

1336 reflections
163 parameters
All H-atom parameters re-
fined

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Cell refinement and data reduction: *SDP* (Frenz, 1978). Program used to solve structure: *SHELX86* (Sheldrick, 1986). Programs used to refine structure: *SHELX76* (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983). Refinement was by full-matrix least-squares methods. The density of the crystal was measured by flotation.

We thank Professor R. Srinivasan for discussions and one of us (JS) thanks UGC (India) for financial assistance.

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 55160 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LJ1005]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O(1)	0.2738 (9)	0.2641 (4)	0.1781 (4)	0.515 (2)
C(2)	0.1111 (14)	0.1672 (6)	0.1831 (6)	0.532 (3)
C(3)	0.1414 (14)	0.0815 (6)	0.0880 (6)	0.506 (3)
C(4)	0.3381 (12)	0.0881 (5)	-0.0272 (5)	0.435 (3)
C(5)	0.7320 (14)	0.2104 (6)	-0.1319 (6)	0.523 (3)
C(6)	0.9032 (12)	0.3082 (5)	-0.1331 (5)	0.456 (3)
O(6)	1.0972 (10)	0.3255 (4)	-0.2345 (4)	0.390 (3)
C(7)	0.8593 (14)	0.3898 (6)	-0.0253 (6)	0.521 (3)
C(8)	0.6550 (13)	0.3740 (5)	0.0754 (6)	0.492 (3)
C(9)	0.4805 (13)	0.2759 (5)	0.0727 (6)	0.444 (3)
C(10)	0.5180 (12)	0.1938 (5)	-0.0290 (5)	0.414 (3)
O(11)	0.3621 (10)	0.0118 (4)	-0.1155 (4)	0.611 (3)
C(1')	-0.0910 (14)	0.1694 (5)	0.3041 (5)	0.480 (3)
C(2')	-0.0730 (15)	0.2471 (6)	0.4031 (6)	0.585 (4)
C(3')	-0.2636 (17)	0.2465 (7)	0.5162 (7)	0.670 (5)
C(4')	-0.4799 (18)	0.1676 (8)	0.5299 (8)	0.731 (5)
C(5')	-0.4952 (15)	0.0916 (7)	0.4333 (8)	0.658 (4)
C(6')	-0.3114 (15)	0.0916 (7)	0.3210 (6)	0.639 (4)

Table 2. Geometric parameters (\AA , $^\circ$)

O(1)—C(2)	1.341 (8)	C(6)—C(7)	1.413 (8)
O(1)—C(9)	1.385 (7)	C(7)—C(8)	1.351 (8)
C(2)—C(3)	1.338 (9)	C(8)—C(9)	1.405 (9)
C(2)—C(1')	1.477 (8)	C(9)—C(10)	1.366 (8)
C(3)—C(4)	1.423 (8)	C(1')—C(2')	1.371 (9)
C(4)—C(10)	1.476 (8)	C(1')—C(6')	1.418 (10)
C(4)—O(11)	1.223 (7)	C(2')—C(3')	1.386 (9)
C(5)—C(6)	1.384 (9)	C(3')—C(4')	1.410 (13)
C(5)—C(10)	1.398 (8)	C(4')—C(5')	1.336 (12)
C(6)—O(6)	1.327 (7)	C(5')—C(6')	1.362 (10)
C(2)—O(1)—C(9)	119.6 (5)	O(1)—C(9)—C(8)	117.4 (5)
O(1)—C(2)—C(1')	111.2 (5)	C(8)—C(9)—C(10)	120.9 (6)
O(1)—C(2)—C(3)	121.7 (6)	O(1)—C(9)—C(10)	121.6 (6)
C(3)—C(2)—C(1')	127.1 (6)	C(5)—C(10)—C(9)	118.7 (6)
C(2)—C(3)—C(4)	123.6 (6)	C(4)—C(10)—C(9)	119.9 (5)
C(3)—C(4)—O(11)	123.7 (6)	C(4)—C(10)—C(5)	121.4 (5)
C(3)—C(4)—C(10)	113.5 (5)	C(2)—C(1')—C(6')	120.8 (5)
C(10)—C(4)—O(11)	122.7 (5)	C(2)—C(1')—C(2')	121.3 (6)
C(6)—C(5)—C(10)	121.5 (6)	C(2')—C(1')—C(6')	117.9 (6)
C(5)—C(6)—C(7)	117.9 (6)	C(1')—C(2')—C(3')	120.3 (7)
C(5)—C(6)—O(6)	120.2 (5)	C(2')—C(3')—C(4')	120.4 (7)
O(6)—C(6)—C(7)	121.9 (5)	C(3')—C(4')—C(5')	119.0 (8)
C(6)—C(7)—C(8)	121.2 (6)	C(4')—C(5')—C(6')	121.6 (8)
C(7)—C(8)—C(9)	119.7 (6)	C(1')—C(6')—C(5')	120.9 (7)

