

Stereochemical Consequences of Dynamic Gearing

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From Molecular Propellers to Molecular Gears

The torsional motions of two or more internal rotors in a molecule may be so strongly coupled that correlated rotation becomes energetically preferred over the independent rotation of the individual groups.¹ In appropriately structured molecules this phenomenon may result in the formation of stereoisomers, as first demonstrated for molecular propellers.² For example, it is possible under ordinary laboratory conditions to separate two conformational diastereomers of (2-methoxynaphthyl)(2-methylnaphthyl)(3-methyl-2,4,6-trimethoxyphenyl)methane, even though all three aryl groups in this triarylmethane are rapidly spinning about their bonds to the central carbon atom on the time scale of isolation. The reason is that, although there are no restrictions on the torsion angle of any one individual ring, correlated rotation under the operation of the two-ring flip mechanism imposes a constraint on the relationship among the torsion angles of all three rings. This constraint blocks a number of interconversion pathways among the full set of conformers, resulting in closed subsets that are identified as "residual stereoisomers". Such stereoisomers may be separated by substantial energy barriers; for example, the diastereomeric triarylmethanes are stable at room temperature and their interconversion requires 30.5 kcal mol⁻¹.

In molecular propellers the aryl rings are twofold rotors. Imagine now a pair of strongly coupled threefold rotors of the type XR₃ attached to a rigid frame: if the R's bound to X are likened to the teeth of a gear, a formal analogy can be drawn between the pair of chemical rotors and their mechanical counterparts, a pair of cogwheels. To extend the analogy, the disrotatory motion of a pair of meshed chemical rotors plainly evokes the image of two engaged gears in motion. Because of the constraint on the relationship between the torsion angles of two gear-meshed rotors, appropriately structured molecules of this type might therefore also exhibit residual stereoisomerism under the operation

of dynamic gearing. As so often happens in science, our two groups at Princeton and Okazaki became interested in the realization of this possibility at the same time, and, without being aware of each other's intentions, independently launched parallel studies to investigate the stereochemical consequences of dynamic gearing.

Correlated rotation is rendered more likely when the rotors are tightly intermeshed, and since previous studies by Ōki and co-workers on hindered rotation in bridgehead-substituted triptycenes had shown that the 9-triptycyl (Tp) group functions as a molecular rotor with an exceptionally high threefold torsional barrier,³ our choice quite naturally fell on derivatives of internally crowded ditriptycyl systems of the type Tp₂X (X = CH₂, O, etc.). Such systems bear an obvious and striking resemblance to three-toothed bevel gears (Figure 1).

As preliminary communications and full papers reporting work from our two laboratories on the design, synthesis, structure, and conformational dynamics of these molecular gear systems started to appear in the literature in the early 1980s, it became evident that our studies, far from representing a duplication of effort, complemented each other and in the event proved to be a source of mutual inspiration and enlightenment. This Account presents the highlights of our findings.^{4,5}

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Hiizu Iwamura obtained his B.S. degree and Ph.D. from the University of Tokyo and joined the faculty there in 1962. In 1977 he moved to the Institute for Molecular Science in Okazaki, and then came back to Tokyo in 1987 to assume the chair of organic chemistry at his alma mater. His research interests include dynamic stereochemistry, elucidation of reactive intermediates, and construction of high-spin organic molecules.

Kurt Mislow was born in Berlin in 1923. He received his B.S. degree from Tulane University and his Ph.D. from the California Institute of Technology under the direction of Linus Pauling. In 1947 he joined the faculty of New York University and in 1964 he moved to Princeton, where he is the Hugh Stott Taylor Professor of Chemistry. The focus of his research has been on the development of stereochemical theory. His interests include the social and public policy aspects of the scientific enterprise, and he is currently teaching a course in Princeton's Chemistry Department on social responsibilities and rights of scientists.

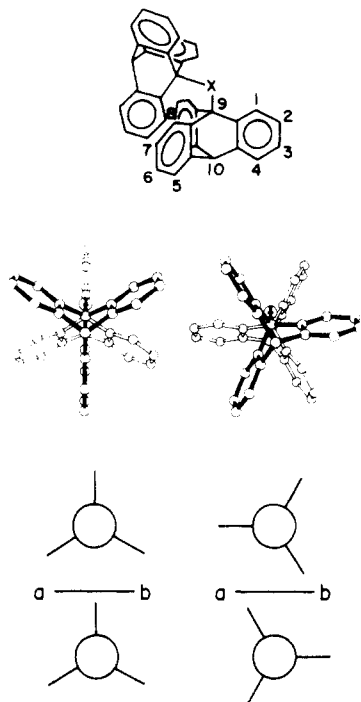


Figure 1. Top: molecular bevel gears consisting of two 9-triptycyl (Tp) groups joined by the bridgehead carbons to a central atom X, as in Tp_2CH_2 or Tp_2O . Middle: perspective views of the C_s conformation (left) and one of the enantiomeric C_2 forms (right). Bottom: schematic representations of the C_s and one of the C_2 conformations ($a = b$). The view is along the bisector of the central C-X-C angle, from the outside of the molecule in the direction from C(9) to C(10). The horizontal line symbolizes X and its ab ligands, if any (e.g., $a = b = \text{H}$ in H-C-H), the circles represent the C(9) carbons of the two triptycyl moieties, and the three lines radiating from each circle represent the three arene blades of each triptycyl group.

