

(m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.10-7.40 (m, 5 H, Ar), 5.20 (q, $J_{\text{H-F}}$ = 7 Hz, 1 H, CH), 4.07-4.59 (AB q, J = 6 Hz, 2 H, CH_2), 2.90 (s, 3 H, CH_3); $^{13}\text{C NMR}$ (CDCl_3) δ 139.5 ($\text{C}=\text{N}$), 135.4, 128.9, 128.4, 126.0 (Ph), 123.0 ($^1J_{\text{C-F}}$ = 293 Hz, CF_3), 76.2 (CH_2), 67.8 ($^2J_{\text{C-F}}$ = 30.5 Hz, CH), 41.1 (CH_3). 13e: pale yellow crystals; mp 48 °C. 13h: yellow oil; oven temperature 75 °C (3 Torr). 15: colorless crystals; mp 120 °C; IR 3100 (m), 1170 (s), 1180 (m), 1190 (s), 765 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.12-7.70 (m, 5 H, Ar), 3.34 (br, 1 H, OH), 4.37 (q, 2 H, CH_2), 2.97 (s, 3 H, CH_3); $^{13}\text{C NMR}$ (CDCl_3) δ 140.0 ($\text{C}=\text{N}$), 135.4, 128.5, 127.9 (Ph), 127.5 ($^1J_{\text{C-F}}$ = 299 Hz, CF_3), 89.0 ($^2J_{\text{C-F}}$ = 33.0 Hz, CCF_3), 74.0 (CH_2), 40.7 (CH_3). 16 (Ar = Ph): pale yellow crystals; mp 83 °C. 16 (Ar = *p*- MeC_6H_4): pale yellow crystals; mp 84 °C; IR 1675 (s), 1190 (s), 1150 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 8.10, 7.17 (d, 4 H, Ar), 4.00-5.00 (br, 2 H, OH), 2.40 (s, 3 H, CH_3). 16 (Ar = *o*- ClC_6H_4): colorless crystals; mp 128 °C. 16 (Ar = *p*- ClC_6H_4): colorless crystals; mp 120 °C. 16 (Ar = *p*- $\text{O}_2\text{NC}_6\text{H}_4$): pale yellow crystals; mp 83 °C. 16 (Ar = *m*- $\text{O}_2\text{NC}_6\text{H}_4$): colorless oil; oven temperature 90 °C (1 Torr). 16 (Ar = *p*- $\text{O}_2\text{NC}_6\text{H}_4$): orange oil. 16 (Ar = *p*- MeOC_6H_4): colorless crystals; mp 81 °C. 16 (Ar = *p*- $\text{Me}_2\text{NC}_6\text{H}_4$): yellow crystals; 80 °C dec; IR 3040-3640 (s, br), 1608 (s), 1434 (m), 1385 (s), 1288 (s), 1200 (s), 1150 (s), 1062 (m), 1002 (m), 823 (m), 608 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 8.15 (d, 2 H, Ar), 6.57 (d, 2 H, Ar), 5.00 (br, 2 H, OH), 3.07 (s, 6 H, CH_3). 16 (Ar = 4-(trifluoroacetyl)-2-furyl): yellow oil; oven temperature 130 °C (2 Torr); IR 3000-3600 (m, br), 1708 (s), 1639 (m), 1352 (m), 1246 (m), 1204 (s), 1160 (s), 1044 (s), 1011 (s), 884 (m), 820 (m), 762 (m), 736 (m) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.46 (br, 1 H, furan), 7.25 (d, 1 H, furan), 5.73-5.93 (br,

2 H, OH). 17: yellow crystals; mp 115 °C; IR 1180 (s), 1125 (s), 1070 (s), 768 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.10-8.27 (m, 8 H, Ar), 2.43 (s, 3 H, CH_3). 18: yellow oil; oven temperature 175 °C (2 Torr); IR 2250 (w), 1610 (s), 1145 (m), 1130 (m), 1085 (s), 750 (s) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.24-7.57 (q, 4 H, Ar), 2.40 (s, 3 H, CH_3).

