

Crystal and Molecular Structure of Bis(9-triptycyl) Ether

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Abstract: The molecular structure of a benzene solvate of bis(9-triptycyl) ether, $\text{Tp}_2\text{O}\cdot 2\text{Bz}$ (**1**), has been determined by an X-ray analysis; monoclinic, space group $P2_1/c$, $a = 20.868$ (2) Å, $b = 10.405$ (1) Å, $c = 18.912$ (1) Å, $\beta = 114.12$ (1)°, $V = 3747.7$ (5) Å³, $d_m = 1.207$ g cm⁻³, and $Z = 4$. The entire molecule constitutes a crystallographic asymmetric unit and thus has no rigorous symmetry. However, there is an approximate symmetry plane including the ether unit, C(9)-O-C(9'). The molecule adopts a beveled gear-shaped structure in which the ethereal C-O bond lengths average 1.412 (5) Å and the bond angle subtended at the oxygen which links the two triptycyl groups is widened to 135.8 (2)°. There are other modes of molecular deformation noted which would be effective in minimizing nonbonded interactions between the biting teeth of the gear; the C-O bonds are not collinear with the threefold symmetry axes of the triptycene units but deviate by 9.5° and 11.7°. In order to reproduce the observed large COC angle by a force-field calculation, the potential energy expression for the COC bending has to be modified in such a way that the energy must not increase drastically at a large angle. The structure of **1** with the C_2 point group was reproduced by the force-field calculation using this MM2' parametrization. The C_2 conformation was shown to be an energy minimum but 0.24 kcal/mol higher in steric energy than the C_s structure. The relative stability between these two conformers is opposite to the known stability order in bis(9-triptycyl) carbon derivatives. About 70 points near the gearing coordinates have been calculated and smoothed to give the potential energy surface on which the dynamic gearing of **1** takes place. The gearing is expected to proceed along an almost flat valley flanked by steep cliffs. There is a very low unsymmetrical barrier of height 0.93 kcal/mol between the two energy minima.

Correlated internal rotation in molecules is a subject of much stereochemical interest. Recently, disrotatory coupling of the internal rotation around two adjacent C-X bonds was designed and achieved in Tp_2X (X = CH₂ and O; Tp = 9-triptycyl) molecules.^{2,3} The molecules undergo rapid internal rotation as revealed by showing only one kind of the benzene ring in their NMR spectra at low temperature.^{2a,b} The strictly geared rotation in these molecular bevel gears was established by demonstrating the newly generated stereoisomerism in the labeled derivatives. When the biting teeth of the wheel (benzene rings) are appropriately labeled, the phase relationship is established between them and stereoisomers with different phases can be isolated. The racemic and meso isomers of bis(2- and 3-chloro-9-triptycyl)-methanes and bis(2- and 3-chloro-9-triptycyl) ethers and bis-(2,3-dimethyl-9-triptycyl)methane were successfully separated.^{2b,d,3a,b} The racemates of bis(2- and 3-chloro-9-triptycyl)-methanes and bis(2- and 3-chloro-9-triptycyl) ethers were further separated into their optical antipodes.^{2e} The interconversion between isomers is effected by a gear-slipping process. The observed high barrier to this isomerization indicates that the repulsive nonbonded interaction between the two triptycene units should be very large in the gear-clashing conformations relative to the gear-meshing ones. The latter were also shown to be suffering from substantial steric strain. In the methane and other carbon-bridged series (X = CH₂, CHO, and C=O),^{3b,d} the central CCC angles are expanded to as much as 129° to release some

of the nonbonded repulsive interaction between the two triptycene units. Since our previous work has shown that the ether series always has more tightly biting gears than the corresponding methanes owing presumably to the shorter C-O bond length than the C-C,^{2d} it is of great interest to see how the internal strain is dissipated within the ether molecules.

The potential energy functions associated with the valence angle deformation of water and simple ethers are another subject of recent interest.⁴ Linearization of the valence angle at the dis-coordinated oxygen is estimated to require an energy of about 35 kcal/mol. In this connection, the C-O-C bond lengths and angle in bis(9-triptycyl) ether (**1**) are of paramount interest.

The potential energy surface on which the geared motion proceeds smoothly appears to consist of a deep valley in which there is only a small up-and-down defining the potential energy barrier to the gear-meshing process and the ground-state conformation. The energy minimum structure of the methanes has been shown by the molecular mechanics method⁵ to be of C_2 symmetry. The structure is reproduced approximately in the crystal lattice.^{3b,d} The ether, on the other hand, was suggested to have a C_s ground-state conformation by the CP/MAS NMR spectra of the powder sample.^{2d}

We have therefore undertaken work on the crystal and molecular structure of bis(9-triptycyl) ether (**1**) to clarify the above.

Experimental Section

Preparation of the Sample. The ether **1** was prepared as described previously.^{2a,d} Plate-like crystals of $\text{Tp}_2\text{O}\cdot 2\text{Bz}$ used for the X-ray work were grown slowly from benzene.

X-ray Analysis. Diffraction data were obtained on a Rigaku AFC-5 four circle diffractometer with graphite-monochromatized Cu K α radiation. Crystal data: $\text{C}_{52}\text{H}_{36}\text{O}$ (= $\text{Tp}_2\text{O}\cdot 2\text{Bz}$), monoclinic, space group $P2_1/c$, $a = 20.868$ (2) Å, $b = 10.405$ (1) Å, $c = 18.912$ (1) Å, $\beta = 114.12$ (1)°, $V = 3747.7$ (5) Å³, $Z = 4$, $d_c = 1.203$ g cm⁻³, and $d_m = 1.207$ g cm⁻³. Within the range $2\theta < 120^\circ$, 4494 independent reflections with $|F| > 3\sigma(F)$ were obtained and used in the structure analysis. The

(1) (a) Institute for Molecular Science. (b) Ibaraki University. (c) Hokkaido University.

