

PHASE ISOMERISM IN GEAR-SHAPED MOLECULES

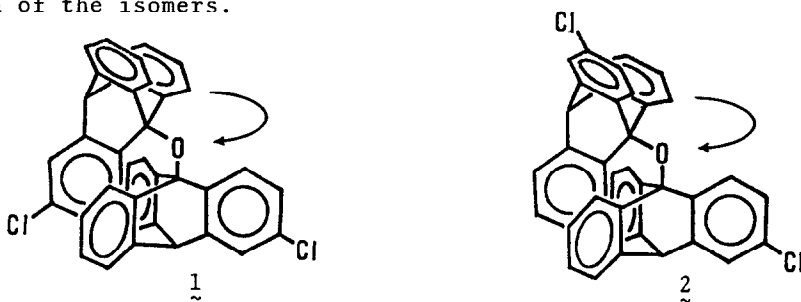
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Abstract: The concept of new stereoisomerism due to different phase relations between the labeled cogs in a smoothly geared molecule is described.

The gear effect or the correlated rotation in systems that contain sterically crowded groups has been the much-discussed subject of recent conformational studies. These effects govern preferred spatial disposition of the bulky groups in a molecule which could carry far-reaching conformational information through the molecular system and may be responsible for many stereochemical consequences of importance. Conformational transmission,¹ induced fit theory, and allosteric effects² are some of the examples.

To what extent the geared rotation in a molecule can be correlated? As one of the most dramatic demonstrations of the smoothly geared cogs, we recently communicated the preparation and separation of a new type of stereoisomers 1 and 2 of the gear-shaped molecules of bis(4-chloro-1-triptycyl) ether.³ We would like here to develop a general idea underlying the experimental findings of the phase isomers, propose the rule describing the number of such isomers, and finally discuss on the mechanism for inter-conversion of the isomers.



Our rule is based on the observation that, when one of the cogs on each wheel is labeled in perfectly correlated geared molecules, a phase relationship is established with respect to the labeled cogs and the phase isomers can result in spite of rapid rotation of the gear. Let us take a bevel gear in Figure 1 as representing the molecule in question. When the number of the

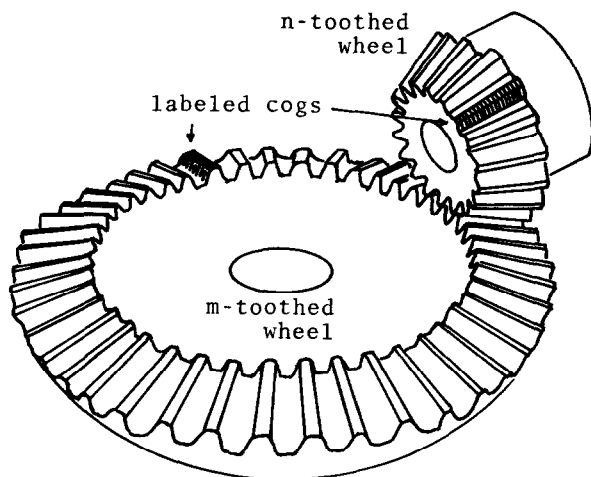


Figure 1

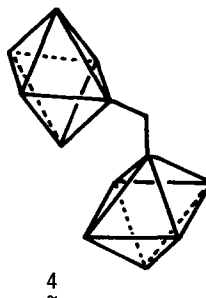
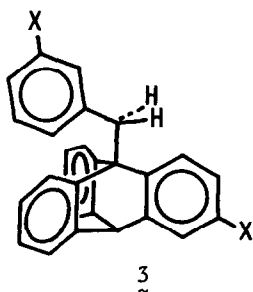
Table 1. The number of the phase isomers possible for a bevel gear (Figure 1) carrying the m - and n -toothed wheels

the greatest common divisor of m and n		achiral	d_l
N	odd	1	$\frac{N-1}{2}$
	even	0	$\frac{N}{2}$
none	one or both of m and n odd	1	0
	both m and n even	0	1