Registry No. 3a, 1075-70-3; 3b, 7422-93-7; 3c, 2035-89-4; 3d, 966-88-1; 3e, 24459-52-7; 3f, 5051-47-8; 3g, 22699-29-2; 3h, 10424-94-9; 3i, 32787-76-1; 3j, 10424-92-7; 3k, 14371-13-2; 3l, 32787-73-8; 3m, 14064-21-2; 3n, 59670-91-6; 4a, 111269-36-4; 4c, 111269-38-6; 4d, 111291-46-4; 4e, 111269-40-0; 4f, 111269-41-1; 4g, 111269-42-2; 4h, 111269-43-3; 4i, 111269-44-4; 4j, 111269-45-5; 4k, 111269-46-6; 4m, 111269-58-0; 4n, 111269-57-9; 5b, 111269-37-5; 6c, 111269-39-7; 8 (X = H), 100-52-7; 8 (X = 4-Me), 104-87-0; 8 (X = 2-Cl), 89-98-5; 8 (X = 4-Cl), 104-88-1; 8 (X = 2- NO_2), 552-89-6; 8 (X = 3- NO_2), 99-61-6; 8 (X = 4- NO_2), 555-16-8; 8 (X = 4-OMe), 123-11-5; 8 (X = 4-NMe₂), 100-10-7; 9k, 111290-74-5; 9l, 111269-53-5; 10k, 111269-54-6; 10l, 111269-55-7; 11m, 111269-56-8; 12a, 111269-47-7; 12e, 111269-49-9; 12h, 111269-51-3; 13a, 111269-48-8; 13e, 111269-50-2; 13h, 111269-52-4; 15, 111269-59-1; 16a, 36750-88-6; 16e, 111269-60-4; 16f, 111269-61-5; 16g, 111269-62-6; 16h, 111269-63-7; 16i, 111269-64-8; 16j, 111269-65-9; 16k, 111269-66-0; 16l, 111269-67-1; 16m, 111269-68-2; 17, 111269-69-3; 18, 111269-70-6; TFAA, 407-25-0; EtCHO, 123-38-6; $(\text{CH}_2\text{O})_x$, 30525-89-4; Me_2NNH_2 , 57-14-7; Ph_2NNH_2 , 530-47-2; *i*-Pr₂NNH₂, 921-14-2; 2- $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$, 95-54-5; $\text{NCC}(\text{NH}_2)=\text{C}(\text{NH}_2)\text{CN}$, 1187-42-4; furfural, 98-01-1; nicotinaldehyde, 500-22-1.

Static and Dynamic Stereochemistry of Chloropentakis(dichloromethyl)benzene

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Chloropentakis(dichloromethyl)benzene (2) was synthesized by photochlorination of chloropentamethylbenzene. The barrier for internal rotation of the side chains was measured by the spin saturation transfer technique and by the coalescence approximation. Empirical force field calculations show that the preferred conformation is the all geared, in agreement with the NMR data, and that the mechanism of topomerization involves stepwise rotation of the side chains. The calculations closely reproduce the topomerization barrier (experimental 20 kcal mol⁻¹; calculated 22 kcal mol⁻¹).

In recent years, there has been an active interest in the stereochemistry of systems bearing isopropyl groups attached to a planar sp^2 frame (such as ethylene or benzene).^{2,3} Some of these systems avoid repulsive nonbonded interactions by assuming a gear-locked conformation in which each of the isopropyl methine hydrogens is tucked into the notch created by the methyl groups of a neighboring isopropyl group. Examples of this kind of system include hexaisopropylbenzene⁴ and tetraisopropylethylene,⁵ both of which display homodirectional isopropyl

groups in their lowest energy conformation (C_{6h} and C_{2h} symmetry respectively). This tight geared interaction raises the barrier to rotation of the isopropyl groups: empirical force field calculations (EFF) predict a topomerization barrier of 19.5 kcal mol⁻¹ for tetraisopropylethylene,^{6,7} and of ca. 35 kcal mol⁻¹ for hexaisopropylbenzene.⁸ In both cases, the calculated topomerization mechanism of lowest activation energy (threshold mechanism) does not involve correlated rotation but a stepwise rotation of the isopropyl groups,^{6,8} i.e. the systems show static but not dynamic gearing.⁹ Groups that are similar

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(2) Berg, U.; Liljefors, T.; Roussel, C.; Sandstrom, J. *Acc. Chem. Res.* 1985, 18, 80 and references therein.

(3) (a) Pettersson, I.; Berg, U. *J. Chem. Res., Synop.* 1984, 208. (b) Pettersson, I.; Berg, U. *J. Chem. Soc., Perkin Trans. 2* 1985, 1365. (c) Anderson, J. E.; Bettels, B.; Gharagozloo, P.; Koon, K. H. *J. Chem. Res., Synop.* 1986, 420.

(4) (a) Arnett, E. M.; Bollinger, J. M. *J. Am. Chem. Soc.* 1964, 86, 4729. (b) Hopff, H.; Gati, A. *Helv. Chim. Acta* 1965, 48, 509.

(5) (a) Langer, R. F.; Tidwell, T. T. *Tetrahedron Lett.* 1975, 777. (b) Bomse, D. S.; Morton, T. H. *Tetrahedron Lett.* 1975, 781.