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Table I. Fractional Positional Parameters ($\times 10^5$) with Esd's in Parentheses

atom	x	y	z
O	73061 (7)	12411 (16)	18411 (9)
C(1)	65822 (13)	35556 (23)	12601 (13)
C(2)	61745 (17)	46543 (25)	9436 (15)
C(3)	55114 (16)	47657 (27)	9248 (16)
C(4)	52306 (14)	37993 (24)	12029 (14)
C(5)	58050 (12)	15310 (25)	33341 (14)
C(6)	63441 (13)	14415 (25)	40655 (14)
C(7)	70258 (13)	13043 (24)	41413 (13)
C(8)	71801 (11)	12512 (21)	34930 (13)
C(9)	66784 (10)	13517 (20)	19568 (12)
C(10)	54052 (11)	15706 (23)	18609 (13)
C(11)	54981 (11)	4006 (22)	14372 (12)
C(12)	61808 (10)	2872 (20)	14842 (12)
C(13)	63431 (12)	-6962 (22)	10863 (14)
C(14)	58227 (14)	-15637 (22)	6575 (14)
C(15)	51549 (14)	-14606 (24)	6189 (15)
C(16)	49885 (12)	-4808 (24)	10156 (14)
C(4a)	56259 (11)	27192 (22)	15223 (12)
C(8a)	66491 (10)	13454 (19)	27586 (12)
C(9a)	63053 (11)	26073 (20)	15635 (12)
C(10a)	59512 (11)	14723 (21)	26849 (13)
C(1')	78992 (13)	-10116 (23)	28856 (14)
C(2')	82337 (15)	-20405 (25)	33564 (18)
C(3')	89503 (17)	-20833 (27)	37256 (18)
C(4')	93608 (14)	-10980 (26)	36357 (16)
C(5')	94807 (12)	32140 (26)	37412 (14)
C(6')	91411 (14)	42314 (25)	38991 (15)
C(7')	84182 (14)	43251 (23)	35410 (14)
C(8')	80231 (11)	33944 (22)	30186 (13)
C(9')	80289 (10)	12082 (20)	23208 (12)
C(10')	93932 (11)	10877 (23)	29970 (14)
C(11')	91217 (11)	11448 (22)	21219 (13)
C(12')	83897 (11)	12120 (20)	17572 (13)
C(13')	80543 (12)	12660 (22)	9570 (14)
C(14')	84604 (13)	12620 (25)	5226 (14)
C(15')	91762 (14)	11930 (27)	8840 (16)
C(16')	95159 (12)	11391 (26)	16871 (16)
C(4a')	90346 (12)	-592 (23)	31758 (14)
C(8a')	83620 (11)	23474 (21)	28697 (12)
C(9a')	83026 (11)	-138 (21)	28061 (13)
C(10a')	90955 (11)	22611 (22)	32303 (13)
C(1b)	67350 (16)	52942 (30)	37497 (21)
C(2b)	64533 (16)	56199 (33)	29870 (19)
C(3b)	63166 (14)	68707 (37)	27844 (17)
C(4b)	64492 (16)	77964 (30)	33335 (22)
C(5b)	67361 (16)	74685 (34)	40917 (20)
C(6b)	68853 (17)	62125 (33)	43084 (17)
C(7b)	85611 (20)	98047 (51)	65664 (24)
C(8b)	86517 (17)	101287 (32)	59153 (24)
C(9b)	86398 (18)	92030 (39)	54187 (20)
C(10b)	85633 (18)	80059 (40)	55562 (23)
C(11b)	84829 (23)	76370 (42)	61899 (30)
C(12b)	84902 (27)	85363 (57)	67106 (26)

intensity data were corrected for Lorentz and polarization factors and for absorption ($\mu = 0.544 \text{ mm}^{-1}$). The size of the crystal used for data collection was approximately $0.60 \times 0.54 \times 0.18 \text{ mm}$.

The structure was solved by a direct method and refined by block-diagonal least squares. The weights (w) were taken as $w = [\sigma_c^2 + (0.015|F|)^2]^{-1}$. The atomic scattering factors for non-hydrogen atoms were taken from ref 6 and those for hydrogen from Stewart et al.⁷ All the hydrogen atoms were located by Fourier difference syntheses, and their positional and isotropic thermal parameters were refined. The final R and R_w values were 0.052 and 0.072, respectively. Positional parameters for non-hydrogen atoms are listed in Table I.

All the calculations were carried out on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science using Library Programs MULTAN and UNICS III.⁸

(6) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(7) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(8) The programs used were MULTAN (written by P. Main) and UNICS III (written by T. Sakurai and K. Kobayashi).

