
H1B	0.5770	0.1045	−0.1011	0.034*
C2	0.50063 (7)	0.07293 (7)	0.07787 (11)	0.0233 (2)
H2	0.4383	0.0484	0.0969	0.028*
C3	0.53165 (7)	0.01523 (7)	0.14585 (11)	0.0242 (2)
H3	0.5944	0.0414	0.1285	0.029*
C4	0.55013 (8)	0.16503 (7)	0.13456 (12)	0.0283 (3)
C5	0.51702 (8)	0.00882 (8)	0.30236 (12)	0.0267 (3)
O1	0.62253 (6)	0.19739 (7)	0.18327 (13)	0.0471 (3)
H4	0.5352 (17)	0.2558 (18)	0.151 (3)	0.083 (8)*
O2	0.50596 (8)	0.20615 (8)	0.12244 (15)	0.0543 (3)
O3	0.46919 (7)	0.03210 (7)	0.35746 (9)	0.0380 (3)
O4	0.55716 (7)	−0.02417 (7)	0.37025 (10)	0.0400 (3)
H5	0.5485 (19)	−0.0245 (19)	0.467 (3)	0.110 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0389 (6)	0.0247 (5)	0.0218 (5)	0.0171 (5)	0.0021 (4)	0.0033 (4)
C2	0.0259 (5)	0.0227 (5)	0.0214 (5)	0.0123 (4)	0.0009 (4)	0.0002 (4)
C3	0.0274 (5)	0.0268 (5)	0.0198 (5)	0.0147 (4)	0.0014 (4)	0.0015 (4)
C4	0.0309 (6)	0.0246 (5)	0.0267 (5)	0.0119 (5)	0.0041 (4)	0.0008 (4)
C5	0.0310 (6)	0.0282 (5)	0.0214 (5)	0.0153 (5)	−0.0010 (4)	0.0009 (4)
O1	0.0302 (5)	0.0342 (5)	0.0672 (8)	0.0088 (4)	−0.0056 (5)	−0.0095 (5)
O2	0.0559 (7)	0.0333 (5)	0.0820 (9)	0.0285 (5)	−0.0212 (6)	−0.0187 (5)
O3	0.0517 (6)	0.0540 (6)	0.0237 (4)	0.0380 (5)	0.0042 (4)	0.0031 (4)
O4	0.0531 (6)	0.0611 (7)	0.0238 (4)	0.0420 (6)	0.0015 (4)	0.0059 (4)

Geometric parameters (Å, º)

C1—C3ⁱ	1.5370 (16)	C3—H3	0.9800
C1—C2	1.5386 (15)	C4—O1	1.2049 (16)
C1—H1A	0.9700	C4—O2	1.3126 (16)
C1—H1B	0.9700	C5—O3	1.2295 (15)
C2—C4	1.5130 (15)	C5—O4	1.2961 (14)
C2—C3	1.5251 (15)	O2—H4	0.81 (3)
C2—H2	0.9800	O4—H5	0.94 (3)
C3—C5	1.5108 (15)		
C3ⁱ—C1—C2	111.06 (9)	C5—C3—C1ⁱ	109.53 (9)
C3ⁱ—C1—H1A	109.4	C2—C3—C1ⁱ	110.89 (9)
C2—C1—H1A	109.4	C5—C3—H3	108.3
C3ⁱ—C1—H1B	109.4	C2—C3—H3	108.3
C2—C1—H1B	109.4	C1ⁱ—C3—H3	108.3
H1A—C1—H1B	108.0	O1—C4—O2	123.84 (12)
C4—C2—C3	111.15 (9)	O1—C4—C2	123.74 (11)
C4—C2—C1	108.23 (9)	O2—C4—C2	112.41 (11)
C3—C2—C1	110.07 (9)	O3—C5—O4	124.14 (11)
C4—C2—H2	109.1	O3—C5—C3	121.25 (10)
C3—C2—H2	109.1	O4—C5—C3	114.60 (10)
C1—C2—H2	109.1	C4—O2—H4	109.5 (18)
C5—C3—C2	111.43 (9)	C5—O4—H5	111.8 (17)
C3ⁱ—C1—C2—C4	178.45 (9)	C1—C2—C4—O1	−95.39 (14)
C3ⁱ—C1—C2—C3	56.81 (13)	C3—C2—C4—O2	−155.53 (11)
C4—C2—C3—C5	61.11 (12)	C1—C2—C4—O2	83.49 (13)
C1—C2—C3—C5	−179.00 (9)	C2—C3—C5—O3	14.47 (16)
C4—C2—C3—C1ⁱ	−176.60 (9)	C1ⁱ—C3—C5—O3	−108.61 (13)
C1—C2—C3—C1ⁱ	−56.70 (13)	C2—C3—C5—O4	−166.81 (10)
C3—C2—C4—O1	25.59 (16)	C1ⁱ—C3—C5—O4	70.12 (13)

Symmetry code: (i) −*x*+1, −*y*, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H4···O1ⁱⁱ	0.81 (3)	1.93 (3)	2.705 (2)	160 (3)
O4—H5···O3ⁱⁱⁱ	0.94 (3)	1.70 (3)	2.632 (1)	176 (3)

Symmetry codes: (ii) −*x*+*y*+1, −*x*+1, *z*; (iii) −*x*+1, −*y*, −*z*+1.