Molecular Bevel Gear Systems of the Type Tp_2X

The resemblance of Tp_2X molecules to mechanical bevel gear systems, obvious from inspection of molecular models, was confirmed by X-ray crystallography. Quantitative information on the mechanism and energy requirements of the torsional processes was obtained from empirical force field (EFF) calculations.

X-ray Structures.^{4d,5h} There are two sets of independent molecules in the unit cells of Tp_2CH_2 , Tp_2CHOH , and Tp_2CO , and one set in the unit cell of Tp_2O . In every case but one the molecules occupy general positions, with the Tp_2C and Tp_2O skeletons adopting approximate C_s symmetry; the exception is Tp_2CO , in which one set occupies general positions of approximate C_s symmetry whereas the other consists of molecules located on twofold rotation axes that pass through the C-O bonds. The coexistence of two independent structures in the unit cell, one of C_2 and the other of approximate C_s symmetry, implies that these conformations do not differ much in energy. Furthermore, the structural correlation⁶ between the two independent torsional parameters, one for each Tp rotor in Tp_2X ($\text{X} = \text{CH}_2, \text{CHOH}, \text{CO}$), maps a minimum-energy region in the torsional space that corresponds to the dynamic gearing trajectory for Tp_2CH_2 calculated by the EFF method. The crystallographic data are therefore entirely consistent with the results of the EFF

calculations described below.

The most striking feature of the X-ray structures is the extraordinary widening of the C-X-C bond angles to $128.5\text{--}129.5^\circ$ ($\text{X} = \text{CH}_2, \text{CHOH}, \text{CO}$) and 135.8° ($\text{X} = \text{O}$). These values represent record angle deformations and indicate that nonbonded repulsion between the two tightly meshed Tp groups is a source of considerable internal strain. While the C(9)-C-C(9') angles only slightly exceed the 128.0° observed for the central C-C-C bond angle in bis(triphenylmethyl)methane,⁷ the value for the C-O-C bond angle is the highest by far ever reported for an ether and is appreciably larger than the C-O-C angle in bis(triphenylmethyl) ether (127.9°).⁸ This effect is due in all probability to the short C-O bond lengths (1.407 and 1.418 Å); the concomitant increase in the repulsion between the two Tp groups results in a further spread of the central angle.

The calculated (MM2) central angles of 130.5 and 129.6° for C_s - and C_2 - Tp_2CO and of 129.4° for C_s - Tp_2CH_2 are in excellent agreement with the experimental values. However, the C-O-C angle of 126.3° calculated for Tp_2O is grossly underestimated, indicating that the anharmonicity term which is designed to respond reasonably to such large angle deformations in the bending force field is not adequately parameterized in MM2. A modification introduced in the force field to reduce the bending potential energy at large deformations without affecting the potential function in the small deformation region significantly reduces the discrepancy and yields a calculated C-O-C angle of 131.8° .

Computational Exploration of the Potential Energy Surface.^{4d,e,5h} EFF calculations were carried out in order to survey the potential energy hypersurface for internal rotation in Tp_2CH_2 and Tp_2CO (MM2) and in Tp_2O (modified MM2). These calculations revealed that the Tp groups in Tp_2CH_2 and Tp_2CO undergo correlated disrotation by way of C_s transition structures only 0.2 and 1.9 kcal mol⁻¹ above the C_2 ground state, respectively. Similarly, correlated disrotation in Tp_2O requires only 0.9 kcal mol⁻¹; in this case the ground state has C_s symmetry and the C_2 structure lies 0.2 kcal mol⁻¹ above the ground state. All of these molecules therefore undergo virtually unhindered dynamic gearing by way of essentially isoenergetic C_2 and C_s structures. By contrast, net *conrotation* of the Tp groups in Tp_2CH_2 , a process analogous to gear slippage, was found to require 30.1 kcal mol⁻¹; in the transition structure two benzene rings within one Tp group are squeezed together and tucked into the expanded notch between two rings in the other group. According to these calculations, the Tp rotors thus behave as highly mobile (i.e., almost frictionless) and tightly meshed (i.e., securely interlocked) bevel gears; the cogs are benzene rings that fit snugly into the V-shaped notches formed by two rings in the other rotor. The gearing trajectory is virtually flat and runs along the bottom of a deep and narrow canyon on the potential energy hypersurface.

Labeling Strategies for Molecular Gears

As previously demonstrated for molecular propellers, the observation of stereoisomerism crucially depends on the appropriate desymmetrization, i.e., on the ap-

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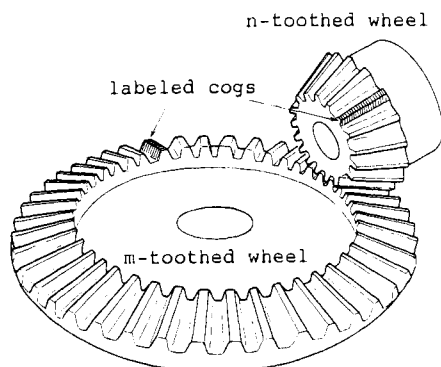


Figure 2. Labeling the cogs of a bevel gear.

appropriate labeling of—or, in the chemical sense, substitution on—the basic molecular framework.² What are the appropriate substitution patterns in molecular bevel gears? An answer to this question may be approached in several ways: the analogy to mechanical gears may be usefully employed, or an exhaustive enumeration of substitution patterns in Tp_2X molecules may be used as the basis for judging the suitability of these patterns in the design of molecules capable of exhibiting stereoisomerism under dynamic gearing but in the absence of gear slippage.