Table II. Selected Bond Lengths and Bond Angles of Tp_2O

bond	bond length, Å	bond	bond angle, deg
O-C(9)	1.418 (3)	C(9)-O-C(9')	135.8 (2)
O-C(9')	1.407 (2)	O-C(9)-C(8a)	124.2 (2)
C(9)-C(8a)	1.542 (4)	O-C(9)-C(9a)	108.0 (2)
C(9)-C(9a)	1.547 (3)	O-C(9)-C(12)	107.5 (2)
C(9)-C(12)	1.531 (3)	O-C(9')-C(8a')	119.0 (2)
C(9')-C(8a')	1.541 (3)	O-C(9')-C(9a')	116.4 (2)
C(9')-C(9a')	1.535 (3)	O-C(9')-C(12')	104.6 (2)
C(9')-C(12')	1.536 (4)	C(9')-O-C(9)-C(8a) ^a	-6.3 (4)
C(4a)-C(10)	1.514 (4)	C(9')-O-C(9)-C(9a)	117.4 (2)
C(10a)-C(10)	1.512 (3)	C(9')-O-C(9)-C(12)	-131.0 (2)
C(10)-C(11)	1.513 (4)	C(9)-O-C(9')-C(8a')	-58.0 (3)
C(4a')-C(10')	1.518 (4)	C(9)-O-C(9')-C(9a')	71.1 (3)
C(10a')-C(10')	1.515 (4)	C(9)-O-C(9')-C(12')	-174.2 (2)
C(10')-C(11')	1.516 (3)		

^a Torsion angle in degrees.

Table III. Comparison of the Corresponding Bond Lengths (Å) and Angles (deg) of R_2O and R_2CH_2

R	R_2O		R_2CH_2	
	$l(\text{R}-\text{O})$	$\angle\text{ROR}$	$l(\text{R}-\text{CH}_2)$	$\angle\text{RCR}$
$\text{CH}_3^{19,21}$	1.416	111.5	1.533	112.0
$\text{CPh}_3^{20,22}$	1.454 ^a	127.9	1.571	128.0
	1.465		1.567	
$\text{Tp}^{b,3}$	1.407 ^a	135.8	1.532, 1.578	129.3 ^{a,c}
	1.418		1.609, 1.557	129.5
$\text{SiH}_3^{28,29}$	1.631	142.2	1.873	114.4
$\text{SiPh}_3^{26,27}$	1.616	180.0	1.850	128.8

^a Unequivalent bond lengths. ^b This work. ^c Two slightly different molecular structures in a unit cell.

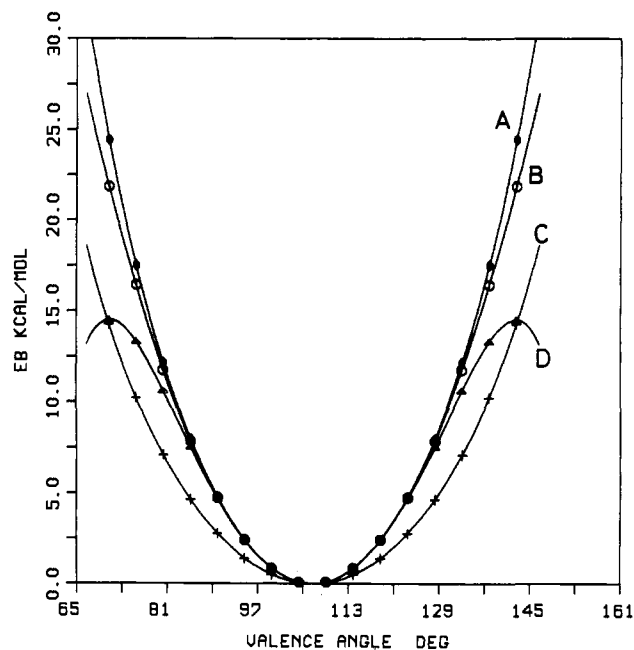


Figure 1. Angle bending potential curve (eq 1, $\theta_0 = 106.8$, $n = 4$) for the C-O-C type illustrating the effect of changing the quadratic force constant k_θ and the sign of anharmonicity constant k'_θ . (A) $k_\theta = 0.77$, $k'_\theta = 0.007 \times 10^{-5}$ (MM2 original). (B) $k_\theta = 0.77$, $k'_\theta = 0.0$. (C) $k_\theta = 0.45$, $k'_\theta = 0.007 \times 10^{-5}$. (D) $k_\theta = 0.77$, $k'_\theta = -0.02 \times 10^{-5}$.

Computational Technique. For a molecule the size of **1**, conventional computational techniques like the MMPI method,⁹ where molecular mechanics⁹ is combined with the π -MO method, are too slow, and the fastest molecular mechanics technique involving "mechanical benzene ring treatment"¹⁰⁻¹² appears to be the only practical one. When **1** was

(9) (a) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893. (b) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *Ibid.* **1974**, *96*, 5100. (c) Allinger, N. L. *QCPE* **1976**, *11*, 318.

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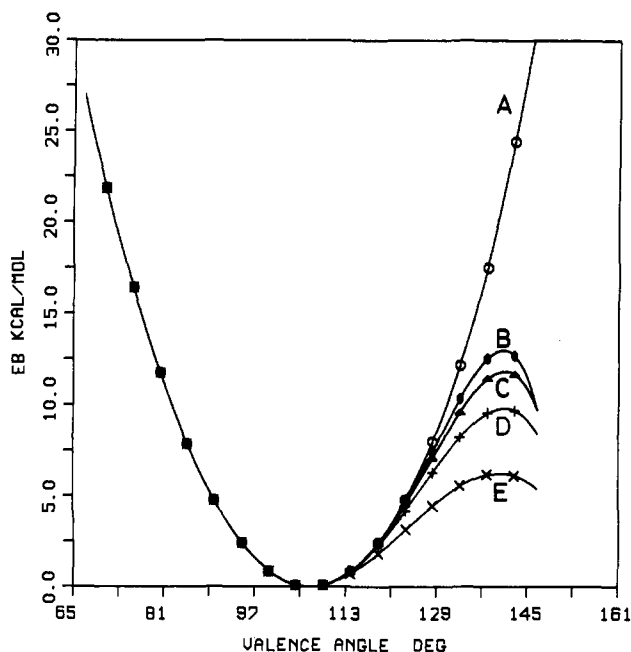