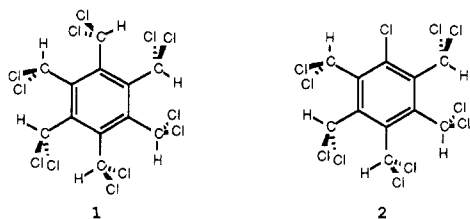
(6) Ermer, O. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 998.

(7) The measured topomerization barrier for tetraisopropylethylene is 17 kcal mol⁻¹.^{5b}

(8) Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* 1986, 108, 1569.

(9) Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczyński, R. J.; Mislow, K. *Isr. J. Chem.* 1980, 20, 65.

in shape to isopropyl (such as dichloromethyl) also show a tendency to statically gear. An example of this kind of system is hexakis(dichloromethyl)benzene¹⁰ (1), first synthesized in 1964 by Imhof.¹¹ According to space-filling models and spectroscopic data, 1 exists in an all-gear-ed conformation. In this conformation each dichloromethyl methine proton is tucked into the cleft formed by the chlorines of a vicinal dichloromethyl group. A recent single-crystal X-ray analysis showed that the geared conformation (approximate symmetry C_{6h}) is the one observed in the solid state.¹² EFF calculations carried out on the compound satisfactorily reproduced the bonding parameters of 1 and showed the special role played by a complete gearing circuit in the conformational stabilization of compounds such as 1. For example, while for 1 the energy difference between the all-gear-ed conformation and the conformation with one dichloromethyl group effectively turned by 180° ¹³ was calculated to be $12.3 \text{ kcal mol}^{-1}$, for 1,2-bis(dichloromethyl)benzene the energy difference between the gear-meshed C_s conformation and the conformation in which the two methine protons face each other (C_2) was only $1.7 \text{ kcal mol}^{-1}$.¹² To the best of our knowledge, no pentasubstituted gear-meshed system has been synthesized, nor has the static and dynamic stereochemistry of such a system been analyzed. These systems are of theoretical interest because they bridge the gap between the hexasubstituted and disubstituted systems and because their lower symmetry allows an assessment of the importance of the relative positions of the "gear tooth" in the topomerization mechanism. Moreover, the barrier to topomerization for these systems can be measured directly by conventional NMR techniques (the high symmetry of a system such as 1 precludes such direct measurement), and since it is expected to be in the dynamic NMR range, the experimental value can be used to test the barrier calculated by the EFF method. Since poly(dichloromethyl)benzenes are readily available from polymethylbenzenes by photochemical chlorination, we decided to synthesize and investigate chloropentakis(dichloromethyl)benzene (2).



Results and Discussion

In analogy to a report by Hojo and Masuda,¹⁴ when pentamethylbenzene was reacted with SO_2Cl_2 in CCl_4 in the presence of silica gel, chloropentamethylbenzene was obtained. Photochemical chlorination of this material afforded 2 in good yield. As in the case of 1, it seems plausible that the chlorination stopped at the dichloromethyl stage because the four methine protons are sterically shielded by the neighboring chlorines, and replacement of the methine hydrogen pointing to the aromatic chlorine (the only methine proton which is relatively "exposed") will result in severe steric interactions between

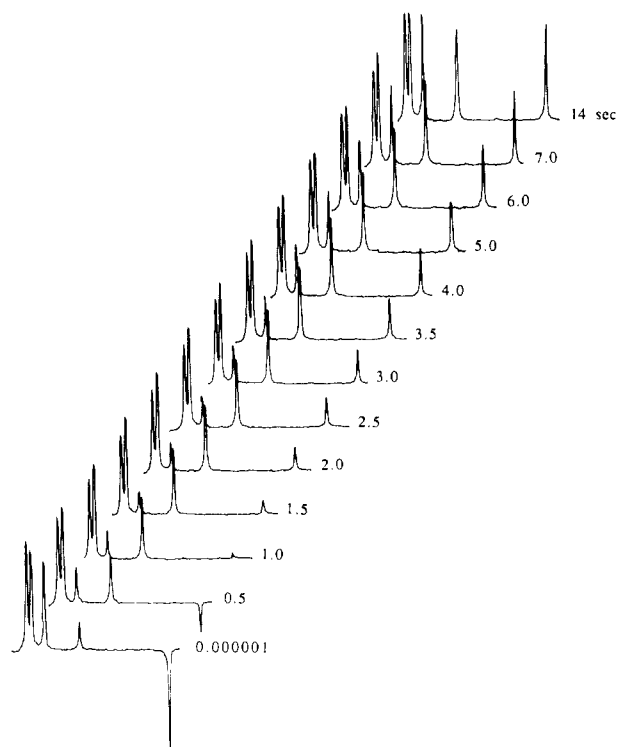


Figure 1. Saturation spin transfer experiment of chloropentakis(dichloromethyl)benzene (2) at 336 K in $\text{CDCl}_2/\text{CDCl}_2$. Numbers beside the spectra correspond to the time delay in seconds between inversion and acquisition. The selective 180° pulse was delivered on the high-field singlet. The loss in intensity of the signal closest to the irradiated peak is due not to saturation transfer but to partial irradiation from the 180° pulse.

the resulting ortho trichloromethyl and chlorine groups.

