J. Am. Chem. Soc. **1981**, *103*, 957-958

Stereoisomerism and Correlated Rotation in Molecular Gear Systems. Residual Diastereomers of Bis(2,3-dimethyl-9-triptycyl)methane

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Received September 29, 1980

Empirical force-field calculations[1] have revealed that the 9-triptycyl (Tp) groups in bis(9-triptycyl)methane (Tp_2CH_2)[2] undergo nearly unhindered cogwheeling through a C_2 transition state which lies only ca. 1.0 kcal mol^{-1} above the C_s ground state.[3,4] We recently pointed out[1] that appropriately ring-substituted derivatives of Tp_2CH_2 and related molecules,[5] which resemble meshed bevel gear systems,[1,2] are capable of exhibiting residual stereoisomerism[6] under the constraint of dynamic gearing, i.e., of coupled disrotation of the Tp groups. We now report the realization of this prediction and present conclusive experimental evidence for correlated rotation in systems of this type.[9]

The compound chosen for this study, bis(2,3-dimethyl-9-triptycyl)methane (**1**), was prepared by addition of a fourfold excess of 4,5-dimethylbenzyne (from 4,5-dimethylanthranilic acid[10] and isoamyl nitrite) to bis(9-anthryl)methane[11] and was purified by column chromatography on silica, eluant 98:2 pentane/ether. Further chromatography on silica Woelm (particle size 32–63 μm) using the same solvent mixture yielded two products, **1a** and **1b**, which were readily differentiated by the properties listed in Table I and characterized as diastereomers by their ^{13}C and ^1H NMR spectra and thermal equilibration (see below).[12]

Nine conformers are expected[1] for **1**: one achiral form and four diastereomeric *dl* pairs. Under the operation of dynamic gearing these nine conformers undergo rapid interconversion in three sets of three conformers each, so that three residual stereoisomers remain: a residual meso isomer, consisting of a mixture of one achiral conformer and one *dl* pair (Figure 1) and two enantiomeric D and L residual isomers, each consisting of a mixture of three chiral, diastereomeric conformers (Figure 2).[13] Our observation

Table I. Some Characteristic Properties of 1a and 1b

isomer	mp, °C (sealed tube)	NMR spectrum (methyl region),[a] δ[b] ^1H	^{13}C
1a	324–327	1.75, 2.12 (1.77, 2.07)	19.25, 19.44
1b	382–385	1.97, 2.18 (1.93, 2.07)	19.29, 19.75

[a] Solvent $CDCl_3$ or $C_6D_5NO_2$ (parenthesized values). [b] In ppm downfield from internal Me_4Si, ambient temperature.

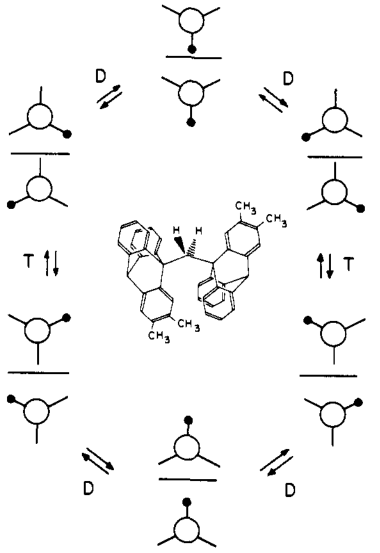

Figure 1. The conformational gearing circuit for the residual meso isomer of bis(2,3-dimethyl-9-triptycyl)methane (**1**). One of the three conformers of the molecule is depicted in the center. In the schematic projections around the perimeter, the view is along the bisector of the H–C–H angle, symbolized by a horizontal line. The circles represent C9 and C9′ of the 2,3-dimethyl-9-triptycyl moieties, and the three lines radiating from each circle represent the three aryl blades of each triptycyl group. The methyl-substituted benzene ring is marked by a heavy dot. Each gearing step, a disrotatory motion involving a ca. 60° twist of each moiety, is either a topomerization (T) or a diastereomerization (D).