Phase Isomerism.^{5c} The bevel gear analogy can be generalized and extended to allow determination of the isomer count in labeled two-rotor systems. Consider a smoothly rotating mechanical bevel gear system that consists of a pair of m - and n -toothed cogwheels, and in which one of the cogs in each wheel is labeled so as to differentiate it from all the others (Figure 2). The labeling of one cog on each wheel establishes a unique phase relationship between the labeled cogs; this relationship remains fixed and invariant regardless of the rate of rotation or the number of revolutions. The number of labeled gear systems with different phase relationships depends on the parity of the greatest common divisor (N) of m and n . Expressed in terms of the chemical systems represented by this model, there are $N/2$ pairs of enantiomers and no achiral isomers when N is even, and there are $(N-1)/2$ pairs of enantiomers and one achiral isomer when N is odd. Derivatives of Tp_2CH_2 and Tp_2O with one substituted ring in each Tp unit ($m = n = N = 3$) thus form one pair of enantiomers and one achiral isomer.

The intimate connection between the phase relationship of labeled cogs and that of substituted benzene rings in Tp_2X systems suggests the term "phase isomerism" as a description for this type of stereoisomerism. The term "residual stereoisomers", though originally introduced in connection with molecular propellers,² has no specific mechanistic connotations: it refers more generally to closed subsets of interconverting isomers that are generated from the full set at a particular time scale of observation and under the operation of a particular stereoisomerization mode. Phase isomerism is thus recognized to be a special case of residual stereoisomerism, i.e., residual stereoisomerism generated under the operation of correlated rotation. Accordingly, any residual stereoisomerism in molecular propellers that depends on a fixed phase relationship among the aryl rings undergoing correlated rotation, i.e., that is generated under the operation of one of the flip mechanisms, may also be characterized

Table I
Classes of Residual Stereoisomers for All Substitution Patterns of Tp_2X under the Full Operation of the Gearing Mode

class	residual isomer or species isomer count ^a		substitution pattern ^b	pattern no.
	gear slippage disallowed	gear slippage allowed		
I	1/0	1/0	$a = b, 1 = 2 = 3 = 4 = 5 = 6$	1
	1/0	1/0	$a = b, 1 = 2 = 3 \neq 4 = 5 = 6$	2
	1/0	1/0	$a = b, 1 = 2 = 3; 4 = 5 \neq 6$	3
	1/0	1/0	$a \neq b, 1 = 2 = 3 = 4 = 5 = 6$	4
II	0/1	0/1	$a = b, 1 = 2 = 3; 4 \neq 5 \neq 6$	5
	0/1	0/1	$a \neq b, 1 = 2 = 3 \neq 4 = 5 = 6$	6
	0/1	0/1	$a \neq b, 1 = 2 = 3; 4 = 5 \neq 6$	7
	0/2	0/2	$a \neq b, 1 = 2 = 3; 4 \neq 5 \neq 6$	8
III	1/1	1/0	$a = b, 1 = 2 = 4 = 5 \neq 3 = 6$	9
	1/1	1/0	$a = b, 1 = 2 \neq 3; 4 = 5 \neq 6$	10
	1/1	1/0	$a = b, 1 = 4 \neq 2 = 5 \neq 3 = 6$	11
	1/1	1/0	$a \neq b, 1 = 2 = 4 = 5 \neq 3 = 6$	12
	2/2	2/0	$a \neq b, 1 = 4 \neq 2 = 5 \neq 3 = 6$	13
IV	0/3	0/1	$a = b, 1 = 2 \neq 3; 4 \neq 5 \neq 6$	14
	0/3	0/1	$a = b, 1 = 4 \neq 2 = 6 \neq 3 = 5$	15
	0/3	0/1	$a \neq b, 1 = 2 \neq 3; 4 = 5 \neq 6$	16
	0/3	0/1	$a \neq b, 1 = 4 \neq 2 = 6 \neq 3 = 5$	17
	0/6	0/2	$a = b, 1 \neq 2 \neq 3; 4 \neq 5 \neq 6$	18
	0/6	0/2	$a \neq b, 1 = 2 \neq 3; 4 \neq 5 \neq 6$	19
	0/12	0/4	$a \neq b, 1 \neq 2 \neq 3; 4 \neq 5 \neq 6$	20

^a For each entry (x/y), x = number of meso (achiral) isomers, and y = number of racemic pairs. The isomer count refers to achiral ensembles observed under achiral conditions. ^b A semicolon between sets {1, 2, 3} and {4, 5, 6} signifies that the two sets may share some, but not all, of their elements.

as phase isomerism. The diastereomeric triaryl-methanes discussed at the beginning of this Account therefore fully qualify as phase isomers.

