Table 1. *Selected geometric parameters (Å, °)*

Br—C4	1.911 (4)	C1—C2	1.487 (7)
O1—C6	1.353 (4)	C2—C3	1.511 (6)
O1—C10	1.433 (5)	C3—C4	1.368 (6)
O2—C7	1.361 (5)	C3—C8	1.395 (6)
O2—C9	1.431 (5)	C4—C5	1.388 (5)
N1—C1	1.133 (6)	C5—C6	1.378 (6)
N2—C12	1.443 (5)	C6—C7	1.384 (6)
N2—C2	1.454 (6)	C7—C8	1.378 (5)
N2—C11	1.459 (5)		
C6—O1—C10	116.8 (4)	C3—C4—C5	122.7 (4)
C7—O2—C9	117.5 (4)	C3—C4—Br	121.2 (3)
C12—N2—C2	112.8 (4)	C5—C4—Br	116.1 (4)
C12—N2—C11	111.4 (4)	C6—C5—C4	119.5 (4)
C2—N2—C11	111.9 (4)	O1—C6—C5	124.4 (4)
N1—C1—C2	173.9 (6)	O1—C6—C7	116.3 (4)
N2—C2—C1	111.1 (4)	C5—C6—C7	119.3 (4)
N2—C2—C3	112.7 (4)	O2—C7—C8	125.0 (4)
C1—C2—C3	111.8 (4)	O2—C7—C6	115.1 (4)
C4—C3—C8	116.7 (4)	C8—C7—C6	119.9 (4)
C4—C3—C2	121.9 (4)	C7—C8—C3	121.9 (4)
C8—C3—C2	121.4 (4)		

An absorption correction by integration from crystal form was performed, but results were not satisfactory, probably due to the uncertainty in the indexing of the crystal faces. Owing to crystal loss, we were forced to use the *XABS*2 procedure (Parkin, Moezzi & Hope, 1995). The H atoms were apparent in the difference map but they were included in the refinement as riding atoms in calculated positions with two common isotropic displacement parameters. The only exception was the H2 atom, for which the positional parameters were refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON*94 (Spek, 1994*a*) and *PLUTON*94 (Spek, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

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References

Berger, B. & Bolte, M. (1994). *Acta Cryst.* C**50**, 773–775.
Chiaroni, A., Riche, C., Guerrier, L., Royer, J., Grierson, D. S. & Husson, H.-P. (1993). *Acta Cryst.* C**49**, 1786–1789.
Davis, F. A., Portonovo, P. S., Reddy, R. E. & Chiu, Y.-H. (1996). *J. Org. Chem.* **61**, 440–441.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
Kokila, M. K., Puttaraja, Kulkarni, M. K. & Shivaprakash, N. C. (1996). *Acta Cryst.* C**52**, 2078–2081.
Matier, W. L., Owens, D. A. & Comer, W. T. (1973). *J. Med. Chem.* **16**, 901–908.
Parfonry, A., Declercq, J.-P., Tinant, B., Van Meerssche, M. & Schweiss, P. (1988). *Acta Cryst.* B**44**, 435–440.
Parfonry, A., Tinant, B., Declercq, J.-P. & Van Meerssche, M. (1986). *Acta Cryst.* C**42**, 1266–1267.
Parkin, S., Moezzi, B. & Hope, H. (1995). *J. Appl. Cryst.* **28**, 53–56.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1994*a*). *PLATON94. Program for the Automated Analysis of Molecular Geometry*. University of Utrecht, The Netherlands.
Spek, A. L. (1994*b*). *PLUTON94. Program for the Display and Analysis of Crystal and Molecular Structures*. University of Utrecht, The Netherlands.
Taillades, J., Rossi, J. C., Garrel, L., Marull, M. & Commeyras, A. (1996). *Bull. Chim. Soc. Fr.* **133**, 89–100.
Verschave, P., Vekemans, J. & Hoornaert, G. (1984). *Tetrahedron*, **40**, 2395–2404.
Weinstock, L. M., Davis, P., Handelsman, B. & Tull, R. (1967). *J. Org. Chem.* **32**, 2823–2829.

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2-[2-(Hydroxyethyl)phenoxy]benzoic Acid

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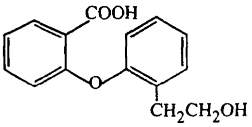
Abstract

The three-dimensional structure of the title compound, $C_{15}H_{14}O_4$, has been determined. The molecule assumes a skew conformation, the angle between the two phenyl rings being 84.8 (1)°. The carboxylic acid substituent is essentially coplanar with the ring. The molecules are connected by O···O intermolecular hydrogen bonds ranging from 2.6 to 2.9 Å. Distorted bond angles at the substituted phenyl C atoms were observed and they agree with the values reported in the literature for other bridged diphenyls.