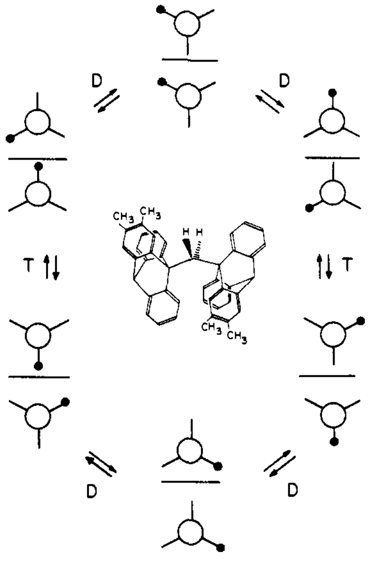

Figure 2. Same as Figure 1, but for the residual D or L isomer of **1**.

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[1] Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961.

[2] Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547.

[3] More refined calculations (R. B. Nachbar, Jr., unpublished results) suggest that the energy difference is even smaller and that the C_s and C_2 structures are almost isoenergetic. Further details will be provided in the full paper.

[4] The observation[2] of a low barrier (≤8 kcal mol^{-1}) to internal rotation in Tp_2CH_2 and bis(9-triptycyl) ether (Tp_2O), though consistent with our calculations, could also be accounted for by rapid rotation of the Tp groups *without* cogwheeling and therefore does not by itself constitute direct evidence for dynamic gearing.

[5] The first representative of this class of molecules, bis(9-triptycyl) selenide (Tp_2Se), was described some 20 years ago: Wittig, G.; Tochtermann, W. *Liebigs Ann. Chem.* **1962**, *660*, 23.

[6] Residual stereoisomerism results whenever closed subsets of appropriately substituted interconverting isomers are generated from the full set of isomers at a particular time scale of observation and under the operation of a given stereoisomerization mode.[7,8]

[7] Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.

[8] Residual diastereoisomerism has been demonstrated for molecular propellers under the operation of the two-ring flip mechanism: (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3198. (b) Glaser, R.; Blount, J. F.; Mislow, K. *Ibid.* **1980**, *102*, 2777.

[9] (a) For a critical discussion on the subject of dynamic gearing, see: Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* **1980**, *20*, 65. (b) Correlated rotation has been demonstrated for molecular propellers.[7]

[10] Brändström, A.; Carlsson, S. A. I. *Acta Chem. Scand.* **1967**, *21*, 983.

[11] Applequist, D. E.; Swart, D. J. *J. Org. Chem.* **1975**, *40*, 1800.

[12] All new compounds gave high-resolution mass spectra consistent with the assigned structures.

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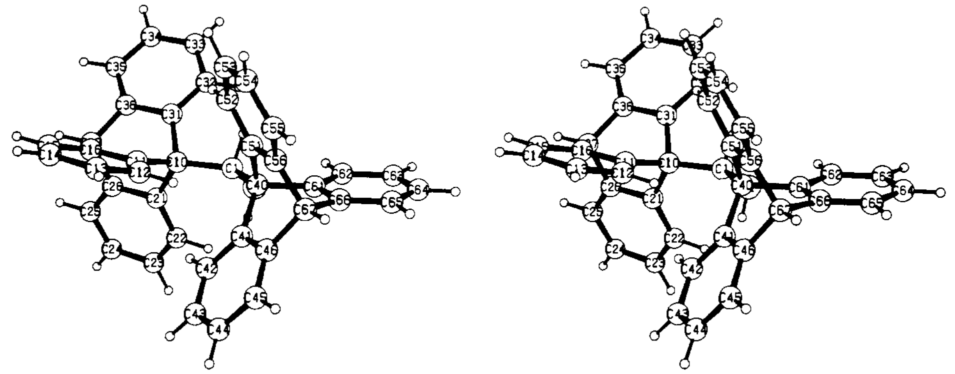