Enumeration and Classification of Substitution Patterns.^{4a,e,f} A group-theoretical (permutational) analysis of isomers and isomerization shows that there are no more than 20 possible substitution patterns for Tp_2X , provided the substituents are nonstereogenic. These patterns are listed in Table I. The symmetry of the central frame to which the two Tp rotors are attached is either C_{2v} ($a = b$; e.g., $\text{X} = \text{CH}_2, \text{CO}, \text{O}$) or C_s ($a \neq b$; e.g., $\text{X} = \text{CHOH}$). The 20 patterns may be partitioned into four classes. The characteristic property of each class is the isomer count under two conditions: disallowed and allowed gear slippage, corresponding to gearing without and with gear slippage, respectively. Isomers under the constraint of the first condition are phase isomers. The eight patterns that constitute classes I and II are unsuitable for our purposes since the isomer count is the same whether gear slippage takes place or not. The 12 patterns that constitute classes III and IV are suitable for an experimental demonstration of phase isomerism. Class III is characterized by systems that consist of n residual meso phase isomers and n racemic pairs of phase isomers under the operation of gearing and in the absence of gear slippage, and that reduce to n residual meso (but not phase) isomers under the full operation of gear slippage. Class IV contains systems in which $3n$ racemic

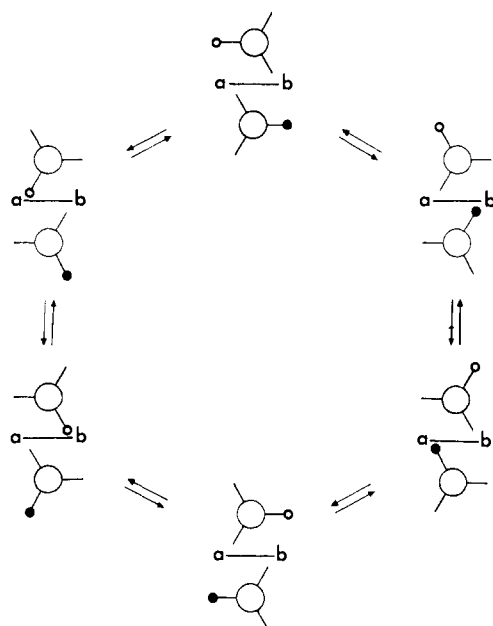


Figure 3. Conformational gearing circuit for meso phase isomers of Tp_2X with substitution patterns 9, 10, and 12 (Table I). Schematic projections around the perimeter follow the convention in Figure 1 and are based on the C_2 conformation. The filled and open circles denote substituted benzene rings. For pattern 9, $a = b$ and $\bullet = \text{O}$; for pattern 10, $a = b$ and $\bullet \neq \text{O}$; for pattern 12, $a \neq b$ and $\bullet = \text{O}$.

pairs of phase isomers similarly reduce to n racemic pairs that are not phase isomers. Since the separation of phase isomers was the prime objective of the proposed experimental study, our choice initially narrowed down to the systems with the fewest such isomers, i.e., those with substitution patterns 9–12 in class III. Figures 3 and 4 depict conformational gearing circuits for phase isomers in a subset of this class, patterns 9, 10, and 12; note that derivatives with one substituted ring in each Tp unit (see above) conform to pattern 9 or 10. As seen by inspection of these circuits, the labeled benzene rings never get near one another in the meso phase isomer, whereas in the D and L isomers they are brought into close proximity in the course of gearing.

Phase Isomers of Tp_2X Derivatives: Synthesis, Separation, and Identification

Given the selection of suitable substitution patterns, the remaining choices in the design of phase isomers concerned the identity and positioning of chemical labels. Phase isomers with isotopic labels would be difficult to separate, and we therefore selected methyl and chlorine substituents as chemical labels, in conjunction with substitution patterns belonging to classes III and IV. Our choice of substituent sites on the benzene rings was governed by the results of EFF calculations, which showed that introduction of methyl groups in positions 2, 3, or 4 of the Tp ring (Figure 1) does not significantly modify the potential energy hypersurface along the gearing trajectory.

Synthesis.^{4f,5d,1,n} Derivatives of Tp_2CH_2 and Tp_2CHOH were prepared by an adaptation of the standard method for the synthesis of triptycenes,⁹

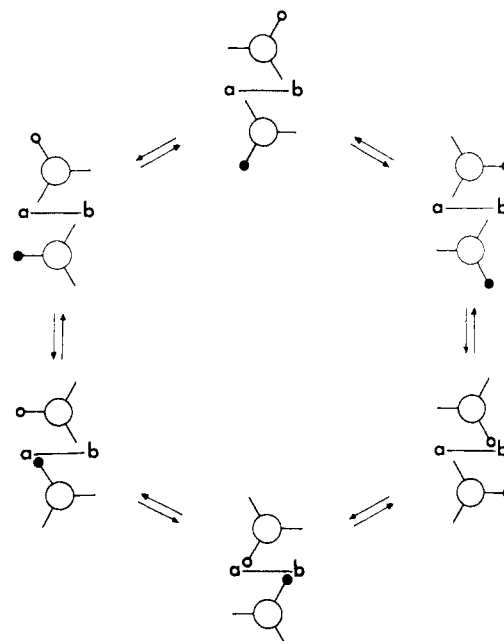


Figure 4. Same as Figure 3 but for the D or L phase isomer. The structures in the circuit of the other enantiomer are the mirror images of the ones shown in this figure.