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Acta Cryst. (1992). **C48**, 1715-1717

1,4-Dibenzoylbenzene

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(Received 8 May 1992; accepted 26 June 1992)

Abstract

The structure determination of the title compound was undertaken in order to obtain more structural information about phthalic acid derivatives and the effects of different benzoyl group positions on the conformation of these compounds. The benzoyl fragments of the centrosymmetric molecule are coplanar and form an angle of $121.4(1)^\circ$ with the central phenylene ring. The bond angles around the C atom of the carbonyl group do not deviate significantly from 120° , indicating sp^2 hybridization. The torsion angles C(7)—C(6)—C(4)—O(5) and C(2)—C(3)—C(4)—O(5) are $23.5(5)$ and $36.9(5)^\circ$, respectively; bond distances and angles are within the normal ranges.

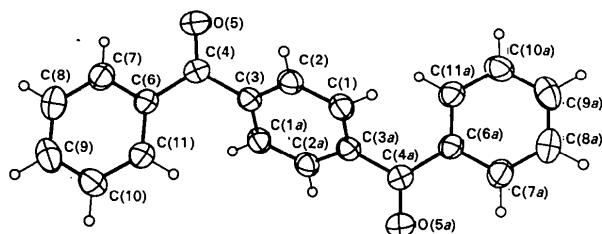


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries; H atoms are shown as spheres of arbitrary radius. The molecule resides on a centre of symmetry.

Comment

Acceptance of an electron into the first antibonding molecular orbital can easily transform the title compound into the corresponding anion radical; this is of great interest as an intermediate species in some electrochemical reactions (Kolev, 1982; Svaan & Parker, 1984, 1988; Juchnovski & Kolev, 1985).

Experimental

Crystal data

$C_{20}H_{14}O_2$

$M_r = 286.33$

Triclinic

$P\bar{1}$

$a = 6.532$ (4) Å

$b = 7.387$ (6) Å

$c = 8.743$ (7) Å

$\alpha = 70.23$ (6)°

$\beta = 83.25$ (6)°

$\gamma = 66.32$ (5)°

$V = 363.5$ (5) Å³

$Z = 1$

$D_x = 1.308$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 40 reflections

$\theta = 7.5$ – 15.1 °

$\mu = 0.08$ mm⁻¹

$T = 293$ (1) K

Plate

$0.50 \times 0.48 \times 0.26$ mm

Colourless

Data collection

Nicolet *R3m/V* diffractometer

$\theta/2\theta$ scans

Absorption correction: none

2802 measured reflections

1288 independent reflections

1061 observed reflections

$[F > 4.0\sigma(F)]$

$R_{int} = 0.040$

$\theta_{max} = 25$ °

$h = -8 \rightarrow 6$

$k = -9 \rightarrow 9$

$l = -11 \rightarrow 11$

6 standard reflections

frequency: 240 min

intensity variation: none

Refinement

Refinement on F

Final $R = 0.039$

$wR = 0.062$

$S = 0.85$

1061 reflections

101 parameters

Only H-atom U 's refined

Calculated weights $w = 1/[\sigma^2(F) + 0.004F^2]$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.1328$ e Å⁻³