Figure 3. Stereoview of the X-ray structure of bis(9-triptycyl)carbinol (Tp_2CHOH).

of two and only two residual diastereomers is fully consistent with this analysis. Configurational assignments were made on the basis of the appearance of the aromatic $^{13}C\{^1H\}$ NMR region, which featured 18 signals for **1b** but only 12 for **1a**,[14] and by an analysis of the aromatic ^1H NMR region, which featured two ABCD spin systems for **1b** but only one for **1a**. Accordingly, **1a** was identified as the residual meso isomer and **1b** as the residual DL pair.[15]

That gear slippage is slow on the laboratory time scale is established by the isolation of two diastereomers of **1** at ambient temperature. This is also consistent with the extraordinarily large central C–C–C bond angle of 129° in a closely related compound, bis(9-triptycyl)carbinol (Tp_2CHOH, Figure 3):[16-20] the magnitude of the angle deformation indicates that the molecule is under considerable internal strain, with the Tp groups tightly meshed, and implies that gear slippage, which would require further expansion of the central bond angle, should be a highly unfavorable process. Indeed, interconversion of the diastereomers becomes readily observable only at elevated temperatures. In nitrobenzene-d_5, thermal equilibrium is attained within several hours at 156 °C; the equilibrium constant, $K(\mathbf{1b}/\mathbf{1a}) = 1.8 \pm 0.1$, corresponds to an almost statistical ratio of DL and meso isomers. The diastereomerization barriers, $\Delta G^{\ddagger} = 34.1$ and 33.6 kcal mol^{-1} at 156 °C,[23] are significantly higher than the topomerization barrier of ca. 20 kcal mol^{-1} calculated[1] for Tp_2CH_2, as might be expected considering that diastereomerization of **1a** or **1b** forces at least one of the two 2-methyl groups into the overcrowded central region of the transition state.[24,25]

Acknowledgments. We thank the National Science Foundation (CHE-8009670) for support of this work, Mary Baum for valuable technical assistance, and the Consiglio Nazionale delle Ricerche for a fellowship to one of us (F.C).

Supplementary Material Available: Structure factors, final positional and thermal parameters, bond lengths, bond angles, and selected torsion angles, with standard deviations, for Tp_2CHOH (28 pages). Ordering information is given on any current masthead page.

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[13] If the gearing barrier is less than RT kcal mol^{-1},[3] a distinction between the three conformers within each of the three sets may become meaningless: Eliel, E. L. *Isr. J. Chem.* **1977**, *15*, 7.

[14] Meso isomer (**1a**): $^{13}C\{^1H\}$ NMR (25.2 MHz, $CDCl_3$) δ 147.2, 146.4, 144.3, 143.7, 132.6, 131.7, 126.8, 125.0, 124.7, 124.6, 124.2, and 123.2 (aromatic carbons); 54.8, 54.7, 25.7, 19.4, and 19.2 (aliphatic carbons). DL isomer (**1b**): δ 147.3, 146.5, 146.5, 146.1, 144.8, 144.3, 132.9, 132.0, 125.7, 125.6, 125.0, 124.9, 124.9, 124.7, 124.3, 124.0, 123.2, and 123.1 (aromatic carbons); 54.8, 54.7, 25.7, 19.7, and 19.3 (aliphatic carbons).