The 250-MHz ^1H NMR spectrum of 2 in $\text{CDCl}_2/\text{CDCl}_2$ at room temperature displays five separate singlets, in agreement with the rotation of the dichloromethyl groups being frozen on the NMR time scale. While four of the five signals are grouped together and are relatively deshielded (δ 8.13–8.27), the fifth dichloromethyl signal appears at higher field (δ 7.89). These results can be interpreted as being the result of a gear-meshed conformation of the five dichloromethyl groups in which only a single methine proton is not tucked into the cleft of a neighboring dichloromethyl group, causing it to be shielded relative to the others.¹⁵

When the temperature of a solution of 2 was raised, four of the five proton signals broadened and finally coalesced, while one signal remained sharp at all temperatures. This signal can be assigned to the methine proton of the dichloromethyl group para to the chlorine substituent since it is the only proton that does not exchange between magnetically nonequivalent sites as a result of rotation. The saturation spin transfer method (SST)¹⁶ was used for a double purpose: (a) to identify pairs of mutually exchanging signals (i.e. the pair of *o*-dichloromethyl protons and the pair of *m*-dichloromethyl protons) and (b) to measure the barrier for the topomerization process. The experiment was carried out at 336 K by delivering a selective 180° pulse to the signal at 7.89 ppm and recording the spectra by a nonselective 90° pulse after increasingly longer delay times (Figure 1). Treatment of the data

(10) Mark, V.; Pattison, V. A. *J. Chem. Soc. D* 1971, 553.

(11) Imhoff, W.; Dissertation ETH, Zurich, 1964 (prom. no. 3507), pp 22–24, 48–49. Also see: Hopff, H. *Chimia* 1964, 18, 140.

(12) Kahr, B.; Biali, S. E.; Schaefer, W.; Buda, A. B.; Mislow, K. *J. Org. Chem.* 1987, 52, 3713.

(13) The actual dihedral angle θ ($\text{C}_{ar}\text{--C}_{ar}\text{--C}_t\text{--H}$) was calculated to be 146° .

(14) Hojo, M.; Masuda, R. *Synth. Commun.* 1975, 5, 169.

(15) Similarly, in the ^1H NMR spectrum of 4,5,6-trichloro-1,2,3-tris(dichloromethyl)benzene, two signals appear at δ 8.06 and 8.08, while the third is at 7.89 ppm.¹⁰ This spectrum was interpreted by Mark and Pattison¹⁰ as indicating the presence of an all-gear-ed conformation.

(16) Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* 1975, 17, 400.

according to a literature procedure¹⁶ allowed us to calculate the rate constant for topomerization of **2** as 0.75 s^{-1} . By use of Eyring equation, and assuming a transmission coefficient equal to unity, a barrier of $19.8 \text{ kcal mol}^{-1}$ was calculated. The barrier to rotation was also evaluated by using the Gutowsky-Holm equation¹⁷ and the coalescence temperature for the pair of signals belonging to the *m*-dichloromethyl groups ($k_c = 73 \text{ s}^{-1}$ at 404 K , $\Delta G_c^\ddagger = 20.3 \text{ kcal mol}^{-1}$). The topomerization barrier for **2** is only $2.5 \text{ kcal mol}^{-1}$ higher than the reported barrier for 3,4,5,6-tetrachloro-1,2-bis(dichloromethyl)benzene ($17.7 \text{ kcal mol}^{-1}$).¹⁰

Static Stereochemistry of 2. Compound **2** can be viewed as the sum of a chlorobenzene skeleton of C_{2v} symmetry and five dichloromethyl ligands; therefore, the different possible conformers of **2** should belong either to the C_{2v} point group, or to its subgroups, i.e. C_s , C_2 , or C_1 . If we assume that the conformations in which the dichloromethyl groups are bisected by the phenyl ring correspond to local minima in the potential energy hypersurface, all minimum energy conformations should ideally have C_s point group symmetry. Since each of five groups can be oriented in two directions, the total number of possible configurations^{18,19a} should be $2^5 = 32$. This number does not, however, correspond to the number of different conformations. For example, the all-gearred conformation can be described as having all dichloromethyl groups oriented either clockwise or anticlockwise. Since each conformer of **2** is represented by two configurations,²⁰ the total number of isomers should be $32/2 = 16$.