Comment

The present work is part of a long-term project concerned with the synthesis of artificial receptors for antiviral compounds. The molecule under investigation, (I), is an intermediate compound for the synthesis of an artificial receptor with a xanthonic nucleus. The compound was obtained from an Ullmann ether synthesis (Rewcastle, Atwell, Baguley, Calveley & Denny, 1989) giving diphenyl ethers and its stereochemistry established by crystal structure determination. Knowledge of the three-dimensional structure of the molecule could be useful for the understanding of this synthesis and for predicting the conformation of other diphenyl ethers. NMR studies had revealed the presence of two aromatic rings, a carboxyl group and the alcohol, but gave no information on a possible intramolecular bond between O3 and the O4—H group.



(I)

Furthermore, molecular modelling was used to predict the structure of this molecule and the energies corresponding to different conformations were calculated using the *CHEM-X* program (Chemical Design Ltd, 1993). The results showed that the molecule could assume a conformation for which O3 and O4—H were within a reasonable distance for a hydrogen bond; however, the calculations also indicated that this situation was energetically less favorable than conformations for which those groups were further apart.

The title molecule (Fig. 1) is a bridged diphenyl compound with a skew conformation (Van der Heijden, Griffith, Chandler & Robertson, 1975). The torsion angle C3—C2—O1—C1′ is −88.3 (2)° and C6′—C1′—O1—C2 is 2.9 (2)°.

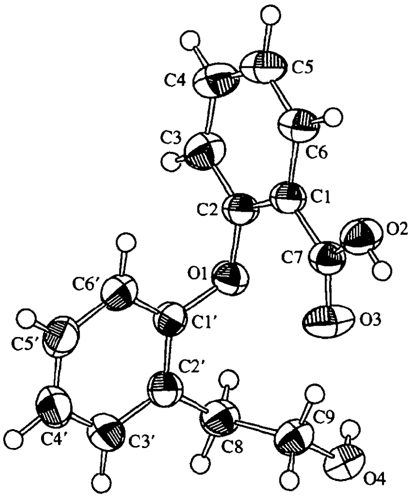


Fig. 1. The molecular structure of the title compound showing the atom-labelling scheme. H atoms are depicted as spheres of arbitrary radii. Displacement ellipsoids are shown at the 50% probability level.

The angle between the (hydroxyethyl)phenyl ring and the the central C2—O1—C1′ plane is 2.8 (2)°. The carboxyphenyl ring is nearly perpendicular to this central plane, the angle being 86.6 (1)°, and the carboxyl group is nearly coplanar with the phenyl ring [torsion angle C2—C1—C7—O2 −171.2 (1)°].

The internal ring angles at the two substituted C atoms (C1 and C2′) are decreased by 2.5 and 3.0°, respectively, from the value of 120° expected for a hexagonally symmetrical ring. This deviation has been observed in other bridged diphenyls (Gurtu, Chandler & Robertson, 1975). Furthermore, the O1—C1′—C6′ angle is 8.04° larger than the O1—C1′—C1′ angle. This is probably due to a steric interaction between the H atom on C6 and the carboxyphenyl ring.

The crystal structure shows no unusual intermolecular contacts. There are two intermolecular hydrogen bonds [O4—H···O3(1 + *x*, *y*, *z*) 2.901 (2) and O2—H···O4(−*x*, −*y*, 2 − *z*) 2.635 (2) Å].

The X-ray crystallography results confirm that there are no intramolecular hydrogen bonds in the crystal structure.

Experimental

The synthesis of (I) was carried out by reaction of the sodium salt of 2-chlorobenzoic acid and the sodium salt of (2-hydroxyphenyl)ethyl alcohol (molar ratio 1:1) in dry dioxane. CuCl and TDA-1 were added and the mixture was heated under reflux in an N_2 atmosphere for 20 h. After purification, the product was recrystallized from ethyl acetate.

Crystal data

$C_{15}H_{14}O_4$
$M_r = 258.26$
Triclinic
$P\bar{1}$
$a = 4.832\ (2)$ Å
$b = 10.222\ (6)$ Å
$c = 13.426\ (6)$ Å
$\alpha = 73.30\ (4)°$
$\beta = 81.43\ (3)°$
$\gamma = 88.83\ (4)°$
$V = 627.9\ (5)$ Å^3
$Z = 2$
$D_x = 1.366$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 1100 reflections
$\theta = 4.8–23.2°$
$\mu = 0.099$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.8 \times 0.3 \times 0.2$ mm
Colourless

Data collection

Stoe IPDS diffractometer
Image plate scans
Absorption correction: none
7464 measured reflections
2789 independent reflections
1988 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0551$

$\theta_{max} = 28.22°$
$h = -5 \rightarrow 5$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$
100 standard reflections
frequency: 6 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0389$
$wR(F^2) = 0.1235$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.145$ e Å^{-3}
$\Delta\rho_{min} = -0.139$ e Å^{-3}

