Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O7*A*	0.1774 (1)	0.1790 (2)	0.0307 (2)	0.0686 (7)
O8*A*	0.12290 (9)	0.0437 (2)	0.1996 (2)	0.0479 (6)
N1*A*	−0.0903 (1)	0.3627 (2)	0.1649 (2)	0.0443 (7)
C2*A*	−0.0150 (1)	0.2886 (2)	0.1827 (2)	0.0353 (7)
C3*A*	0.0343 (1)	0.2285 (2)	0.0831 (2)	0.0371 (7)
C4*A*	0.0043 (2)	0.2488 (3)	−0.0403 (2)	0.0477 (9)
C5*A*	−0.0724 (2)	0.3250 (3)	−0.0597 (3)	0.0516 (9)
C6*A*	−0.1177 (2)	0.3778 (3)	0.0443 (3)	0.0501 (9)
C7*A*	0.1190 (1)	0.1498 (3)	0.1004 (2)	0.0441 (9)
C8*A*	0.2057 (2)	−0.0233 (4)	0.2282 (4)	0.0657 (13)

Table 2. *Geometric parameters* (Å, °)

O7*A*—C7*A*	1.204 (2)	C2*A*—C2*B*	1.493 (2)
O8*A*—C7*A*	1.332 (2)	C3*A*—C4*A*	1.390 (3)
O8*A*—C8*A*	1.447 (3)	C3*A*—C7*A*	1.490 (2)
N1*A*—C2*A*	1.342 (2)	C4*A*—C5*A*	1.371 (3)
N1*A*—C6*A*	1.345 (3)	C5*A*—C6*A*	1.372 (3)
C2*A*—C3*A*	1.388 (2)		
O8*A*···C2*B*	2.849 (3)	N1*A*···C7*B*	3.001 (3)
O8*A*···N1*B*	2.913 (3)		
C7*A*—O8*A*—C8*A*	115.4 (2)	C4*A*—C3*A*—C7*A*	118.1 (2)
C2*A*—N1*A*—C6*A*	117.2 (2)	C3*A*—C4*A*—C5*A*	119.5 (2)
N1*A*—C2*A*—C3*A*	122.9 (2)	C4*A*—C5*A*—C6*A*	118.6 (2)
N1*A*—C2*A*—C2*B*	114.6 (2)	N1*A*—C6*A*—C5*A*	123.7 (2)
C3*A*—C2*A*—C2*B*	112.3 (2)	O8*A*—C7*A*—C3*A*	113.2 (2)
C2*A*—C3*A*—C7*A*	123.8 (2)	O7*A*—C7*A*—C3*A*	122.9 (2)
C2*A*—C3*A*—C4*A*	118.1 (2)	O7*A*—C7*A*—O8*A*	123.9 (2)

The diester (3) was obtained by oxidation of 1,10-phenanthroline to 2,2′-bipyridine-3,3′-dicarboxylic acid (Baxter, Connor, Povey, Powell & Wallis, 1992), esterification with methyl orthochloroformate/*N*-methylmorpholine (Rebek, Trend, Wattley & Chakravorti, 1979) and crystallization from acetone.

We thank Professor M. B. Hursthouse and the SERC X-ray Crystallography Service, University of Wales, Cardiff, for collecting the diffraction data, Professor J. A. Ballantine and the SERC Mass Spectrometry Service for some data and the University of Kent for a studentship (to CRR) and further financial help.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71395 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1057]

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Structure of Pentaerythritol Tetrabenzoate

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(*Received* 30 *June* 1992; *accepted* 8 *April* 1993)

Abstract

Distances and angles about the central C atom are in agreement with literature values for pentaerythritol and its ester derivatives; three C—'central C'—C angles are < 109° while two are > 109°. The O···O distances are incompatible with metal complexation; this is consistent with unsuccessful attempts to form complexes with various metal cations.