Figure 2. Angle bending potential curve (eq 1, $\theta_0 = 106.8$, $k_\theta = 0.77$) for the C—O—C type illustrating the effect of changing two anharmonicity constants (k'_θ and n). $k'_\theta = 0$ for angles smaller than the natural angle. (A) $k'_\theta = 0.007 \times 10^{-5}$, $n = 4$ (MM2 original). (B) $k'_\theta = -0.025 \times 10^{-5}$, $n = 4$. (C) $k'_\theta = -1.0 \times 10^{-5}$, $n = 3$. (D) $k'_\theta = -4.3 \times 10^{-4}$, $n = 2$. (E) $k'_\theta = -2.0 \times 10^{-2}$, $n = 1$.

subjected to MM2 calculations¹³ using this benzene ring treatment, however, the critical C—O—C angle in the energy-minimized structure with C_s symmetry (**1a**) was 126.3° , much smaller than the observed value of 135.8° (Table II).¹⁴ The somewhat smaller C—O—C angle of bis(triphenylmethyl) ether (**2**, 127.9° , Table III) was also underestimated by the MM2 method (124.4°).

In order to overcome these difficulties, a modification of the force field has been attempted. The force field has been designed to respond to such large angle deformation as observed in **1** by means of the anharmonicity term which was intended to compensate for some of the excessive angle strain arising from the quadratic term (eq 1)¹³

$$E \text{ (kcal/mol)} = 0.021914k_\theta(\theta - \theta_0)^2[1 + k'_\theta(\theta - \theta_0)^n] \quad (1)$$

where k_θ = bending force constant (mdyn Å/rad²), k'_θ = anharmonicity constant, θ = bond angle, and θ_0 = natural bond angle. However, the positive k'_θ (7×10^{-5}) and large power n (4) used for this term in the original MM2 strongly resist the occurrence of very large deformations (compare curves A and B in Figure 1). Reducing the k_θ constant is effective in decreasing the strain at large deformations (curve C), but then the strain at small deformations is also greatly reduced.¹⁵ Instead, retaining the original k_θ and θ_0 and using negative k'_θ seem promising (curve D) in that it has little effect in the small deformation region but greatly reduces the strain in the large deformation region.¹⁶ This approach was further tested as shown in Figure 2. Under these conditions, the contribution of the correction term overwhelms the quadratic contribution when the angle exceeds about 140° . This is certainly an unrealistic disadvantage in using this type of equation for molecules like **1**. The best compromise was achieved when $k'_\theta = -4.3 \times 10^{-4}$ and $n = 2$ (curve D). When this modified bending potential was used in conjunction with the MM2' force field, a new version of MM2,¹⁷ the calculated

C—O—C angle as well as other key structural parameters of **1a** and **2** were reasonably well reproduced (vide infra).

Results and Discussion

X-ray Crystallographic Results. Figure 3 shows the crystal structure of $\text{Tp}_2\text{O} \cdot 2\text{Bz}$. There are two crystallographically independent benzene molecules of crystallization in the unit cell. All molecules including the benzene molecules are well separated, with all contacts of the non-hydrogen atoms being greater than 3.6 Å. Thus, their packing cohesions are normal van der Waals interactions.

Molecular Structural Features of 1. A stereoscopic view of the molecular structure of Tp_2O (**1**) is given in Figure 4 along with the atom numbering scheme. Selected bond lengths and angles of interest are collected in Table II.

The entire molecule constitutes a crystallographic asymmetric unit and thus has no rigorous symmetry. However, as Figure 4 shows, there is an approximate symmetry plane formed by the ether linkage C(9)—O—C(9'). One of the most striking features of this approximate C_s structure is that the C—O—C angle is expanded to as much as 135.8° , the highest angle ever reported for a divalent oxygen attached to two carbon atoms. This seems to be the obvious outcome of the nonbonded repulsive interaction present between the two triptycyl units in the ground-state conformation of the molecule (Table III). The angle increases as we go from water (104.52°)¹⁸ to dimethyl ether (111.5°)¹⁹ and to bis(trityl) ether (127.9°).²⁰ In the methane series, the angles are 109.5° (methane), 112.0° (propane),²¹ 127.2° (bis(trityl)methane,²² and 129.3 – 129.5° (bis(9-triptycyl)methane).^{3d} The difference in the last two compounds is only about 2° . We therefore did not predict the angle of **1** to be considerably larger than 130° .²³ The reason the C—O—C angle is so large here and the MM2 method is not successful in reproducing such a large angle (vide infra) may be due to the short C—O bond lengths, which are 1.407 (2) and 1.418 (3) Å and even shorter on the average than that of dimethyl ether (1.416 Å). Nonbonded interaction between the biting teeth (benzene rings in **1**) of the gear would then be increased proportionally. To avoid this effect, the C—O—C bond angle has to be stretched out further. In bis(trityl) ether (**2**), the bond lengths are 1.454 and 1.465 Å. Thus, the bond lengths seem to be governed not only by the repulsive interaction between the attached ligands but also by a quantum mechanical electronic effect. This may be the different bond hybridization of the carbon atoms attached to the oxygen atom. The trityl-to-oxygen bond is expected to be rich in p-character, while the bond extending out of the bridgehead of the triptycene units is known to have high s-character. They are not typical C_{sp^3} —O bonds but ca. $sp^{2.5}$ hybridized.²⁴

We then note the barely nonequivalent C—O bond lengths: C(9)—O is longer than C(9')—O by 0.011 (4) Å.²⁵ The conformation of the C(9)—O bond is fixed in such a way that the two sp^3 -like lone pairs of electrons and two C—C bonds forming the

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(19) Kimura, K.; Kubo, M. *J. Chem. Phys.* **1968**, *30*, 151.