teeth in each wheel is the same ($m = n = N$), the cycle of rotation is the same to the two wheels and the phase relationship is kept definitely once the labeling is made. Out of the possible N relationships, the labeling patterns in which one of the wheels is 1, 2, 3... tooth ahead of the other are enantiomeric to those in which the former is 1, 2, 3... tooth behind of the latter, respectively. Therefore, there are $N/2$ d_l pairs present for even number of N . For odd number of N , $(N-1)/2$ isomers are similarly chiral and consist of d_l pairs. When the labeling is made $(N+1)/2$ teeth apart, this particular isomer contains a doubly degenerate labeling pattern with a plane of symmetry and $(N-1)/2$ enantiomeric pairs of the labeling patterns during each 360° rotation, and is therefore achiral.

When the number of the teeth on each wheel is different ($m \neq n$), the cycle of rotation is now different between the two wheels. As a result, the phase difference between the labeled teeth changes during the course of rotation. The initial phase relationship comes back after the m - and n -toothed wheels turn round by the number of times corresponding to the least common multiple of m and n divided by m and n , respectively. The number of isomers possible is then governed by the greatest common divisor of m and n . When they have the greatest common divisor N , the number of different phases is equal to that of the symmetrical N -toothed gear as described above. If there is no common divisor between m and n , all phase relations between the labeled cogs are achieved during the n - and m -times rotation of the m - and n -toothed wheels. No phase isomer is born under these circumstances except that, when both m and n are even, the molecule is chiral and should be present as a d_l pair. The labeled gear is achiral if either one of m and n is odd. The rules obtained from these considerations are summarized in Table 1.

The bis(1-triptycyl) ether and the di-(1-triptycyl)methane in which one of the benzene rings of each triptycene moiety is equally labeled provide the case $N = 3$.³ According to Table 1, one achiral and one dl isomers (as 1 and 2, respectively) should be present as verified in our previous paper.³ Correlated rotation in 1-benzyltriptycenes (3) reported by Yamamoto and Ōki corresponds to the example of $m = 3$ and $n = 2$.⁴ There is no common divisor and one of the wheels carries odd number of teeth. Therefore, no phase isomerism emerges in this system, although it is necessary for the phenyl-CH₂ and 1-triptycyl-CH₂ bonds to rotate by $3 \times 360^\circ$ and $2 \times 360^\circ$, respectively, to get back to the original conformation.⁵



As long as tetracoordinated carbon atoms are employed as materials for constructing the gear, it would be difficult to envisage a molecule in which $N > 3$. Effective use of the corner of octahedral metal complexes as in 4 or some carboranes⁶ could produce gear-shaped molecules with $N > 3$ and our rule would be operationally extended.

It is easily expected that at elevated temperatures the smoothly geared cogs could get stripped and, as a result, the phase isomers would interchange each other. This was realized for 1 and 2 in the temperature range 250-300 °C to give the activation energy value of 42.7 kcal mol⁻¹ ($\log A = 12.6$) for the interconversion. A preliminary result shows that the stripped gear of di-(4-chloro-1-triptycyl)methane molecule can be obtained about 10^4 times faster in these temperature range than that of the corresponding ether. Thus the degree of correlation in the geared motion appears to depend sensitively on the bond lengths and angles forming the gear-shaped molecules.⁷

REFERENCES AND NOTES

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- 4) G. Yamamoto and M. Ōki, Chemistry Lett., 1251, 1255 (1979).
- 5) We thank Prof. M. Ōki of The University of Tokyo for pointing out this possibility. The rotational isomers due to restricted geared motion⁴ are the subject outside of the present discussion.
- 6) This was pointed out to us by Prof. E. Osawa of Hokkaido University.
- 7) We had originally thought that the ether would isomerize faster than the methane and that it might be possible to have an experimental measure for the barrier height of divalent oxygen inversion. The shorter C-O bond length and probably smaller COC angle appear to be more effective in making the more tight gear.

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