double addition of benzynes to bis(9-anthryl)methanes or carbinols. Where this method was not applicable because of the lack of appropriate bis(9-anthryl) derivatives, the synthesis of Tp_2X derivatives was accomplished by connecting two Tp units prepared in advance. A Tp_2SiH_2 derivative was obtained by nucleophilic substitution reaction of trichlorosilane with (9-triptycyl)lithium to give the corresponding Tp_2SiHCl derivative, which was then reduced with lithium aluminum hydride.¹⁰ The synthesis of Tp_2O derivatives was accomplished by cage recombination of the 9-triptycyl/9-triptycyloxy radical pairs obtained by thermolysis of 9-triptycyl 9-triptyceneperoxy-carboxylates; a similar approach, involving homolysis, removal of a small molecular fragment, and recombination of the remaining radical pair yielded appropriately labeled derivatives of Tp_2NH and Tp_2S .

Separation and Identification.^{4f,5d,e,g,l,n} The meso and DL phase isomers of bis(2,3-dimethyl-9-triptycyl)methane were separated by column chromatography on silica gel, and those of bis(2- or 3-chloro-9-triptycyl)methane, ether, amine, and sulfide by normal-phase HPLC. The DL isomers were obtained in approximately twofold excess over the meso isomers, i.e., in approximately statistical ratio.

All of these Tp_2X compounds conform to pattern 9. Under conditions of rapid gearing, i.e., on the NMR time scale at ambient temperature, the two unsubstituted benzene rings in each Tp unit of the meso phase isomer are enantiotopic. The two substituted and the four unsubstituted rings of this isomer therefore fall into two classes and give rise to 12 aromatic carbon NMR signals. Under the same conditions the two unsubstituted benzene rings in each Tp unit in the D or L isomer are diastereotopic; therefore three classes and 18 aromatic carbon signals are produced. The phase isomers were thus readily differentiated and identified.

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Furthermore, optical resolution of the DL isomers of the chloro-substituted methanes and ethers could be effected by means of HPLC on a column of microsilica coated with (+)-poly(triphenylmethyl methacrylate). The separation of the diastereomeric phase isomers and the optical resolution of DL pairs is compelling evidence that gear slippage does not take place in these compounds under normal conditions of laboratory manipulation.

In Tp_2NH and its derivatives, pyramidal inversion at nitrogen is extremely fast on the time scale of gear slippage, so that the isomer count conforms to patterns with $a = b$ rather than $a \neq b$. Bis(2-chloro-9-triptycyl)amine therefore conforms to pattern 9 rather than 12, and (2-chloro-9-triptycyl)(3-chloro-9-triptycyl)amine to pattern 10 rather than 16. The phase isomers of the latter were separated by HPLC and identified by observation of most of the 24 and 36 aromatic carbon NMR signals theoretically predicted for the meso and DL isomers, respectively.

Bis(2,3-dimethyl-9-triptycyl)carbinol conforms to pattern 12. The meso and DL phase isomers were separated by column chromatography and identified by NMR. The meso isomer, like Tp_2CHOH itself, though chemically achiral, is an ensemble of chiral molecules that enantiomerize exclusively through a chiral gearing pathway so long as gear slippage is disallowed. That is, all structures in the gearing circuit of the meso isomer (see Figure 3) are pairwise related as mirror images, and none are achiral. The two 2,3-dimethyl-9-triptycyl groups are pairwise enantiotopic by external comparison, and three sets of pairwise equivalent rings are produced under conditions of rapid gearing. The meso isomer therefore features 18 aromatic carbon NMR signals. In the D or L phase isomer all conformations are symmetry nonequivalent (see Figure 4) and all six rings remain nonequivalent under conditions of rapid gearing. The DL isomer therefore features 36 aromatic carbon signals. Note that transposition of H and OH on the central carbon atom does not interconvert D and L isomers; that is, the central carbon atom is not stereogenic.

The three rings in each triptycyl unit of bis(2,6-dichloro-9-triptycyl)methane differ in constitution, and the bridgehead atoms are therefore stereogenic. Under conditions of gear slippage this compound exists as a conventional set of diastereomers, a meso form (*RS*) and a racemic pair (*RR/SS*). But, as we saw, gear slippage does not take place under normal laboratory conditions. The *RS* compound conforms to pattern 11 and is therefore expected to give rise to meso and DL phase isomers (Figures 5 and 6). The phase isomers bear a certain resemblance to those of bis(2,3-dimethyl-9-triptycyl)carbinol: all conformations in the gearing circuits are chiral, all are pairwise related as mirror images in the meso form, and all are symmetry nonequivalent in the D and L forms. In contrast, the *RR/SS* compound conforms to pattern 15 and yields three diastereomeric DL pairs under the constraint of gear meshing. In accord with these expectations, five fractions were isolated with HPLC on microsilica. Two of these were unambiguously identified as the meso and DL phase isomers derived from the *RS* compound: one fraction (meso), on heating in *o*-dichlorobenzene under reflux for 5 h, i.e., under conditions conducive to gear