(20) Glidewell, C.; Liles, D. C. *Acta Crystallogr. Sect. B* **1978**, *B34*, 696.

(21) Lide, D. R. *J. Chem. Phys.* **1960**, *33*, 1514.

(22) Winter, W.; Moosmayer, A.; Rieker, A. *Z. Naturforsch., B* **1982**, *37B*, 1623. See also ref 3d.

(23) See footnote 37 in ref 2d and footnote 12 in ref 3d. The reasoning is based on the possible similarity in the space-demanding properties of triptycyl and trityl groups. However, comparison of structural features of **1** and **2** revealed significant differences between these groups. Both the central angle (135.8° for **1a**, 127.9° for **2**) and the largest angle around the C_{sp^2} carbon atoms (124.2° for **1a**, 114.6° for **2**) are much larger for triptycyl. Likewise, the tilt angle, the angle between the O—C bond axis and the approximate three fold axis of the bulky group (19.8° for **1**, 11.7° for **2**, both being the sum of two tilt angles), is also larger for **1a**. Hence, the reasoning is not warranted at least for **1** vs. **2**.

(24) (a) Theilacker, W.; Albrecht, K.; Uffmann, H. *Chem. Ber.* **1965**, *98*, 428. (b) Iwamura, H., unpublished work.

(25) The difference between the two bond lengths is comparable to and not greater than 3σ , 99.9% confidence limit, and therefore should not be taken very seriously. We thank a referee for pointing this out. However, the nonequivalent bond lengths are reproduced by our MM2' calculation and suggested by the CP/MAS ¹³C NMR spectra (see text).

(11) After completion of this work, Beckhaus¹² recommended changing the C_{sp^2} — C_{sp^2} — C_{sp^2} bending force constant and torsional constants about the C_{sp^2} — C_{sp^2} bond along with the stretch constants of the latter. In a rigid system like **1**, these additional changes should not give significantly different results.

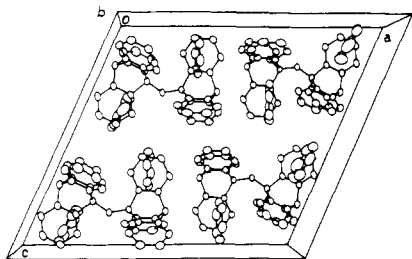
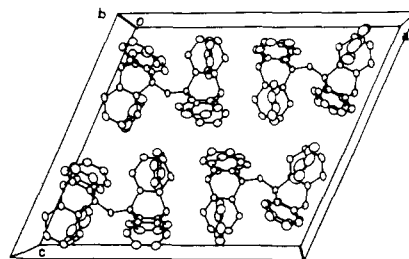
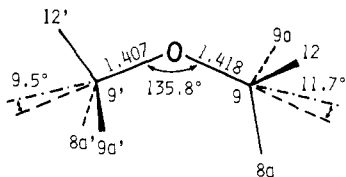
(12) Beckhaus, H.-D. *Chem. Ber.* **1983**, *116*, 86.

(13) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *11*, 395.

(14) MM2 well reproduces structural features of bis(9-triptycyl)methane including the central bond angle.^{3d}

(15) In Allinger's MM scheme, parameters k'_θ and n are universal for all types of atoms. Hence, any modification that affects small deformation region disturbs hydrocarbon part as well.

(16) A negative k'_θ has been used in the Engler force field (Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005) and also in MM1 (Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579).

Figure 3. Packing arrangement of $Tp_2O \cdot 2Bz$ viewed along the b axis.Figure 4. Stereoviews of the X-ray structure of bis(9-triptycyl) ether (**1**).Figure 5. Structural features of the ether linkage in **1**.

tritycene framework are eclipsed, while they are staggered in $C(9')-O$ (Figure 5). From a different point of view, a lone pair of electrons in the sp^2 inplane orbital at the oxygen is in a better position to overlap with the $C-C \sigma^*$ orbital at $C(9')$. In any event, the different bond lengths appear to be of conformational origin. Previously, the powder sample of **1** showed two separate ^{13}C signals (1.3 ppm apart) for $C(9)$ and $C(9')$, a result compatible with the molecule with the C_s point group. The C_2 symmetry of the molecule had not been rigorously excluded since, unless the molecule lies on a crystallographic symmetry element, it could show nonequivalent $C(9)$ and $C(9')$ due to different crystal fields.² The latter was now shown not to be the case.

