

Of particular interest with disaccharides of this type is the conformation around the glycosidic linkage. In this case the respective φ and ψ angles [defined as $\varphi = \text{O5}(i)-\text{C1}(i)-\text{O4}(i-1)-\text{C4}(i-1)$ and $\psi = \text{C1}(i)-\text{O4}(i)-\text{C4}(i-1)-\text{C3}(i-1)$ from IUPAC-IUB Joint Commission on Biochemical Nomenclature (1983)] are $-83.23(41)$ and $131.70(35)^\circ$ with a glycosidic angle [C(1)—O(1)—C(14)] of $117.1(3)^\circ$. It has been suggested by Perez & Marchessault (1978) that the *exo*-anomeric effect is important in the conformational analysis of polysaccharides. This effect occurs when there are sequences of atoms with alternating polarity and having free electron pairs. A sequence such as this is found in the disaccharide between the ring oxygen, O(5), and the ring carbon, C(14), via C(1) and O(1). This phenomenon is thought to give a conformational bias to the dihedral values related to rotation about the glycosidic linkage. With the occurrence of an intramolecular hydrogen bond, the values of φ and ψ normally lie in a very narrow range for a selection of disaccharides of this type, e.g. the values found for mannobiose (Sheldrick, Mackie & Akrigg, 1984) are -96.1 and 95.1° for φ and ψ with a glycosidic angle of 114.8° . However, when free of this restriction, instead of the larger range of φ and ψ angles that would be expected, φ still appears to be limited to a range of 30° , whereas ψ varies by as much as 100° . Therefore, it would appear that for all oligosaccharides, φ is limited to a narrow range, whilst ψ will only be restricted in compounds with intramolecular hydrogen bonds. An example of this is β -maltose (Gress & Jeffrey, 1977) which has no hydrogen bond and $\varphi = 121.7^\circ$ and

$\psi = 132.8^\circ$, with this latter value corresponding to the value in this study. In conclusion, 4-*O*- β -D-galactopyranosyl- α -D-mannose fits the general trend of having a biased conformation of dihedral angles due to the *exo*-anomeric effect which has been shown to exist in many other oligosaccharide crystal structures.

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A Bis(anisyl)cyclohexanone: A Non-Macrocyclic Model for Some Features of Spherand Structures

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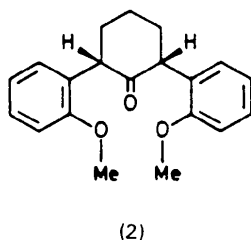
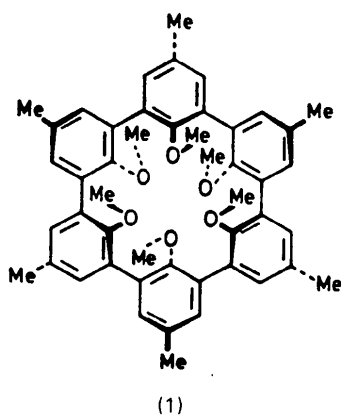
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Abstract. *cis*-2,6-Bis(2-methoxyphenyl)cyclohexan-1-one, $\text{C}_{20}\text{H}_{22}\text{O}_3$, $M_r = 310.4$, orthorhombic, $P2_12_12_1$, $a = 9.364(1)$, $b = 7.865(1)$, $c = 23.219(5)$ Å, $V = 1710.0$ Å³, $Z = 4$, $D_m = 1.23$, $D_x = 1.21$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.74$ cm⁻¹, $F(000) = 664$,

$T = 295$ K, $R = 0.057$ for 1445 unique observed reflections with $I > \sigma(I)$. The methoxy O and C atoms in this structure are nearly coplanar with the aromatic rings to which they are attached and the rings themselves are planar rather than folded, quite in contrast to the situation in the related macrocyclic spherands and hemispherands containing similar rings.

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Introduction. The first spherands and hemispherands (Cram & Trueblood, 1981) were prepared from anisyl or 4-methylanisyl moieties joined in the 2- and 6-positions; the prototype spherand is represented by formula (1).



More recently, spherands and hemispherands containing cyclic urea groups and other moieties as well as anisyl groups have been prepared (Cram, Dicker, Lauer, Knobler & Trueblood, 1984). In all of these molecules, the anisyl rings are invariably folded (by as much as 13°) and their methoxy methyl groups are twisted far out of the best plane through the ring atoms. The present compound, (2), an intermediate in the preparation of certain spherands (Cram, Moran, Maverick & Trueblood, 1983), provides a good control for some of the distortions and conformational features found in the structures of many spherands and hemispherands.