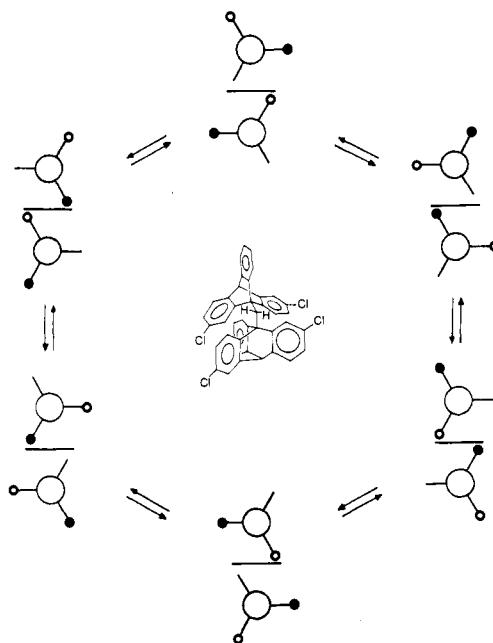


Figure 5. Conformational gearing circuit for the meso phase isomer of (9*R*,9'*S*)-bis(2,6-dichloro-9-triptycyl)methane (pattern 11, Table I). Schematic projections follow the convention in Figure 1 ($a = b$). The filled and open circles denote 2- and 6-chloro substituents, respectively.

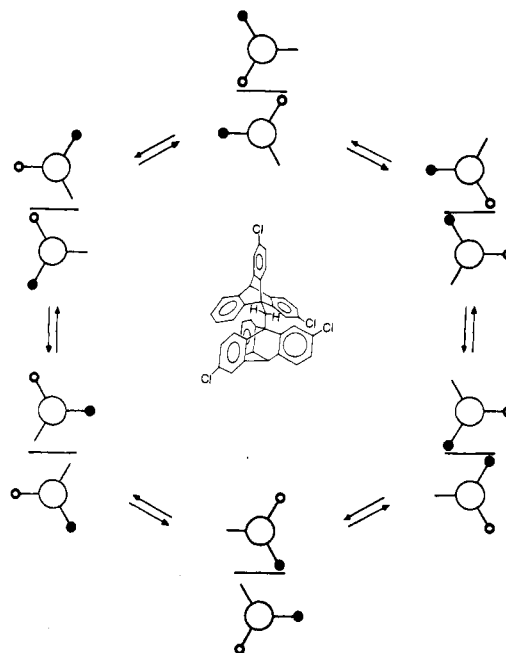


Figure 6. Same as Figure 5 but for the D or L phase isomer.

slippage (see below), yielded a mixture of meso and DL fractions in an intensity ratio of ca. 1:2; the two fractions were identified as such by the number of quaternary aromatic carbon NMR signals, 8 and 16 for the meso and DL phase isomer, respectively. The remaining three fractions, derived from the *RR/SS* compound, could each be resolved by HPLC on chiral packing material.

Torsional Barriers in Tp_2X Derivatives: An Experimental Approach

In harmony with the prediction of EFF calculations, the observation that phase isomers can be separated and are stable at room temperature clearly shows that gear slippage is slow on the laboratory time scale. What

Table II
Activation Parameters for Gear-Slippage Processes:
Diastereomerization of Tp_2X Derivatives

substitution pattern ^a			E_a , ^c kcal mol ⁻¹	log A	K^d (DL/meso)	ref
X	2	3				
CH ₂	CH ₃	CH ₃	34 ^b		1.8 ± 0.1	4f
CH ₂	Cl	H	32.2 ± 0.1	12.1 ± 0.1	1.65 ± 0.01	5d
CH ₂	H	Cl	33.1 ± 0.2	12.2 ± 0.1	1.86 ± 0.01	5d
O	Cl	H	42.0 ± 0.5	12.3 ± 0.2	1.90 ± 0.03	5d
O	H	Cl	43.2 ± 0.3	12.5 ± 0.1	1.89 ± 0.01	5d
NH	Cl	H	39.1 ± 0.5	12.4 ± 0.2	1.82 ± 0.01	5l
SiH ₂	Cl	H	21.1 ± 0.4	13.9 ± 0.2	2.08 ± 0.02	5o
S	Cl	H	29.3 ± 0.3	12.2 ± 0.2	1.73 ± 0.01	5n

^aNumbers refer to positions on the ring (Figure 1). ^b ΔG^\ddagger at 145–165 °C. ^cArrhenius activation energy for the process DL → meso. ^dEquilibrium constant of phase diastereomers under conditions described in the text.

does it take to throw the molecules out of gear, so that the torsional motions of the two Tp units are no longer correlated? An answer to this question was provided by the experiments described below.

The Height of Barriers to Gear Slippage.^{4f,5d,n,o} An experimental estimate of the energy requirement for gear slippage can in principle be obtained either from the rates of interconversion of D and L phase isomers (enantiomerization) or from the rates of interconversion of meso and D (or L) phase isomers (diastereomerization). In the present work the latter approach proved the more convenient, and we therefore resorted to a study of diastereomerization kinetics. Our results are collected in Table II. With the exception of the silane, data for which were obtained by variable-temperature ¹H NMR measurements, the tabulated information was obtained by monitoring DL/meso isomer ratios as a function of time using high-boiling solvents (nitrobenzene-*d*₅, *o*-dichlorobenzene, diphenylmethane) and temperature intervals ranging from 61–132 °C for the sulfide to 220–330 °C for the ethers. Reaction kinetics were all strictly first order. The log A values are consistent with unimolecular processes. The DL/meso equilibrium ratios are slightly but consistently smaller than the statistical ratio of 2/1, indicating a slight thermodynamic preference for the meso isomer; this preference is attributable to the absence of conformations in which the substituted rings come close to one another.