The significantly shorter than usual $C-O$ bond distance and the unusually expanded $C-O-C$ bond angle are highly reminiscent of the linear μ -oxo bridge in transition-metal complexes. The closest analogy may be seen in bis(triphenylsilyl) ether which has a linear structure.²⁶ The $Si-C-Si$ angle in the corresponding bis(triphenylsilyl)methane is only 128.8° (see Table III). In terms of a Walsh diagram, the $1\pi_u$ orbital in the linear configuration of AB_2 molecules is considered to be stabilized by interaction with the vacant $d_{x^2-y^2}$ orbital on the two silicon atoms. Such a bonding model may also be contributing in stabilizing the widened configuration in the present ether. The three $C-C$ bonds extending from the bridgehead carbons and forming the bicyclo skeleton of the triptycene moieties are known to be bent and rich in p -character.²⁴ The σ^* orbitals may then be low-lying and could interact with the $1\pi_u$ orbitals of the ether oxygen to stabilize them. In the trityl derivative **2**, it is obvious that the $Ph-C$ bonds are

rich in s -character and the $C-O$ bonds tend to be rich in p -character. The trend is just the opposite of our case.

Severe steric crowding in the internal region of the molecule of C_s-1 that caused the great opening of the $C-O-C$ angle manifests itself in several other features as well. Valence angles about the bridgehead carbon atoms ($C(9)$ and $C(9')$) are unusual: $O-C(9)-C(8a)$ (124.2°) as well as $O-C(9')-C(8a')$ and $O-C(9')-C(9a')$ are abnormally expanded (Tables II and IV³⁰). Strain in this molecule is concentrated at the cog most deeply nested in the notch (the benzene ring $C(8a)-C(10a)-C(5)-C(6)-C(7)-C(8)$). This is indicated by the very large $O-C(9)-C(8a)$ angle and also by the fact that the $O-C(9)$ is longer than $O-C(9')$. Tilting of the $C-O$ bond direction from the threefold symmetry axis of each triptycene unit is also noted. These distortions amount to 11.7° and 9.5° . Such a deformation mode was first pointed out in a *tert*-butyltritycene derivative for which the tilt angle was 4.3° .³¹

Computational Results on Energy-Minimized Structure of **1**.

The crystal conformation of **1** with the C_s point group (**1a**) is also an energy minimum on the MM2' energy surface. The C_2 conformation (**1b**) is also an energy minimum, but 0.24 kcal/mol higher in steric energy than **1a**. The calculated structural parameters are collected in Table V. The relative stability of these two conformers is the reverse of the known stability order in bis(triptycyl) carbon derivatives where C_2 conformers are 0.2–1.9 kcal/mol more stable than the C_s form.^{3b,d} This contrasting behavior of the oxygen-bridged and carbon-bridged bis(triptycyl)s is due to the destabilization of the C_s form in the latter by the eclipsing interaction between the $C(9)-C(9a)$ and $C(9)-C(12)$ bonds on the one hand and the $C-H$ and $C-O$ bonds at the central carbon in the methane and carbinol derivatives.³² There is no such destabilization in **1a**.

The calculated structural features follow quite nicely those experimentally determined except that the calculated $C-O-C$

(26) Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 124. $Si-O$ π bonding is not necessarily popular in the current theory of silicon chemistry, but a similar π bonding may be more important in the $C-O$ bonds.

(27) Glidewell, C.; Liles, D. C. *J. Organomet. Chem.* **1982**, *234*, 15.

(28) Almenningen, A.; Bastlansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455.

(29) Almenningen, A.; Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1970**, *24*, 1697.

(30) Unusual bond angles also appear in bis(9-triptycyl)methane, bis(9-triptycyl)carbinol, and bis(9-triptycyl)ketone. They are shown in Table IV based on the crystal coordinates in ref 3b,d. Note the extraordinarily large angles at $C(1)-C(10)-C(11)$. For the numbering, see ref 3b,d.

(31) Mikami, M.; Torumi, K.; Konno, M.; Saito, Y. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2474.

(32) It is well-known that the carbonyl double bond ($C=O$) acts as a pair of bent bonds as far as steric behavior is concerned: Dale, J. "Stereochemistry and Conformational Analysis"; Verlag Chemie: Weinheim/Bergstr., Germany, 1978; p 74.

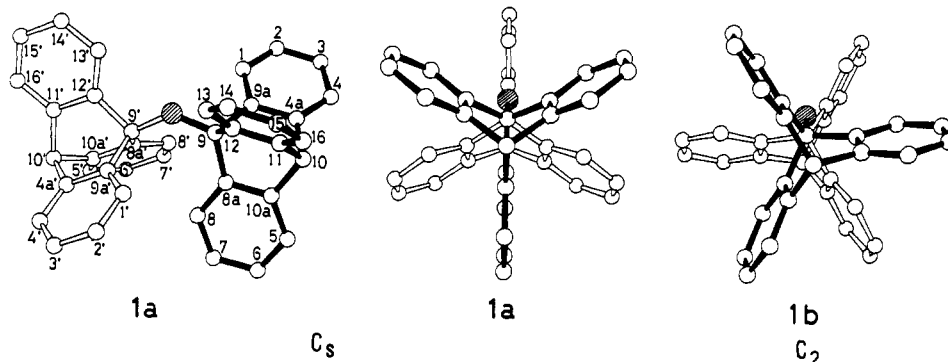


Table IV. Valence Angles about the Bridgehead Carbon Atoms in Tp_2X ($\text{X} = \text{CH}_2, \text{CHOH}, \text{CO}$)^a

angle	methane		carbinol	ketone	
	C(1)	C(1')	C(1)	C(1)	C(2)
C(1)-C(10)-C(11)	122.7°	(123.6°)	121.3°	124.5°	122.6°
C(1)-C(10)-C(21)	111.5°	(108.9°)	107.2°	108.1°	106.7°
C(1)-C(10)-C(31)	109.9°	(108.9°)	115.6°	109.5°	113.3°
C(1)-C(40)-C(41)	119.9°	(117.7°)	118.0°	116.7°	122.6°
C(1)-C(40)-C(51)	115.4°	(114.4°)	113.0°	109.9°	106.7°
C(1)-C(40)-C(61)	109.7°	(106.5°)	112.4°	115.2°	113.3°

^a For the numbering, see ref 3b,d.