Comment

This project was undertaken to explore the usefulness of the title compound (PETB) as a metal ligand. Atomic coordinates and isotropic thermal parameters are given in Table 1, bond lengths and angles in Table 2. The molecular structure with atom labelling is shown in Fig. 1.

Acta Crystallographica Section C
ISSN 0108-2701 ©1993

Each carbonyl appears to align *roughly* in a 'head-to-tail' fashion around a pseudo-C_3 axis along the C—C1 bonds. The C—C distances around the central C atoms in PETB, pentaerythritol (Eilerman & Rudman, 1979) and the tetranitrate (Conant, Cady, Ryan, Yarnell & Newsam, 1979), tetraacetate (Goodwin & Hardy, 1938), tetrathionobenzoate (Moore & Palmer, 1991) and tetracinnamate (Tieghi & Zocchi, 1972) derivatives of pentaerythritol are equal. Many of these compounds are similarly distorted around the central C atom with, usually, two angles greater than and two less than 109°. In PETB, three of the C—'central C'—C angles are significantly ($> 3\sigma$) less than 109°; two are greater.

When viewed down any of the four C(n)—C1 (n = 2, 3, 4, 5) bonds, two of the non-carbonyl O atoms point in the general direction of the viewer ('up') and the other points away ('down'). Fig. 1 illustrates this along the C2—C1 bond; the torsion angles C2—C1—C3—O2 and C2—C1—C5—O4 are 70.8 (4) and 61.3 (4)°, respectively (average 66.1°, difference between up torsion angles 9.4°), while C2—C1—C4—O3 is − 170.9 (3)° (≡ + 189.1°, *i.e.* down); there are three other sets of three torsional angles about the C1—C(n) bonds which are similarly disposed (*cf.* Table 2). In all four instances, the pairs of torsion angles involving the two up O atoms are within 5–10° of each other and the magnitudes of all the up torsion angles range between 50 and 71° (*cf.* Table 2). The four complementary torsion angles for all the down O atoms are 123–128° from the average value of the corresponding up torsional angles. For example, C2—C1—C4—O3 differs by 123.1° from the average of C2—C1—C3—O2 and C2—C1—C5—O4. Examination of the non-bonded O···O distances listed in Table 2 reveals that only the O2···O3 distance [3.131 (5) Å] is comparable to the ~2.8 Å O···O distance expected in oxalate-containing compounds. Not only does the 'two up – one down' phenomenon (probably the result of steric influences) destroy ideal C_3 symmetry, but the resultant distance incompatibility and the fact that O2 and O3 are non-carbonyl O atoms greatly diminish the probability of PETB being useful as a bidentate ligand. This is consistent with attempts to form complexes with Zn^{2+}, Be^{2+}, NH_4^+, Na^+, Ca^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Co^{3+} and Ni^{2+} dissolved in a series of solvents (acetone/water, acetonitrile/water, chloroform, dioxane, tetrahydrofuran/water) which all produced crystals of the pure tetrabenzoate, but no complexes.

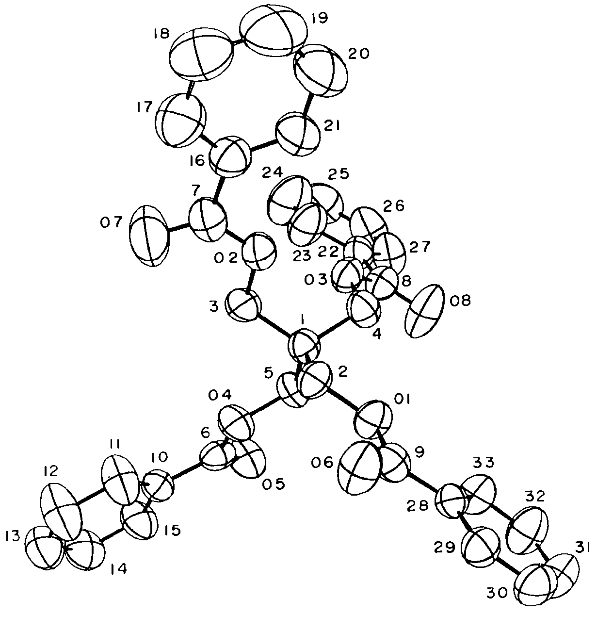

Fig. 1. The pentaerythritol tetrabenzoate molecule showing 50% probability ellipsoids.