Activation energies for gear slippage in the methanes (32–34 kcal mol⁻¹) are in reasonable agreement with the value of 30.1 kcal mol⁻¹ calculated (EFF) for Tp_2CH_2 and thus lend credence to the transition structure described above. The substantially higher barrier for gear slippage in the ethers (42–43 kcal mol⁻¹), like the large central angle deformation, may be ascribed to shorter C–X bond lengths which bring the Tp groups closer together, as well as to larger C–X stretching and C–X–C bending force constants. Since linearization of the ether oxygen leads to facile gear slippage, the observed barrier heights also provide a lower limit for the linearization energy of these ethers. By comparison, a value of 36–37 kcal mol⁻¹ has been calculated for the linearization of water.¹¹

The barrier observed for the amine is intermediate between those observed for the methanes and ethers. This result is not unexpected given that C–X bond lengths as well as C–X stretching and C–X–C bending force constants for X = N all fall between the corresponding values for X = O and C.

The gear-slippage barrier of the silane is too low to permit isolation of phase isomers at room temperature. The decrease in barrier height is primarily a consequence of the increase in C–X bond length; as a result the Tp groups are pushed further apart, the gear system is loosened up, and slippage becomes easier. Related observations have recently been reported for internal rotation in hexakis(dimethylsilyl)benzene.¹² On the other hand, phase isomers of the sulfide are easily separated at room temperature despite the elongation of the C–S bond. The smaller C–S–C angle, as compared to C–Si–C, evidently plays an important role in tightening the gear system and raising the gear-slippage barrier. The value of that barrier is also a lower limit for the linearization energy of the sulfide.

The Height of Barriers to Gearing.^{5i,m} As noted above, correlated rotation of the Tp groups in Tp_2X systems is virtually unhindered: according to EFF calculations, the gearing barrier in Tp_2X (X = CH₂, CO) and Tp_2O is only 1–2 kcal mol⁻¹. Furthermore, ¹H and ¹³C NMR spectra of Tp_2O and TpCH_2 derivatives show no splitting of the benzene ring signals down to ca. –90 °C, consistent with an upper limit of 7–8 kcal mol⁻¹ for the gearing barrier.

Since the rate of the gear-meshing torsional motions is expected to be very fast, in the order of 10⁹ s⁻¹, the Tp_2X system appeared appropriate for the inspection of exciplex fluorescence dynamics. For this purpose a Tp_2O derivative was designed that conformed to pattern 10 and in which a ring in one Tp unit carried a CH₂N(CH₃)₂ group in the 2-position (amino chromophore, D) while a ring in the other unit carried a benzo group fused to the 2,3-positions (naphtho chromophore, A). The meso and DL phase isomers were separated by HPLC. Upon excitation at 290 nm, the meso phase isomer showed typical fluorescence due to A* in the 320–360-nm region, indicating that there is no conformation available for this isomer in which D and A come next to each other. The DL phase isomer showed a characteristic exciplex (D·A*) fluorescence at longer wavelength (maximum at 407 nm in *n*-butyl ether) in addition to the weakened fluorescence due to A*. Since there is no D/A interaction in the ground state as revealed by the normal absorption spectra, the exciplex fluorescence in the DL isomer indicates that, when A* is formed by light absorption, the internal rotation that takes place during the lifetime of A* brings A* into the proximity of D and thus generates the D·A* complex. The system was analyzed both under photostationary conditions and under pulsed excitation. In the former, the temperature dependence of the fluorescence intensities due to A* and D·A* was determined. In the latter, a dual-exponential decay curve of locally excited state emission and a grow-in and decay curve of exciplex state emission were obtained by irradiating the naphthalene chromophore at 290 nm with a flash lamp. During the time that the naphtho group is in the electronically

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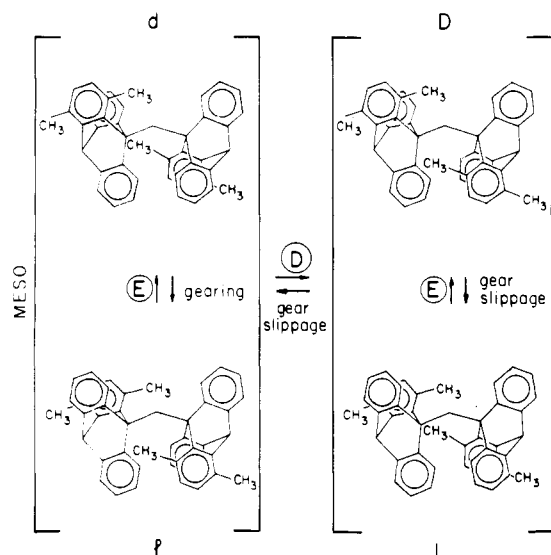


Figure 7. Representative conformations of stereoisomers of bis(1,4-dimethyl-9-triptycyl)methane. Enantiomers are paired in brackets. The mechanism of stereomutation is indicated next to the circled E (enantiomerization) and D (diastereomerization).

excited state, the gear framework of the molecule should not be very different from that of the ground state. The measured activation energy for these processes, 4.2 kcal mol⁻¹, therefore corresponds to the height of the barrier that separates the conformer with proximal D and A* from the one with distal D and A* and may be taken as an upper limit of the gearing barrier.