$\Delta\rho_{min} = -0.1609$ e Å⁻³

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C(1)	0.6502 (3)	0.9157 (2)	0.6303 (2)	0.0417
C(2)	0.5310 (3)	0.8056 (2)	0.6115 (2)	0.0410
C(3)	0.3813 (2)	0.8881 (2)	0.4817 (2)	0.0383
C(4)	0.2534 (3)	0.7647 (2)	0.4680 (2)	0.0428
O(5)	0.1892 (2)	0.6640 (2)	0.5914 (1)	0.0681
C(6)	0.2145 (2)	0.7591 (2)	0.3054 (2)	0.0401
C(7)	0.0403 (3)	0.7057 (2)	0.2838 (2)	0.0488
C(8)	0.0125 (3)	0.6847 (3)	0.1368 (2)	0.0575
C(9)	0.1574 (3)	0.7140 (3)	0.0117 (2)	0.0599
C(10)	0.3313 (3)	0.7654 (3)	0.0326 (2)	0.0574
C(11)	0.3602 (3)	0.7885 (2)	0.1783 (2)	0.0474

Table 2. Geometric parameters (Å, °)

C(1)—C(2)	1.387 (3)	C(6)—C(7)	1.395 (3)
C(1)—C(3a)	1.396 (2)	C(6)—C(11)	1.394 (2)
C(2)—C(3)	1.390 (3)	C(7)—C(8)	1.386 (3)
C(3)—C(4)	1.500 (3)	C(8)—C(9)	1.378 (3)
C(4)—O(5)	1.222 (2)	C(9)—C(10)	1.382 (4)
C(4)—C(6)	1.490 (3)	C(10)—C(11)	1.385 (3)
C(2)—C(1)—C(3a)	119.8 (3)	C(4)—C(6)—C(7)	119.4 (2)
C(1)—C(2)—C(3)	120.6 (3)	C(7)—C(6)—C(11)	119.1 (3)
C(2)—C(3)—C(1a)	119.6 (3)	C(6)—C(7)—C(8)	120.0 (3)
C(2)—C(3)—C(4)	118.7 (3)	C(7)—C(8)—C(9)	120.5 (3)
C(4)—C(3)—C(1a)	121.7 (3)	C(8)—C(9)—C(10)	119.8 (3)
C(3)—C(4)—C(6)	119.8 (3)	C(9)—C(10)—C(11)	120.3 (3)
C(3)—C(4)—O(5)	119.4 (3)	C(6)—C(11)—C(10)	120.2 (3)
O(5)—C(4)—C(6)	120.8 (3)	C(3)—C(1a)—C(2a)	119.8 (3)
C(4)—C(6)—C(11)	121.2 (3)		

Symmetry code: (a) $-x, -y, -z$.

Data collection: Nicolet *R3m/V* software, release 4.11. Cell refinement: Nicolet *R3m/V* software. Data reduction: Nicolet *R3m/V* software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXTL-Plus*, *SHELX76* (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983), *PLATON* (Spek, 1982).

The title compound was obtained by Friedel-Crafts reaction of terephthaloyl chloride and dry benzene following the procedure of Murray & Trozzolo (1961). The reaction product was recrystallized from 95% ethanol to give white crystals of 1,4-dibenzoylbenzene (m.p. 435–436 K). These were sublimed *in vacuo* and recrystallized three times from anhydrous ethanol to give crystals with an m.p. in the range 440–440.5 K. The IR spectrum of the title compound in the solid state shows a band at 1664 cm⁻¹ in the carbonyl stretching region and a Raman band at 1665 cm⁻¹. Refinement was based on full-matrix least-squares methods with H atoms in calculated positions (C—H 0.96 Å). A search for higher symmetry was performed using *MISSYM* (Le Page, 1987); *PCK83* (Williams, 1984) was used to check the crystal packing.

One of us (TK) thanks the Alexander von Humboldt Stiftung for a research fellowship.