Table V. Calculated Structural Parameters and Conformational Energies of Tp_2O (**1**) by MM2^a

	1a (C_s)	1b (C_2)	barrier ^b
O-C(9)	1.413	1.409	1.412
O-C(9')	1.403	1.409	1.405
C(9)-C(8a)	1.540	1.534	1.519
C(9)-C(9a)	1.536	1.534	1.547
C(9)-C(12)	1.536	1.534	1.543
C(9')-C(8a')	1.527	1.534	1.523
C(9')-C(9a')	1.527	1.534	1.516
C(9')-C(12')	1.533	1.534	1.548
C(9)-O-C(9')	131.8	131.6	132.9
O-C(9)-C(8a)	123.2	122.3	123.3
O-C(9)-C(9a)	111.3	112.0	110.7
O-C(9)-C(12)	111.3	111.3	110.8
O-C(9')-C(8a')	117.3	122.3	117.1
O-C(9')-C(9a')	117.3	112.0	117.0
O-C(9')-C(12')	110.4	111.3	109.8
C(9')-O-C(9)-C(8a)	0.0	-31.6	-14.7
C(9')-O-C(9)-C(9a)	124.4	95.8	112.0
C(9')-O-C(9)-C(12)	-124.4	-152.4	-138.7
C(9)-O-C(9')-C(8a')	-65.2	-31.6	-50.4
C(9)-O-C(9')-C(9a')	65.2	95.8	80.5
C(9)-O-C(9')-C(12')	180.0	-152.4	-164.9
ϕ_1^c	0.0 ^d	90.6	106.2
ϕ_2^c	60.0	90.6	75.1
rel E_s^e	0.00	0.24	0.93

^a Modified anharmonicity constants used in the angle bending potential. See text. Bond lengths in Å, angles in degrees, and energies in kcal/mol. ^b C_1 . ^c Torsional coordinates. See text. ^d Equivalent to 120°. ^e Relative energy.

angle and the tilt angles of the Tp moieties from the Tp-O bond axes are somewhat smaller. The unsymmetrical C(9)-O and C(9')-O bond lengths are again obtained.²⁴

It is interesting to compare the steric crowding in the internal part of the geared molecules of **1** and the carbon analogues. We use here the area of a triangle made by three atoms, C(8), C(1'), and C(8'), as a simple measure of the depth of gear-biting.³³ Remarkable constancy of the areas (4.9–5.3 Å² in Table VI) suggests that the deepest possible gearing has been achieved for

(33) The observed C(8a)-C(9)-C(9a') angle (106.8°) of **1** is near normal, and hence the distance C(1')...C(8') or the cog width is supposed to remain nearly constant, at least in the energy minimum conformation. Then, it is the height of this triangle, that is the depth of gearing, which primarily determines the area. The area decreases as the gear tightens and eventually reaches zero when these three atoms become collinear.

Table VI. Area of Triangle (C(8), C(1'), C(8')) in Energy Minimum Conformations of Tp_2X ($\text{X} = \text{O}, \text{CH}_2, \text{CHOH}, \text{CO}$)

compd	X	sym group	area, Å ²
1a	O	C_s	5.17 (4.93) ^a
1b		C_2	— (5.05) ^a
	CH ₂	C_1	5.09
	CHOH	C_1	4.92
	C=O	C_1	5.05
		C_2	5.37

^a Based on the final MM2' coordinates in this work. Otherwise X-ray coordinates are used.

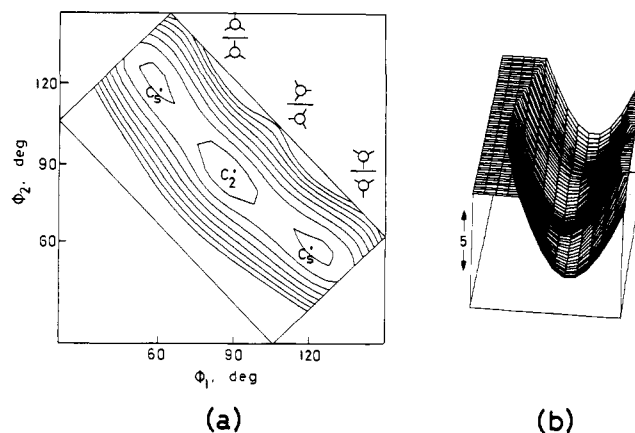


Figure 6. Partial torsional energy surface of Tp_2O (**1**). (a) Contour map with line spacings every 1 kcal/mol. ϕ_1 and ϕ_2 are the torsional coordinates along O-C(9) and O-C(9') bonds, respectively. Schematic representation of C_s and C_2 conformations follows Mislow's convention.³ (b) Perspective view of the three-dimensional surface as seen along the direction of dynamic trajectory. Energy in kcal/mol.

all of the Tp_2X 's examined here. The tendency to form a gear in Tp_2X 's is so large, as can be readily seen by examining framework models, that the primary factor in determining the energy minimum structure must be how to loosen the meshing of the gears to a "permissible" extent, and this extent appears to be the same for all Tp_2X 's irrespective of the type of central atom, X.³⁴ Hence, the different hybridization of carbon and the resultant difference in the natural bond angles and lengths in the carbon derivatives did not greatly alter the structure, giving almost identical central bond angles of about 129°. In **1**, the C-O-C angle had to be expanded to an unprecedented extent in order to make up for the short C-O natural length (1.407 Å in MM2') and to keep the same, deepest possible meshing in the internal part of the molecule.³⁵

(34) The statement may be true of the second-row atoms for X. When the system is extended to the third-row atoms for X as in bis(9-triptycyl)silane (see footnote 35 of ref 3d), the gear can get loose and the gear slipping can take place readily.