Experimental. Colorless, rectangular parallelepiped single crystal grown from cyclohexane, $0.50 \times 0.20 \times 0.30$ mm, D_m by flotation in carbon tetrachloride-cyclohexane; Syntex P1 diffractometer, graphite monochromator, unit-cell parameters by least-squares refinement of 15 reflections ($20.3 \leq 2\theta \leq 26.6^\circ$), $\theta-2\theta$ scan, $4.0^\circ \text{ min}^{-1}$, $2\theta_{\text{max}} = 50^\circ$ for the range $0 \leq h \leq 12$, $0 \leq k \leq 9$, $0 \leq l \leq 27$, three reflections monitored every 97 reflections with no significant variation, 1850 measured intensities, 1822 unique data (not including space-group extinctions), 1640 with $I > 0$, 1445 with $I > \sigma(I)$ used for refinement, Lorentz and polarization but no absorption correction ($\mu = 0.74 \text{ cm}^{-1}$); structure solved by direct methods, all atoms (including H atoms) located on Fourier and difference Fourier maps; for refinement, all C-H bond distances fixed at 1.08 \AA ; methyl groups refined as rigid groups with H geometry tetrahedral and rotation allowed around O-CH₃ bond; other H atoms riding on their attached C atoms with bond angles fixed at standard values; anisotropic displacement parameters for all non-H atoms and fixed

isotropic ones for H; refined by full-matrix least-squares procedure based on F with a maximum $\sin\theta/\lambda = 0.59 \text{ \AA}^{-1}$; refinement of 220 parameters converged to $R = 0.057$, $wR = 0.051$, $w = 1/\sigma^2(F_o)$, goodness of fit = 1.33; $(\Delta/\sigma)_{\text{max}}$ in final cycle was 0.15 in a position parameter [y of C(8)] and 0.24 in a displacement parameter [for H(8C)]; highest positive and negative peaks 0.19 and -0.22 e \AA^{-3} in the final difference map; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations were performed on DEC VAX 11/750 and VAX 11/780 computers using the *UCLA Crystallographic Package* (1984) (locally edited versions of CARESS, PROFILE, MULTAN, ORFLS, ORFFE, ABSORB, ORTEP and SHELX, and local molecular-geometry and thermal-motion programs, MG84 and THMV9) and PLUTO78 (Motherwell & Clegg, 1978).

Discussion. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1. Bond lengths, bond angles and torsion angles involving atoms other than H are given in Table 2.* Fig. 1 is a PLUTO stereoview of the molecule, showing the atom-numbering scheme. The near coplanarity of the methoxy O and C atoms with the aromatic rings is apparent; the angles between the C-O-C planes and the attached aromatic rings are 1.0° for the ring involving atoms C(1) to C(6) and 4.5° for the other aromatic ring, values typical of anisyl derivatives that are not overcrowded. In typical spherands and hemispherands, on the other hand, these angles vary between 65° and 90° (Cram & Trueblood, 1981). Similarly, the bond angles at the methoxy O atoms in the present structure are 118.5° and 118.9° , values quite typical of uncrowded aromatic-aliphatic ethers, whereas in both complexed and uncomplexed spherands and hemispherands similar angles are 3 to 6° smaller. The two aromatic rings in the present molecule show no significant deviations from planarity (the maximum deviation of any atom is 0.007 \AA , the average only 0.002 \AA , with typical e.s.d. 0.005 \AA). In most spherand and hemispherand structures (Cram & Trueblood, 1981), the rings are folded or buckled, occasionally to a considerable degree, as a result of intramolecular constraints. The cyclohexanone ring has a chair conformation, with the aromatic rings inclined to its central plane at quite different angles, about 65° for the ring on the left in Fig. 1 and only 34° for the ring on the right. The bond distances throughout the molecule are unexceptional; the average distance within the aromatic