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 55243 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1018]

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Acta Cryst. (1992). **C48**, 1717–1718

Structure of 1,4,7,10-Tetraazacyclododecane Trihydrate

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(Received 27 April 1992; accepted 23 June 1992)

Abstract

The neutral 1,4,7,10-tetraazacyclododecane molecules exhibit crystallographic twofold rotation symmetry and have a [3333] quadrangular conformation with C atoms occupying corner positions. The H atoms bound to the N atoms at the 1 and 7 ring positions are directed outward, away from the center of the ring, while the H atoms bound to the N atoms at the 4 and 10 ring positions are pointed inward, toward the center of the ring. Each N atom is hydrogen bonded to one water molecule. The quadrangular conformation is important in the preorganization of 1,4,7,10-tetraazacyclododecane and its derivatives prior to complexation to metal ions [$(C-C)_{ave} = 1.518(7)$, $(C-N)_{ave} = 1.464(3)$ Å].

Comment

The structure of the title compound, also known as cyclen, was determined to establish the conformation of the twelve-membered cyclododecane ring. Fig. 1 shows the structure and the numbering scheme used. The ring conformation is important in understanding the effect of preorganization on complex stability and selectivity for metal ions (Hancock & Martell, 1989; Weber & Vogtle, 1981;

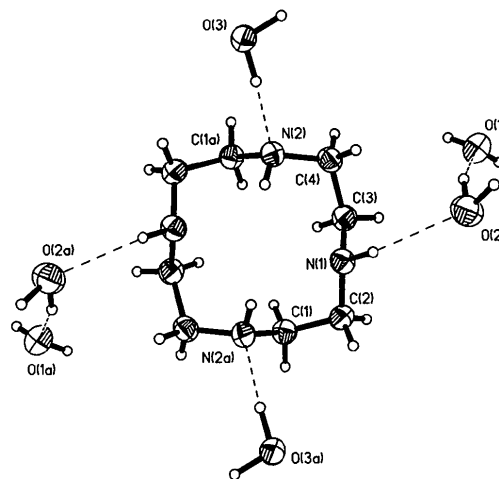


Fig. 1. Thermal ellipsoid plot (50% probability) of cyclen.3H₂O; H atoms are shown as spheres of arbitrary radius.

Cram & Trueblood, 1981). Previous work (Reibenspies & Anderson, 1990) has shown that the twelve-membered ring of the protonated H₄cyclen⁴⁺ cation folds to form four repeating units, each containing two adjacent bonds with *gauche* configuration and one bond with *anti* configuration. The resulting combination of configurations is labeled the [3333] quadrangular conformation (Dale, 1980). The present study shows that the neutral cyclen molecule also prefers the [3333] quadrangular conformation in the crystalline state. The two similar structures (H₄cyclen⁴⁺ and cyclen) differ in the position of the N atoms in the ring with respect to the side and corners of the conformation. For the protonated cyclen cation, the N atoms are located at the corners of the square while for the neutral cyclen molecule the N atoms are located along the sides. As expected, the average C—N distance is significantly shorter for the neutral cyclen molecule [1.464(3) Å] than for the protonated cyclen cation [1.497(3) Å]. The average C—C distances in the cyclen cation and the neutral cyclen molecule [1.527(7) and 1.518(7) Å respectively] do not differ significantly. Three molecules of water are located at special positions. Two water molecules [O(2) and O(3)] are hydrogen bonded to the N atoms of the cyclen molecule [N(1)—O(2) 3.186(3), N(2)—O(3) 2.835(2) Å] and the third water molecule, O(1), is hydrogen bonded to other water molecules [O(1)—O(2) 2.998(3), O(1)—O(3) 2.894(2) Å].

Experimental

Crystal data

C₈H₂₀N₄.3H₂O
 $M_r = 226.3$
 Orthorhombic
Ccca
 $a = 16.636(4)$ Å
 $b = 16.873(3)$ Å
 $c = 8.881(2)$ Å

Mo K α radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 9.19$ – 27.53°
 $\mu = 0.086$ mm⁻¹
 $T = 296$ K