Experimental

Crystal data

$C_{33}H_{28}O_8$
M_r = 552.58
Monoclinic
$P2_1/a$
a = 12.498 (4) Å
b = 18.723 (5) Å
c = 12.680 (3) Å
β = 100.87 (2)°
V = 2914 (1) Å^3
Z = 4
D_x = 1.260 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 20.6–44.5°
μ = 0.753 mm^{-1}
T = 288 K
Prism
0.23 × 0.18 × 0.18 mm
Colourless

Data collection

Siemens $P3$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7751 measured reflections
3875 independent reflections
2074 observed reflections [$F \geq 3\sigma(F)$ and $I \geq 3\sigma(I)$]
$R_{\rm int}$ = 0.057

$\theta_{\rm max}$ = 55°
h = 0 → 14
k = −20 → 20
l = −14 → 14
3 standard reflections monitored every 50 reflections
intensity variation: ±4%

Refinement

Refinement on F
Final R = 0.052
wR = 0.033
S = 2.48
2074 reflections
370 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$\Delta\rho_{\rm max}$ = 0.3 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.2 e Å^{-3}
Extinction correction: none
Atomic scattering factors from Hanson, Herman, Lea & Skillman (1964) (non-H) and Stewart, Davidson & Simpson (1965) (H)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}
O1	0.0591 (2)	0.7591 (2)	0.2494 (2)	4.6
O2	−0.0036 (3)	0.8542 (2)	0.5317 (2)	5.4
O3	0.2437 (3)	0.8591 (2)	0.5173 (2)	5.2
O4	0.0461 (2)	0.9453 (1)	0.2454 (2)	4.5
O5	0.1720 (3)	1.0075 (2)	0.1806 (3)	5.5
O6	−0.0975 (3)	0.7089 (2)	0.1724 (3)	6.3
O7	−0.1412 (3)	0.9236 (2)	0.5493 (3)	10.3
O8	0.3918 (3)	0.8209 (2)	0.4597 (3)	9.2
C1	0.0835 (4)	0.8529 (2)	0.3782 (3)	4.1
C2	−0.0001 (3)	0.8019 (2)	0.3150 (3)	4.0
C3	0.0231 (4)	0.8996 (2)	0.4485 (3)	4.3
C4	0.1762 (4)	0.8100 (2)	0.4463 (3)	4.6
C5	0.1341 (3)	0.9026 (2)	0.3060 (3)	4.2
C6	0.0784 (5)	0.9985 (2)	0.1871 (4)	5.2
C7	−0.0878 (5)	0.8711 (3)	0.5752 (4)	7.3
C8	0.3509 (5)	0.8603 (3)	0.5129 (4)	5.8
C9	0.0002 (4)	0.7138 (2)	0.1794 (4)	4.4
C10	−0.0152 (4)	1.0423 (2)	0.1326 (4)	4.1
C11	−0.1202 (5)	1.0313 (3)	0.1457 (4)	6.9
C12	−0.2031 (4)	1.0735 (3)	0.0914 (5)	7.9
C13	−0.1814 (5)	1.1265 (3)	0.0236 (4)	6.8
C14	−0.0763 (5)	1.1375 (3)	0.0112 (4)	6.5
C15	0.0068 (4)	1.0956 (3)	0.0654 (4)	5.4
C16	−0.1063 (5)	0.8210 (3)	0.6610 (4)	4.7
C17	−0.2025 (5)	0.8246 (3)	0.6990 (5)	6.8
C18	−0.2199 (5)	0.7779 (4)	0.7800 (5)	7.3
C19	−0.1404 (7)	0.7301 (4)	0.8207 (5)	8.7
C20	−0.0451 (6)	0.7268 (3)	0.7829 (5)	8.9
C21	−0.0282 (5)	0.7720 (3)	0.7007 (4)	6.6
C22	0.4094 (5)	0.9170 (2)	0.5833 (4)	5.6
C23	0.3558 (4)	0.9652 (3)	0.6366 (4)	7.3
C24	0.4146 (6)	1.0182 (3)	0.6984 (5)	9.7
C25	0.5257 (7)	1.0222 (3)	0.7083 (5)	7.3
C26	0.5791 (5)	0.9747 (3)	0.6562 (5)	7.3
C27	0.5217 (5)	0.9214 (3)	0.5924 (4)	6.8
C28	0.0660 (4)	0.6734 (2)	0.1152 (4)	4.0
C29	0.0140 (4)	0.6224 (2)	0.0446 (4)	4.6
C30	0.0723 (5)	0.5849 (2)	−0.0191 (4)	5.4
C31	0.1822 (5)	0.5977 (3)	−0.0144 (4)	5.8
C32	0.2332 (4)	0.6488 (3)	0.0570 (5)	6.7
C33	0.1762 (4)	0.6865 (2)	0.1218 (4)	5.3