$S = 1.031$
2544 reflections
220 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.15P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1′	1.383 (2)	C6—C1	1.399 (2)
O1—C2	1.390 (2)	C1—C7	1.496 (2)
O2—C7	1.318 (2)	C1′—C6′	1.386 (2)
O3—C7	1.210 (2)	C1′—C2′	1.399 (2)
O4—C9	1.442 (2)	C6′—C5′	1.387 (2)
C2—C3	1.390 (2)	C5′—C4′	1.376 (3)
C2—C1	1.395 (2)	C4′—C3′	1.383 (3)
C3—C4	1.378 (2)	C3′—C2′	1.392 (2)
C4—C5	1.377 (3)	C2′—C8	1.504 (2)
C5—C6	1.385 (3)	C8—C9	1.508 (2)
C1′—O1—C2	118.39 (11)	O2—C7—C1	112.70 (12)
O1—C2—C3	117.63 (15)	O1—C1′—C6′	123.27 (13)
O1—C2—C1	121.38 (13)	O1—C1′—C2′	115.23 (13)
C3—C2—C1	120.90 (14)	C6′—C1′—C2′	121.50 (14)
C4—C3—C2	120.2 (2)	C1′—C6′—C5′	119.6 (2)
C5—C4—C3	120.2 (2)	C4′—C5′—C6′	120.3 (2)
C4—C5—C6	119.7 (2)	C5′—C4′—C3′	119.5 (2)
C5—C6—C1	121.6 (2)	C4′—C3′—C2′	122.2 (2)
C2—C1—C6	117.49 (14)	C3′—C2′—C1′	116.99 (15)
C2—C1—C7	122.79 (13)	C3′—C2′—C8	121.12 (14)
C6—C1—C7	119.72 (14)	C1′—C2′—C8	121.89 (13)
O3—C7—O2	122.27 (14)	C2′—C8—C9	113.82 (14)
O3—C7—C1	125.03 (14)	O4—C9—C8	111.13 (14)

In the final refinement cycles, the reflections from the outermost resolution shell, 0.78–0.75 Å, were omitted on account of their weakness and poor agreement.

Data collection: Stoe IPDS software package. Cell refinement: Stoe IPDS software package. Data reduction: Stoe IPDS software package. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Zsolnai & Pritzkow, 1995) and *XPMA* (Zsolnai, 1996). Software used to prepare material for publication: *SHELXL*93 and *ORTEP*.

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References

Chemical Design Ltd (1993). *CHEM-X*. Chemical Design Ltd, Oxford, England.
Gurtu, K., Chandler, W. & Robertson, R. E. (1975). *Can. J. Chem.* **53**, 2093–2101.
Rewcastle, G. W., Atwell, G. J., Baguley, B. C., Calveley, S. B. & Denny, W. A. (1989). *J. Med. Chem.* **32**, 793–799.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Van der Heijden, S. P. N., Griffith, E. A. H., Chandler, W. D. & Robertson, B. E. (1975). *Can. J. Chem.* **53**, 2084–2092.
Zsolnai, L. (1996). *XPMA. Molecular Geometry Program for a Silicon Graphics Computer*. University of Heidelberg, Germany.
Zsolnai, L. & Pritzkow, H. (1995). *ORTEP Program for a Silicon Graphics Computer*. University of Heidelberg, Germany.

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Octamethylcuneane and Octamethylcubane: the First X-ray Crystal Structure of a Cuneane

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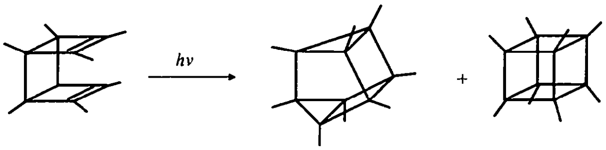
Abstract

In the crystal of octamethylcuneane (1,2,3,4,5,6,7,8-octamethylpentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane), $C_{16}H_{24}$, there are two independent molecules in the asymmetric unit. Octamethylcubane (1,2,3,4,5,6,7,8-octamethylpentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane), $C_{16}H_{24}$, exhibits crystallographic $\bar{3}m$ symmetry. Due to the eclipsed orientation of the methyl groups in octamethylcubane, the average bond length is extended to 1.563 (3) Å compared with cubane itself. In the cuneane derivative, the cage bond lengths vary between 1.517 (2) and 1.573 (2) Å in accordance with their bicyclic character and the repulsive forces between the methyl groups. The exocyclic bonds to the methyl C atoms in both molecules are shortened due to the increased *s* character of the cage C atoms.

Comment

The octamethyl derivative, (III), of *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene gave octamethylcuneane, (I), and traces of octamethylcubane, (II), among others under irradiation with ultraviolet light (Gleiter & Brand, 1994).



(III) (I) (II)

During the course of our studies on strained polycyclic compounds (Irngartinger & Strack, 1994), the

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