The isomers of **2** are depicted in Figure 2 together with their shorthand descriptors.⁸ These descriptors are based on an arbitrary convention in which the different dichloromethyl groups are numbered in a clockwise fashion according to their relative position with respect to the chlorine substituent. The standard structure (the all-gearred) is denoted R_0 , and in the other structures, the subscripts refer to the positions of the rotated dichloromethyl groups relative to R_0 . These descriptors are not unique (e.g. $R_{13} = R_{124}$), and in general, there are two descriptors for each conformation. The relative steric energies of the different isomers were calculated by means of the MM2 force field²¹ as implemented in BIGSTRN-3.^{22,23} According to the calculations, the lowest energy conformer is R_0 , with the R_5 and the R_{45} conformers lying 4.3 and $4.8 \text{ kcal mol}^{-1}$ above the ground state, respectively.²⁴ In these

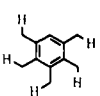

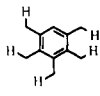

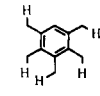

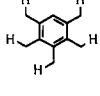

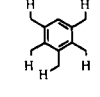

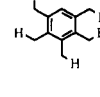

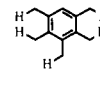

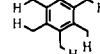

Descriptor	Energy	Descriptor	Energy		
	R_0	0.0		R_1	9.2
	R_2	11.8		R_3	11.8
	R_4	9.6		R_5	4.3
	R_{12}	11.5		R_{13}	21.5
	R_{14}	18.7		R_{15}	13.2
	R_{23}	15.3		R_{24}	18.3
	R_{25}	16.0		R_{34}	13.5
	R_{35}	12.2		R_{45}	4.8

Figure 2. The 16 conformational isomers of **2**, their descriptors, and calculated relative energy. The isomers are schematically represented by figures with lines in the plane of the benzene ring projecting from the methine carbons that point in the direction of the methine hydrogens. All chlorine atoms are suppressed for clarity.

three conformers, no neighboring (ortho) dichloromethyl groups with chlorines oriented toward each other are present. All other conformers involve at least one gear-clashing interaction between the chlorines of neighboring dichloromethyl groups, and their energy is $>9 \text{ kcal mol}^{-1}$ above the ground state. Except for R_0 and R_5 , which display C_s symmetry, the 14 other calculated conformers have C_1 symmetry. All of these 14 conformations are chiral and therefore exist in two enantiomeric forms. It should be noted, however, that during the study of the topomerization mechanism, two additional conformers were found. The first was located on the interconversion pathway between R_1 and R_{13} and the second between R_4 and R_{24} . The relative energies of the two additional conformers are 18.3 and $21.6 \text{ kcal mol}^{-1}$, and their geometries are close to those of R_{13} and R_{24} , respectively. In conclusion, according to the EFF calculations, **2** should exist mainly in the R_0 conformation. This is in agreement with the NMR data, which shows the presence of only a single conformer (R_0) in solution.

Topomerization Mechanism of 2. In order to elucidate the detailed topomerization mechanism of **2**, we decided to explore the energy surface computationally. The profiles for the rotation of different dichloromethyl groups were obtained by the one bond driver technique, initially rotating by 5° increments and subsequently, in the high-energy regions, by 1° increments. The exact location of each saddle point was determined by using the BIGSTRN-3 program. Stationary points on the hypersurface were characterized as partial maxima by the number of negative

(17) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* 1956, 25, 1228.

(18) Willem, R.; Pepermans, H.; Hoogzand, C.; Hallenga, K.; Gielen, M. *J. Am. Chem. Soc.* 1981, 103, 2297.

(19) (a) Brocas, J.; Gielen, M.; Willem, R. *The Permutational Approach to Dynamic Stereochemistry*; McGraw-Hill: New York, 1983; Chapter 4. (b) *Ibid.* Chapter 8.

(20) In accordance with a mathematically proven theorem,^{19b} the number of configurations of a particular isomer is a function of its symmetry number. Because in the case of **2** all conformations have the same symmetry number ($\sigma = 1$), each is represented by the same number of configurations (two).

(21) (a) Allinger, N. L. *J. Am. Chem. Soc.* 1977, 99, 8127. (b) Allinger, N. L.; Yuh, Y. H. *QCPE* 1981, 13, 395. Two modifications for $C_{ar}-C_{ar}$ bonds were $I_0 = 1.3937 \text{ \AA}$ and $k_s = 8.0667 \text{ mdyn \AA}^{-1}$. See also: Osawa, E.; Onuki, Y.; Mislow, K. *J. Am. Chem. Soc.* 1981, 103, 7475.