Table 2. *Selected interatomic distances* (Å), *bond angles* (°) *and torsion angles* (°)

The signs of the torsion angles are as per Klyne & Prelog (1960).

O1—C2	1.455 (4)	C11—C12	1.378 (5)
O1—C9	1.341 (5)	C12—C13	1.373 (6)
O2—C3	1.442 (4)	C13—C14	1.367 (6)
O2—C7	1.315 (5)	C14—C15	1.377 (5)
O3—C4	1.443 (4)	C16—C17	1.378 (6)
O3—C8	1.352 (5)	C16—C21	1.365 (6)
O4—C5	1.456 (4)	C17—C18	1.396 (7)
O4—C6	1.348 (5)	C18—C19	1.364 (7)
O5—C6	1.200 (5)	C19—C20	1.367 (7)
O6—C9	1.210 (5)	C20—C21	1.390 (7)
O7—C7	1.199 (5)	C22—C23	1.375 (6)
O8—C8	1.180 (5)	C22—C27	1.389 (6)
C1—C2	1.527 (5)	C23—C24	1.386 (6)
C1—C3	1.544 (5)	C24—C25	1.373 (7)
C1—C4	1.534 (5)	C25—C26	1.356 (7)
C1—C5	1.524 (5)	C26—C27	1.395 (6)
C6—C10	1.487 (5)	C28—C29	1.384 (5)
C7—C16	1.487 (6)	C28—C33	1.386 (5)
C8—C22	1.488 (6)	C29—C30	1.379 (6)
C9—C28	1.472 (5)	C30—C31	1.384 (6)
C10—C11	1.369 (6)	C31—C32	1.388 (6)
C10—C15	1.373 (5)	C32—C33	1.380 (5)
O2···O3	3.131 (5)	O6···O1	2.223 (4)
O4···O1	3.491 (4)	O7···O2	2.200 (5)
O5···O4	2.235 (4)	O8···O3	2.233 (5)
C2—O1—C9	116.8 (4)	C11—C12—C13	120.5 (5)
C3—O2—C7	118.6 (4)	C12—C13—C14	119.2 (5)
C4—O3—C8	116.9 (4)	C13—C14—C15	120.5 (5)
C5—O4—C6	114.9 (4)	C10—C15—C14	120.2 (5)
C2—C1—C3	107.2 (4)	C7—C16—C17	119.4 (6)
C2—C1—C4	109.8 (3)	C7—C16—C21	119.6 (5)
C2—C1—C5	112.7 (3)	C16—C17—C18	119.6 (6)
C3—C1—C4	111.8 (4)	C17—C18—C19	119.1 (6)
C3—C1—C5	107.7 (3)	C18—C19—C20	121.2 (7)
C4—C1—C5	107.6 (4)	C19—C20—C21	120.0 (6)
C1—C2—O1	105.9 (3)	C16—C21—C20	119.2 (5)
C1—C3—O2	107.1 (3)	C8—C22—C23	122.3 (6)
C1—C4—O3	107.9 (3)	C8—C22—C27	117.8 (5)
C1—C5—O4	107.2 (3)	C22—C23—C24	119.5 (5)
O4—C6—O5	122.5 (5)	C23—C24—C25	120.7 (6)
O4—C6—C10	111.8 (4)	C24—C25—C26	120.1 (6)
O2—C7—O7	122.1 (5)	C25—C26—C27	120.3 (6)
O2—C7—C16	113.7 (5)	C22—C27—C26	119.5 (5)