* Lists of anisotropic displacement parameters, H-atom parameters, structure factors, and some least-squares-plane parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42555 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Position and displacement parameters for *cis*-1,3-bis(2-methoxyphenyl)cyclohexan-1-one

	x	y	z	$\langle u^2 \rangle^*(\text{\AA}^2)$
C(1)	0.9968 (6)	-0.1920 (6)	0.7096 (2)	0.072
C(2)	0.8555 (6)	-0.1739 (7)	0.7219 (2)	0.079
C(3)	0.7761 (5)	-0.0474 (7)	0.6968 (2)	0.076
C(4)	0.8405 (4)	0.0630 (6)	0.6585 (2)	0.060
C(5)	0.9837 (4)	0.0486 (5)	0.6447 (1)	0.048
C(6)	1.0603 (5)	-0.0809 (6)	0.6709 (2)	0.060
O(7)	1.2019 (3)	-0.0891 (4)	0.6561 (1)	0.086
C(8)	1.2883 (7)	-0.2195 (8)	0.6804 (3)	0.108
C(9)	1.0549 (4)	0.1692 (5)	0.6029 (2)	0.050
C(10)	1.0303 (5)	0.3590 (5)	0.6169 (2)	0.063
C(11)	1.1074 (5)	0.4746 (5)	0.5740 (2)	0.069
C(12)	1.0595 (5)	0.4358 (5)	0.5126 (2)	0.064
C(13)	1.0396 (4)	0.2485 (6)	0.4977 (2)	0.050
C(14)	1.0101 (4)	0.1393 (5)	0.5405 (2)	0.046
O(15)	0.9146 (3)	0.0435 (4)	0.5271 (1)	0.067
C(16)	1.0592 (4)	0.1991 (6)	0.4359 (2)	0.053
C(17)	0.9766 (4)	0.2983 (7)	0.3994 (2)	0.067
C(18)	0.9540 (6)	0.2481 (8)	0.3428 (2)	0.085
C(19)	1.0128 (6)	0.1007 (9)	0.3226 (2)	0.089
C(20)	1.0959 (5)	-0.0022 (7)	0.3583 (2)	0.077
C(21)	1.1175 (4)	0.0476 (6)	0.4152 (2)	0.058
O(22)	1.1975 (3)	-0.0404 (4)	0.4536 (1)	0.070
C(23)	1.2541 (6)	-0.2015 (6)	0.4367 (3)	0.092

* $1/8\pi^2 \times$ 'equivalent *B* value' defined by Hamilton (1959).

Table 2. Distances (Å), angles (°) and torsion angles (°) for *cis*-2,6-bis(2-methoxyphenyl)cyclohexan-1-one

E.s.d.'s are in parentheses, in units of the least-significant digit of the corresponding value.