(22) Nachbar, R. B., Jr.; Mislow, K. *QCPE* No. 514. Nachbar, R. B., Jr.; Mislow, K. *QCPE Bulletin* 1986, 6, 96.

(23) Input geometries having C_s symmetry were based on standard bond lengths and angles. Geometry optimizations were routinely begun with the MM2 program and concluded with the full matrix Newton-Raphson method. The final convergence criteria for the Newton-Raphson stage were as follows: root mean square gradient less than $10^{-6} \text{ kcal mol}^{-1}$ and root mean square atom movement less than 10^{-6} \AA .

(24) The R_5 conformation of pentakis(dichloromethyl)benzene lies only $1.6 \text{ kcal mol}^{-1}$ above the R_0 conformation.¹² The higher energy gap between these two conformations in **2** is probably due to the repulsive steric interaction between the chlorines of the twisted dichloromethyl group and the chlorine at the 1 position.

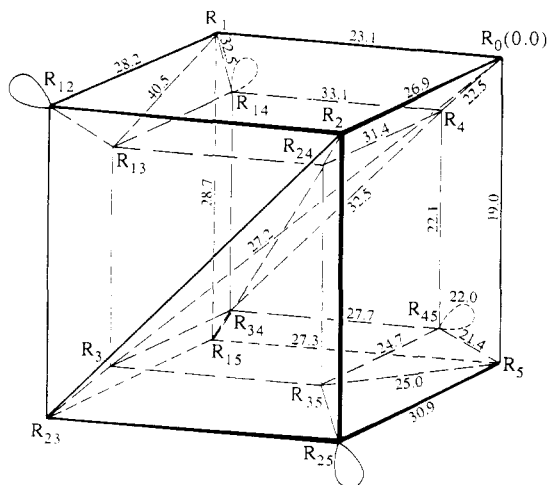


Figure 3. Graph showing the interconversion scheme for the 16 ideal isomers of **2**. The different isomers are represented according to their descriptors (cf. Figure 2), while relevant transition state energies (relative to R_0) are indicated at the edges of the graph. The four closed loops denote topomerization processes.

eigenvalues in the force constant matrix; a single partial maximum (one negative eigenvalue) corresponded to a saddle point (transition state). Convergence criteria for saddle points were the same as for minima.²³ The BIGSTRN-3 eigenvector distortion option was used to obtain the two minima interconnected by these saddle points. This assured that the saddle points indeed connected the expected pair of minima.

The first question to be addressed was whether the threshold rotational mechanism involves a correlated rotation of the dichloromethyl groups (i.e. simultaneous rotation of all groups in a correlated disrotation) or whether, by analogy to other gear-locked systems,^{2,6,8,25} the rotation proceeds via a stepwise mechanism (uncorrelated rotation) of the dichloromethyl groups. We believe that correlated rotation can be safely disregarded as the threshold rotational mechanism, since by driving the different dichloromethyl groups one at a time the other groups do not "follow up". Moreover, the conformation with an alternant "up" and "down" disposition of the dichloromethyl groups (C_s symmetry, presumably the transition state for the correlated process) is 67.1 kcal mol⁻¹ above the R_0 conformation.

In discussing the threshold rotational mechanism, it is very useful to construct a graph for the rotation of the haloalkyl groups in the system. In this graph, the vertices represent the different minimum-energy conformers, and the lines connecting them (the edges) represent symmetry nonequivalent pathways involving rotation of one dichloromethyl group at a time.²⁶ Since in each of the 16 different conformers (of ideal C_s symmetry) the five dichloromethyl groups are symmetry nonequivalent, there are five different single-group rotation pathways emanating from each different conformer; i.e. the degree of each vertex in the graph is equal to five. The graph describing the network of interconversions in **2** is therefore composed of 16 vertices and 42 edges. Among the possible geometric realizations of this graph, we chose the one depicted in Figure 3, which has as its "skeleton" the form of a three-dimensional projection of a hypercube, and on which ad-

ditional lines were added in order to increase the connectivity of each vertex from four (as in a "regular" hypercube) to five.^{27,28} In four of the conformers (R_{12} , R_{14} , R_{45} , and R_{25}), rotation of the dichloromethyl group para to the aromatic Cl leads to homomerization and not to isomerization. These processes are represented in the graph by loops at the previously mentioned vertices.