O3—C8—O8	123.7 (5)	C9—C28—C29	118.0 (5)
O3—C8—C22	111.4 (5)	C9—C28—C33	121.8 (5)
O1—C9—O6	121.2 (5)	C28—C29—C30	119.7 (5)
O1—C9—C28	113.3 (4)	C29—C30—C31	121.1 (5)
C6—C10—C11	123.3 (4)	C30—C31—C32	118.5 (5)
C6—C10—C15	117.2 (5)	C31—C32—C33	121.1 (5)
C10—C11—C12	120.1 (5)	C28—C33—C32	119.5 (4)
C3—C1—C2—O1	179.7 (7)	C2—O1—C9—O6	−1 (1)
C4—C1—C2—O1	−58.6 (4)	C2—O1—C9—C28	179.1 (4)
C5—C1—C2—O1	61.4 (4)	C3—O2—C7—O7	−1.6 (8)
C2—C1—C3—O2	70.8 (4)	C3—O2—C7—C16	−179.1 (4)
C4—C1—C3—O2	−49.6 (5)	C4—O3—C8—O8	−4.6 (7)
C5—C1—C3—O2	−167.7 (3)	C4—O3—C8—C22	175.4 (3)
C2—C1—C4—O3	−170.9 (3)	C5—O4—C6—O5	4.1 (6)
C3—C1—C4—O3	−52.0 (5)	C5—O4—C6—C10	−176.7 (4)
C5—C1—C4—O3	66.1 (4)	O4—C6—C10—C11	3.3 (6)
C2—C1—C5—O4	61.3 (4)	O4—C6—C10—C15	−176.1 (4)
C3—C1—C5—O4	−56.8 (4)	O2—C7—C16—C17	−168.0 (5)
C4—C1—C5—O4	−177.5 (3)	O2—C7—C16—C21	11.7 (7)
C1—C2—O1—C9	−174.7 (3)	O3—C8—C22—C23	−5.6 (7)
C1—C3—O2—C7	−154.0 (4)	O3—C8—C22—C27	175.8 (4)
C1—C4—O3—C8	−124.3 (4)	O1—C9—C28—C29	176.6 (4)
C1—C5—O4—C6	172.1 (3)	O1—C9—C28—C33	−5.2 (6)

The title compound was obtained by recrystallization from acetonitrile-acetone-methanol (6:5:10). All 41 non-H atoms were located by *MULTAN76* (Main, Woolfson & Germain, 1976) using the coordinates for benzoate and neopentane, and a *K* curve to compute the *E* values. Aromatic H atoms were set at 1.00 Å from the respective C atoms while bisecting the C—C—C angle; ethyl H atoms were placed in tetrahedral positions at a distance of 1.10 Å. Anisotropic thermal parameters were used for all H atoms; these were assigned the B_{eq} value of the associated C atom. Programs used: *MULTAN76*; *ALLS* (Lapp & Jacobson, 1979); *FOUR* (Powell & Jacobson, 1980); *ORFFE* (Busing, Martin & Levy, 1964); *ORTEP*II (Johnson, 1971).