C(1)–C(2)	1.361 (8)	C(1)–C(6)	1.387 (6)
C(2)–C(3)	1.372 (7)	C(3)–C(4)	1.382 (7)
C(4)–C(5)	1.383 (5)	C(5)–C(6)	1.386 (6)
C(5)–C(9)	1.513 (5)	C(6)–O(7)	1.371 (5)
O(7)–C(8)	1.423 (7)	C(9)–C(10)	1.546 (5)
C(9)–C(14)	1.526 (5)	C(10)–C(11)	1.529 (6)
C(11)–C(12)	1.526 (6)	C(12)–C(13)	1.539 (6)
C(13)–C(14)	1.511 (6)	C(13)–C(16)	1.512 (5)
C(14)–O(15)	1.210 (5)	C(16)–C(17)	1.388 (6)
C(16)–C(21)	1.396 (6)	C(17)–C(18)	1.389 (7)
C(18)–C(19)	1.366 (9)	C(19)–C(20)	1.396 (7)
C(20)–C(21)	1.393 (6)	C(21)–O(22)	1.354 (5)
O(22)–C(23)	1.429 (6)		
C(2)–C(1)–C(6)	119.1 (4)	C(1)–C(2)–C(3)	121.0 (5)
C(2)–C(3)–C(4)	119.5 (4)	C(3)–C(4)–C(5)	121.4 (4)
C(4)–C(5)–C(6)	117.4 (4)	C(4)–C(5)–C(9)	121.6 (3)
C(6)–C(5)–C(9)	121.0 (3)	C(1)–C(6)–C(5)	121.7 (4)
C(1)–C(6)–O(7)	123.2 (4)	C(5)–C(6)–O(7)	115.1 (4)
C(6)–O(7)–C(8)	118.9 (4)	C(5)–C(9)–C(10)	113.9 (3)
C(6)–C(9)–C(14)	113.0 (3)	C(10)–C(9)–C(14)	107.9 (3)
C(9)–C(10)–C(11)	111.5 (3)	C(10)–C(11)–C(12)	110.6 (3)
C(11)–C(12)–C(13)	110.3 (3)	C(12)–C(13)–C(14)	107.8 (3)
C(12)–C(13)–C(16)	115.1 (3)	C(14)–C(13)–C(16)	112.7 (4)
C(9)–C(14)–C(13)	113.7 (3)	C(9)–C(14)–O(15)	123.0 (3)
C(13)–C(14)–O(15)	123.3 (3)	C(13)–C(16)–C(17)	122.7 (4)
C(13)–C(16)–C(21)	118.2 (4)	C(17)–C(16)–C(21)	119.1 (4)
C(16)–C(17)–C(18)	120.2 (4)	C(17)–C(18)–C(19)	120.3 (5)
C(18)–C(19)–C(20)	120.9 (5)	C(19)–C(20)–C(21)	118.7 (4)
C(16)–C(21)–C(20)	120.7 (4)	C(16)–C(21)–O(22)	115.2 (4)
C(20)–C(21)–O(22)	124.1 (4)	C(21)–O(22)–C(23)	118.5 (4)
C(4)–C(5)–C(9)–C(10)	51.5 (5)	C(4)–C(5)–C(9)–C(14)	72.1 (5)
C(6)–C(5)–C(9)–C(10)	-128.3 (4)	C(6)–C(5)–C(9)–C(14)	108.0 (4)
C(1)–C(6)–O(7)–C(8)	1.3 (7)	C(5)–C(6)–O(7)–C(8)	-179.2 (4)
C(5)–C(9)–C(10)–C(11)	178.7 (3)	C(5)–C(9)–C(14)–C(13)	-175.0 (3)
C(5)–C(9)–C(14)–O(15)	8.6 (5)	C(10)–C(9)–C(14)–C(13)	58.1 (4)
C(10)–C(9)–C(14)–O(15)	-118.3 (4)	C(14)–C(9)–C(10)–C(11)	-54.9 (4)
C(9)–C(10)–C(11)–C(12)	57.0 (5)	C(10)–C(11)–C(12)–C(13)	-58.6 (5)
C(11)–C(12)–C(13)–C(14)	58.7 (4)	C(11)–C(12)–C(13)–C(16)	-174.6 (4)
C(12)–C(13)–C(14)–C(9)	-60.2 (4)	C(12)–C(13)–C(14)–O(15)	116.1 (4)
C(12)–C(13)–C(16)–C(17)	-16.2 (6)	C(12)–C(13)–C(16)–C(21)	163.6 (4)
C(14)–C(13)–C(16)–C(17)	107.9 (5)	C(14)–C(13)–C(16)–C(21)	-72.3 (5)
C(9)–C(14)–C(13)–C(16)	171.7 (3)	C(16)–C(13)–C(14)–O(15)	-12.0 (6)
C(16)–C(21)–O(22)–C(23)	176.5 (4)	C(20)–C(21)–O(22)–C(23)	-5.5 (6)

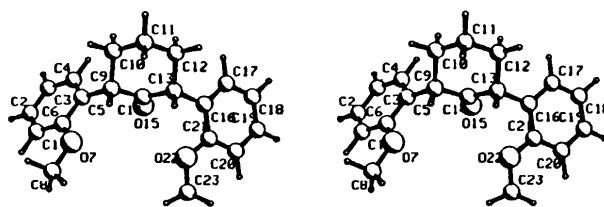


Fig. 1. Stereoview of the molecule, showing the numbering scheme.

rings is 1.383 Å before correction for libration (Schomaker & Trueblood, 1968), and 1.387 Å after such corrections. The anisotropic displacement parameters are of poor quality by the Hirshfeld (1976) test, and the libration corrections to bond distances, which range from 0.002 to 0.006 Å, cannot be considered very meaningful, especially as there is evidence (Rosenfeld, Trueblood & Dunitz, 1978) of significant internal motion (especially of the methoxy groups). The shortest interatomic distances between different molecules are not unusual: no C...C below 3.5 Å; O...C, 3.19 Å between the keto O, O(15), and C(23) at $-\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z$; C...H, 2.88 Å, between C(2) and H(10A) at $2 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; O...H, 2.48 Å, between O(15) and H(23A) at $-\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z$; and H...H, 2.24 Å, between H(3) and H(19) at $\frac{3}{2} - x, -y, \frac{1}{2} + z$.

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