A Molecular Monkey Wrench.^{4c,f} Bis(1,4-dimethyl-9-triptycyl)methane differs from the Tp₂X derivatives described thus far by the presence of methyl groups in the 1-positions of the two Tp units. In the course of gearing, a benzene ring bearing a 1-methyl group is forced into the notch between the two arene rings in the other rotor. Accommodation of this group in an already overcrowded space (to judge by the observed central bond angle deformation in Tp₂CH₂) substantially increases the steric strain of the molecule and profoundly affects the gearing behavior. Figuratively speaking, these methyl groups act as molecular monkey wrenches in the Tp cogwheel system and have an enormous effect on the magnitude of the gearing barrier.

The processes involved are summarized in Figure 7. At temperatures well above 200 °C, i.e., on the time scale of rapid gearing and gear slippage, the compound is a single, achiral species. As the temperature is lowered and gear slippage—but not gearing—is frozen out, enantiomerization of the D and L isomers and diastereomerization of the meso and DL isomers is slowed. That is, three separate phase isomers (meso, D, and L) are formed on that time scale, as expected for a molecule with substitution pattern 9. The diastereomerization barrier (ΔG^\ddagger), 39.4 ± 0.5 kcal mol⁻¹ at 215 °C, is substantially higher than that of related methanes (Table II) due to the steric effect of the 1-methyl groups.

As the temperature is lowered further, the ¹H and ¹³C NMR spectra of the meso isomer become more complex and the ring carbon signal count changes from 12 at 100 °C to 18 at -50 °C, corresponding to a process in which two enantiotopic benzene rings become diastereotopic. At these low temperatures gearing is also frozen out,

and the meso phase isomer is partitioned into a pair of enantiomers (*dl*). Thus there are four stereoisomers (*d*, *l*, *D*, and *L*) on the time scale of slow gearing and gear slippage.

Unlike the *D* and *L* isomers, the *d* and *l* isomers are interconvertible by correlated rotation and are therefore not phase isomers. The magnitude of the *dl* enantiomerization barrier (ΔG^\ddagger), 14.2 ± 0.5 kcal mol⁻¹ at 17–20 °C, far exceeds that of any gearing barrier in comparable systems and attests to the drastic alteration suffered by the potential energy hypersurface because of the presence of the 1-methyl groups.

Conclusion and Future Prospects

Our work has shown that the two 9-triptycyl (Tp) rotors in Tp₂CH₂, Tp₂O, and related molecules behave as a pair of almost frictionless bevel gears: barriers to gearing amount to only a few kcal mol⁻¹. The gears are securely meshed, and gear slippage generally requires activation energies of 30–40 kcal mol⁻¹. The disrotatory cogwheeling motion in these systems, which arises from complementary steric interactions between tightly fitting Tp rotors, is therefore at least as strictly maintained as con- or disrotation in orbital symmetry-controlled reactions.

Derivatives with one substituted ring in each Tp unit form stereoisomers that are separable under ordinary laboratory conditions. Stereoisomers of this type differ in the phase relationship between substituted rings and, by analogy to bevel gear systems with labeled cogs, are designated as “phase isomers”. Phase isomers owe their separate existence to the conservation of phase relationships, and observation of phase isomerism suffices as an operational test for strictly correlated disrotation in these systems.

Our findings may be extended in several directions. For example, in molecular bevel gears as well as in molecular propellers the shafts of the rotors lie along intersecting axes, and phase isomers of molecular spur gears, i.e., gears in which the axes are parallel, have yet to be reported. As another example, molecular gear systems with rotors of periodicity greater than three are still unknown, and it might be possible to design phase isomers with fourfold rotors if advantage is taken of the corners of octahedral coordination complexes.^{5j} Finally, it should in principle be possible to construct macromolecular chains of securely meshed chemical gears so that transfer of information could in principle take place from one end of the molecule to the other via cooperative torsional motions along the chain.^{5j} As a first step in this direction, a doubly connected bevel gear system of the type Tp'OTpOTp' (9,10-bis(3-chloro-9-triptycyloxy)triptycene) has been synthesized in which only the outer two Tp units are labeled; the DL and meso phase isomers of this compound have been separated by HPLC and identified by NMR.^{5f,k} For this system, many conformations are possible, the molecular chain is rather flexible, the labels are very far apart, and yet the phase relationship between the two labeled benzene rings is strictly conserved on the time scale of rapid cogwheeling of the two outer triptycyl groups (Tp') with the middle triptycene unit.

The preceding discussion has been restricted to chemical systems that bear a formal similarity to gears in which the teeth are cut on the outside surfaces of both wheels. Disrotation is a characteristic of such

“external gears”.¹³ In “internal gears” one wheel with teeth cut on the outside moves on the inside of a hollow cylinder with teeth cut on the inner surface; in such gears the motion is conrotatory.¹³ It has been suggested that the motion of a guest molecule within the enclosure

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of the host component in a suitably structured inclusion compound might serve as a chemical analogue of an internal gear system.^{1a}

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