We want to stress that our interest was to find the threshold topomerization mechanism, i.e. the multistep process by which R_0 interconverts to itself with the net result of magnetic site exchange at the pairs of ortho and meta positions in R_0 . Since there are five symmetry nonequivalent dichloromethyl groups, a minimum of five single group rotations are required in order to complete the topomerization process. A two-step, three-step, or four-step process (for example $R_0 \rightarrow R_1 \rightarrow R_{12} \rightarrow R_2 \rightarrow R_0$) while possibly resulting in homomerization (R_0 becomes R_0) cannot result in topomerization. With this limitation in mind, we proceeded to explore the potential energy hypersurface of **2**. The relevant transition states are included in Figure 3.²⁹ Starting from R_0 , the five transition states that interconnect it with R_1 , R_2 , R_3 , R_4 , and R_5 have calculated energies (relative to R_0) of 23.1, 26.9, 27.2, 22.5, and 19.0 kcal mol⁻¹, respectively. Therefore, only the paths emanating from R_1 , R_4 , and R_5 were further explored. As Figure 3 shows, the paths connecting R_4 and R_5 with R_{45} have energies of 22.1 and 21.4 kcal mol⁻¹, respectively, while all other paths leading away from R_1 , R_4 , and R_5 (excluding the reverse of the first step; $R_1 \rightarrow R_0$, $R_4 \rightarrow R_0$, and $R_5 \rightarrow R_0$) have energies > 25 kcal mol⁻¹ and therefore can be safely eliminated. R_{45} can further interconvert to R_{34} or R_{35} (with calculated transition state energies of 27.7 and 24.7 kcal mol⁻¹, respectively) or it can topomerize via rotation of the dichloromethyl group in the para position (denoted in Figure 3 by a loop around the R_{45} vertex) through a transition state of calculated C_s symmetry (22.0 kcal mol⁻¹). Accordingly, the calculated threshold topomerization mechanism involves the following steps: $R_0 \rightarrow R_5 \rightarrow R_{45}$ (with calculated relative transition state energies of 19.0 and 21.4 kcal mol⁻¹) followed by topomerization of R_{45} and reversal of the first two steps (i.e. $R_{45} \rightarrow R_5 \rightarrow R_0$). There is a competing pathway that involves reaching R_{45} through the steps $R_0 \rightarrow R_4 \rightarrow R_{45}$ (with calculated transition state energies of 22.5 and 22.1 kcal mol⁻¹). Although the latter pathway is somewhat higher in energy, we consider the difference to be within the margin of uncertainty of the calculations. In short, the EFF calculations indicate that the topomerization proceeds by the successive rotation of the dichloromethyl groups. The calculated barrier for the preferred interconversion pathways $R_0 \rightarrow (R_4 \text{ or } R_5) \rightarrow R_{45} \rightarrow (\text{topomerization}) R_{45} \rightarrow (R_4 \text{ or } R_5) \rightarrow R_0$ (22 kcal mol⁻¹) is very close to the value experimentally determined by dynamic NMR (20 kcal mol⁻¹).

Experimental Section

Pentamethylbenzene and sulfur chloride were purchased from Aldrich and were used without purification. NMR spectra were

(25) Schuster, I. I.; Weissensteiner, W.; Mislow, K. *J. Am. Chem. Soc.* 1986, 108, 6861.

(26) For clarity, enantiomeric pathways (e.g. the rotations of a given dichloromethyl group in R_0 in a clockwise and anticlockwise manner) are represented by single edges, since the energies of the two transition states must be equal.

(27) Graphs having representations of hypercubes were used for analyzing the isomerizations of molecular propellers (Gust, D.; Mislow, K. *J. Am. Chem. Soc.* 1973, 95, 1535).

(28) The enumeration of edges at the vertices associated with the loops can introduce some ambiguity, since the loops can be treated as a single or double edge. However, because each of the loops represent a single homomerization process, they are counted singularly (see: Ore, O. *Theory of Graphs*; American Mathematical Society, Colloquium Publications: Providence, Rhode Island, 1962; Vol. 38, p 7).

(29) During the exploration of the interconversion mechanism of **2**, it was found that the pathways interconnecting R_1 and R_{13} and interconnecting R_4 and R_{24} involve a two-step processes with an intermediate minimum-energy conformation. In Figure 3, only the energy of the highest transition state is depicted.

recorded on a Bruker WM-250 spectrometer. Temperature measurements were based on the chemical shift separation of an ethylene glycol sample and utilization of the van Geet relationship.³⁰ Mass spectra were measured on a Kratos MS 50 RFA spectrometer. Melting points were recorded on a Thomas-Hoover melting point apparatus and are corrected. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Chloropentamethylbenzene. To a solution of pentamethylbenzene (1 g, 6.8 mmol) in 10 mL of CCl₄ was added 0.6 mL of SO₂Cl₂ (1 g, 7.4 mmol) and 0.3 g of silica gel (60–200 mesh). After the mixture stood for 12 h at room temperature (without stirring), the solvents were evaporated, and the residue was added to the top of a short silica gel column. Elution with hexane afforded 260 mg (21%) of chloropentamethylbenzene, mp 152–153 °C (lit.³¹ mp 153–155 °C).