(35) The larger central angle of **1** compared to those of **3** to **5** does not necessarily mean that the angle of ether oxygen valence is more readily deformed than sp³-carbon valence angles. The universal quadratic force constant for bending of angle C-O-C (0.770 mdyne/Å/rad²) is larger than that for the C-C-C angle (0.450) in MM2'.

Gearing Energy Surface of 1. Because of the stated inadequacy of the angle bending potential function for large deformations (vide supra), attempts at simulating gear slippage were unsuccessful. Hence, we concentrated in this work on covering the part of the torsional energy surface that pertains to the dynamic gearing process.³⁶

The torsional coordinates³⁶ are used to draw the surface:

$$\phi_1 = (\omega_1 + \omega_2 + \omega_3 + \alpha)/3$$

$$\phi_2 = (\omega_4 + \omega_5 + \omega_6 + \alpha)/3$$

where ω_1 , ω_2 , and ω_3 are the three torsional angles passing through the ether linkage and terminating at C(9), whereas ω_4 , ω_5 , and ω_6 are those terminating at C(9'). Angle $\alpha = 0$ when the smallest ω is between 0 and $\pi/3$, and $\alpha = 2\pi$ when the smallest ω is between $\pi/3$ and $2\pi/3$. About 70 points near the gearing coordinates were calculated and smoothed³⁷ to give an energy surface which is reproduced in Figure 6. According to this map, the dynamic gearing of 1 takes place rapidly along an almost flat valley having a finite width. Between the two adjacent energy minima (C_s and C_2) is a very low, unsymmetrical barrier, only 0.93 kcal/mol above C_s . The calculated low barrier is in accord with the failure to detect it in low-temperature NMR experiments on 1.^{2a,d} Our calculations indicate that the C-O-C angle expands further by 1° at the top of the barrier.³⁸

(36) In these calculations, the C-O-C angle had to be fixed at the outset of minimization in order to prevent this angle from expanding beyond the artificial maximum in the potential curve, leading to "explosion" of the molecule. Only at the final stage of minimization was the C-O-C angle relaxed.

(37) E. Ōsawa, *J. Comput. Chem.* 1982, 3, 400.

In the hydrocarbon analogues, C_s conformations (observed in crystals slightly distorted to C_1 point group) are the transition states along the dynamic gearing trajectory with C_2 conformations as the global energy minima.^{3b,d} In 1, both of these conformations are energy minima.

The present X-ray analysis and molecular mechanics calculations give the following partial picture of the novel molecule 1: a slightly worn out but still considerably tightly meshed gear with unusually large deformation at the oxygen bridge and with strain in the internal part as strong as in Mislow's hydrocarbon analogues.³

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Registry No. 1, 90990-93-5.

Supplementary Material Available: Tables of hydrogen atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

(38) The employed potential energy function for the C-O-C valence angle underestimates the increase of the energy and even becomes defective at ca. 140° as the angle increases from the equilibrium value. Therefore, if the valence angle changed drastically along the calculated torsional coordinate, the result should have been regarded invalid. Fortunately, the valence angle change was kept within 1°.

Preparation and Lithiation of Optically Active 2,2'-Dihalo-1,1'-binaphthyls. A General Strategy for Obtaining Chiral, Bidentate Ligands for Use in Asymmetric Synthesis

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Abstract: Chiral, bidentate ligands based on the 1,1'-binaphthyl system have achieved remarkable success in certain asymmetric syntheses that have been reported in the literature. Enantiomeric excesses are often above 90% and may approach 99% or better. In the present paper, it is demonstrated that 2,2'-dibromo-1,1'-binaphthyl and the corresponding diiodide can be obtained in preparative quantities with optical purities in excess of 98%. The compounds can be mono- or dilithiated, and the lithio intermediates are configurationally stable from -131 °C up to at least -44 °C. Yields of the dilithio intermediate are 95% or higher, and the monolithio intermediates can be formed in chemical yields of 80-85%. This discovery provides an efficient, general route for obtaining symmetrical and unsymmetrical chiral, bidentate ligands based on the binaphthyl system. These derivatives are expected to have broad applications in mechanistic studies of asymmetric reactions and in practical synthetic procedures. For example, (*R*)- and (*S*)-BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl), which are reported to give enantiomeric excesses approaching 100% in certain rhodium-catalyzed hydrogenations, have been synthesized from 2-naphthol in overall yields ranging from 16% to 34%.

I. Introduction

In recent years, optically active 2,2'-disubstituted-1,1'-binaphthyl derivatives have been used in the asymmetric hydride reduction of ketones,¹ in the asymmetric hydrogenation of amino

acrylic acid derivatives,^{2a} in the isomerization of allylamines to chiral enamines,^{2b} in the asymmetric alkylation and arylation of

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