[15] A permutational analysis[1] reveals that two residual diastereomers are expected under the operation of any one of six different stereoisomerization modes. However, all but two of these are immediately excluded on the basis of the NMR signal multiplicity. Of the remaining two modes, one corresponds to the gearing motion depicted in Figures 1 and 2 and the other to the corresponding antigearing motion, in which rotation of the moieties is conrotatory instead of disrotatory. Although empirical force-field calculations indicate that gearing is overwhelmingly the preferred mode,[1] the isolation of two residual diastereomers does not *by itself* rigorously exclude antigearing.[1]

[16] Crystals of Tp_2CHOH, prepared as previously described[1] and grown by slow evaporation of a pentane/ether solution, are monoclinic, space group $P2_1/n$. There are two independent molecules, primed and unprimed, of the carbinol in the unit cell. The crystals also contain 9% pentane and 6% ether solvent by NMR. The primed molecule represents a disordered arrangement of two molecules in almost the same orientation; we therefore place greater reliance in the geometry of the unprimed molecule, which is shown in Figure 3. The carbinol crystallizes as rods elongated along the b direction. Crystallographic data for Tp_2CHOH: $a = 21.385$ (5), $b = 17.408$ (6), $c = 17.433$ (5) Å; $\beta = 104.87$ (2)°, and $d_{calcd} = 1.137$ g cm^{-3} for $Z = 8$ ($C_{41}H_{28}O$, $M = 536.67$; solvent excluded from density); $R = 0.068$, $R_w = 0.076$ for 4969 reflections with $I > 2.5\sigma(I)$. Intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). Reflections were measured for $\theta < 48°$. The structure was solved by a multiple solution procedure [Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368]. The final refinement was carried out by block-diagonal least squares in which the matrix was partitioned into two blocks. Anisotropic thermal parameters were used for the nonhydrogen atoms of the unprimed and primed molecules, and isotropic temperature factors were used for the disordered oxygen atom, two solvent atoms, and the hydrogen atoms. The C10–C1–C40 angle assumes a value of 128.9 (3)° and 129.1 (4)° in the unprimed and primed molecule, respectively.

[17] It is noteworthy that this molecule undergoes enantiomerization exclusively through chiral structures under the constraint of gear meshing.[1]

[18] This value is comparable to the central bond angle (125–128°, as determined by electron diffraction) in di-*tert*-butylmethane.[19] We find a value of 123 Hz for the methylene ^{13}C–^1H NMR coupling constant in Tp_2CH_2, which is comparable in magnitude to the value of 125 Hz reported[19] for the methylene coupling constant in di-*tert*-butylmethane.

[19] Bartell, L. S.; Bradford, W. F. *J. Mol. Struct.* **1977**, *37*, 113.

[20] The observation of greatly expanded central bond angles in bis(triphenylmethyl) ether[21] and sulfide[22] suggests that Tp_2Se[5] and Tp_2O[2] may also have extraordinarily large central C–X–C angles, i.e., that the described phenomenon may not be unique to Tp_2X (as compared to $(trityl)_2X$) systems.

[21] Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 696.

[22] Jeffrey, G. A.; Robbins, A. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1820.

[23] The ratio of **1a** and **1b** was determined from the relative peak areas of the upfield methyl proton signals at 1.77 and 1.93 ppm (Table I) and was monitored as a function of time. The cited values of $\Delta G^{\ddagger}$ were obtained from a kinetic treatment[8b] of these data.

[24] We assume that the transition state for gear slippage in Tp_2CH_2 is approximated by the gear-clashed conformation **1B** in ref 1.

[25] By the same token, the barrier to interconversion of D- and L-**1b** is expected to be relatively low.

Bis(4-chloro-1-triptycyl) Ether. Separation of a Pair of Phase Isomers of Labeled Bevel Gears[1]

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Received September 25, 1980

The idea of geared rotation has often been adopted to explain unexpectedly fast internal rotation in apparently congested molecules, e.g., hexamethylbenzene,[2] 1,1,1-tri-*tert*-butyl compounds,[3] and Ar_3Z systems.[4] Coupled rotation of two parts of

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[1] Part 2 of this series. For part 1, see: Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547.

[2] Iroff, L. D. *J. Comput. Chem.* **1980**, *1*, 76 and references cited therein.

0002-7863/81/1503-958$01.25/0