(30) Van Geet, A. L. *Anal. Chem.* 1968, 40, 2227; 1970, 42, 679.

(31) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* 1957, 79, 5169.

Chloropentakis(dichloromethyl)benzene (2). A slow stream of chlorine gas was bubbled through a refluxing solution of chloropentamethylbenzene (130 mg) in 20 mL of CCl₄ while the reaction mixture was irradiated with a 150-W tungsten lamp. After 24 h, the reaction mixture was cooled, and the solid that deposited in the gas inlet was collected. The product was recrystallized from 1,1,2,2-tetrachloroethane to afford 65 mg (14%) of pure 2, mp >300 °C: ¹H NMR (CDCl₂CDCl₂, room temperature) δ 7.89 (s, 1 H, *o*-CH), 8.13 (s, 1 H, *m*-CH), 8.22 (s, 1 H, *o*-CH) 8.25 (s, 1 H, *p*-CH), 8.27 (s, 1 H, *m*-CH); exact mass calcd for C₁₁H₅³⁵Cl₉³⁷Cl₂ 525.6904, found 525.6876. Anal. Calcd for C₁₁H₅Cl₁₁: C, 25.06; H, 0.96. Found: C, 25.12; H, 0.92.

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Registry No. 2, 111351-51-0; chloropentamethylbenzene, 5153-39-9.

Interpretation of Conjugated Oxiranes Behavior toward Nucleophiles

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The behavior of conjugated oxiranes toward nucleophiles has been rationalized by means of perturbational theory and MNDO calculations. Metal ion coordination to the oxiranic oxygen seems to be important in the regioselectivity of the 1,2-addition on α,β -epoxy esters.

Conjugated oxiranes, i.e., oxiranes directly bonded to a π -electron system, are synthetically important frameworks capable of sustaining regioselective reactions (1,2-addition, 1,4-conjugate addition, or 3,4-addition) depending on the reactant.¹ However, this rather diverse behavior toward nucleophiles in neutral or basic conditions has not yet been fully interpreted in terms of a sound theory.

We found it convenient to interpret the results by MNDO^{2,3} calculations on several simple model compounds in terms of a combination of perturbational and hard and soft acid and base (HSAB) theories. We present herein a summary of our study qualitatively interpreted.

According to Klopman–Salem equation,⁴ nucleophilic attack on conjugated oxiranes is governed by the combination of Coulombic interactions between reactant and substrate at the reactive site and the interactions between the occupied molecular orbitals (MO) of the nucleophile and the unoccupied MO of the substrate. In our approach reactants were classified on the basis of HSAB concept, and only the LUMO and atomic charge distribution of oxiranes (obtained by MNDO calculations on model compounds including full geometry optimization) were con-

Table I. Four Types of Conjugate Oxiranes with LUMO and Atomic Charge Distribution Obtained by MNDO. The Experimentally Preferred Sites of Attack by Nucleophiles are Shown by the Arrows

type	model molecule and experimental site of attack ^a	MNDO	
		LUMO ^b	charge distribution
A			
B			
C			
D			

^a Open arrow for soft base and solid arrow for hard base.

^b Numbers refer to $\sum c^2$ for atomic valence orbitals on each atom.

sidered. The compounds studied were grouped into four classes, A, B, C, and D, depending on the π -electron system conjugated to the oxirane being the representative of each class: vinyl- (1), formyl- (2), acetyl-(enolate) (3), and (methoxycarbonyl)oxirane (4), respectively. In Table I these compounds are depicted jointly with the calculated

(1) (a) Rao, A. S.; Pakniker, S. K.; Kirtane, J. G. *Tetrahedron* 1983, 39, 2323. (b) Gorzynski, J. *Synthesis* 1984, 629.

(2) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1979, 99, 4899, 4907. (b) Dewar, M. J. S. *J. Mol. Struct.* 1983, 100, 45.

(3) The best available program for running MNDO calculations is MOPAC. An updated program of MOPAC (version 3.0), QCPE455, is now available: Stewart, J. J. P. *QCPE Bull.* 1985, 5, 133. See also Aquino A. J. A.; Conti, M.; de Silva, A. B. F.; Trsic, M. *QCPE Bull.* 1985, 5, 122; Stewart, J. J. P. *Ibid.* 1985, 5, 126. A version of MNDO program for use on a personal computer is recently being distributed (QCMP002: *QCPE Bull.* 1984, 4, 76).

(4) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, 1978; p 27.