Acknowledgements are due to NMSU's Undergraduate Research Stipend Program and Computer Services for the computer time.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71253 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1019]

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Acta Cryst. (1993). C**49**, 1985–1988

(Z)-Perchlorostilbene

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(*Received* 9 *February* 1993; *accepted* 11 *May* 1993)

Abstract

Steric repulsion of the bulky Cl atoms causes the perchlorophenyl rings to rotate out of the plane of the central double bond eliminating the conjugation between the three π systems. Molecules pack as interlocking dimers and the dimeric pairs adhere by face-to-face π stacking.

Comment

Sterically congested stilbenes (Gano, Park, Subramaniam, Lenoir & Gleiter, 1991; Gano, Park, Pinkerton & Lenoir 1990, 1991; Gano, Subramaniam & Birnbaum, 1990) and the effect that steric congestion has on (*Z*)/(*E*)-isomerization barriers (Gano, Lenoir, Park & Roesner, 1987) have been of some interest to us. Our attention was drawn to the very high isomerization barrier reported for (*Z*)-perchlorostilbene (Ballester & Rosa, 1960), a member of the large class of known perchloroarenes (Ballester, 1989). Alternative explanations for the observed results based on our earlier work prompted an X-ray structural determination of this molecule to verify the structure and reveal the geometry. The original structural assignment for (*Z*)-perchlorostilbene is confirmed and a highly twisted geometry is demonstrated.

The structure of (*Z*)-perchlorostilbene was calculated using force-field programs (*PCModel* with and without the *PI* option; Gilbert & Gyjewski, 1992) and semi-empirical programs (*MOPAC* with the *AM*1 and *PM*3 parameter sets; Dewar, Zoebisch, Healy & Stewart, 1985; Stewart, 1989). All programs gave the same general structure. The force-field calculation which included a *PI* contribution, *MMX(PI)*, gave the best fit and showed no major faults in its structure. The simple force-field program *MMX* greatly underestimated the out-of-plane twisting of the phenyl groups. This failure reoccurs with twisted π systems using this approach. Surprisingly, the semi-empirical programs fail to predict the twist about the central double bond.

The structure of (*Z*)-perchlorostilbene is shown in Fig. 1 and some selected structural features are noted in Table 3. The central double bond is twisted 6.4 (3)°, based on the Cl atoms, or −11.5 (5)° based on the phenyl groups. The phenyl rings are rotated out of the plane of the double bond by, on average, 76° each, preventing the strong conjugation of the three π systems, as would have occurred had the system been planar. The bond length $C_{sp^2}{=}C_{sp^2}$ of 1.336 (3) Å is typical for the $C{=}C{—}C_{ar}$ system (1.339 Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), but the average value of the single bond, 1.484 (3) Å, is closer to that observed in *o*-biphenyls (1.487 Å) than in the conjugated $C{=}C{—}C_{ar}$ system (1.470 Å; Allen *et al.* 1987). The slightly shortened $C_{sp^2}{—}Cl$ bonds of average length 1.727 (2) Å, compared with 1.734 Å (Allen *et al.*, 1987), indicates the involvement of the vicinal Cl atoms in the electronic interactions and support its similarity to *o*-biphenyls. A similar arrangement of the pentachlorophenyl rings has been observed in perchloro-1,2,3-triphenylnaphthalene (Gali, Solans, Miravitlles, Font-Altaba & Armet, 1978), where the perchlorophenyls are rotated out of the plane defined by the C—C—C—C fragment of the naphthalene ring by an average of 73°. The twist of the aromatic rings allows the molecule to adopt a 'staggered' rather than 'eclipsed' conformation (see the Newman