

(2 H, d, $J = 8.5$ Hz), 3.50 (1 H, s), 3.70 (3 H, s), 2.52 (1 H, q, $J = 7.0$ Hz), 2.48 (1 H, q, $J = 7.0$ Hz), 1.22 (3 H, t, $J = 7.0$ Hz); MS m/e (rel intensity) 255 (M^+ , 3), 196 (100), 195 (71).

The Cyclopropanes (20) from 2a and α -Chloroacrylonitrile. A solution of the diazo ester (**1a**, 50 mg) in the acrylonitrile (5 mL) was irradiated as described above and the reaction mixture was separated by preparative TLC (CHCl_3 - n -hexane = 1:1). Removal of the mobile phase under reduced pressure afforded 1-chloro-1-cyano-2-(methoxycarbonyl)-2-(4-nitrophenyl)cyclopropanes (**20**). The major isomer (43 mg, 67.0%) eluted first, followed by the minor isomer (16 mg, 25.0%). The major isomer: NMR (δ , CDCl_3) 8.25 (2 H, d, $J = 8.0$ Hz), 7.68 (2 H, d, $J = 8.0$ Hz), 3.79 (3 H, s), 2.68 (1 H, d, $J = 7.5$ Hz), 2.35 (1 H, d, $J = 7.5$ Hz); MS m/e (rel intensity) 280 (M^+ , 34), 140 (64), 59 (100). The minor isomer: NMR (δ , CDCl_3) 8.25 (2 H, d, $J = 8.0$ Hz), 7.55 (2 H, d, $J = 8.0$ Hz), 3.80 (3 H, s), 2.92 (1 H, d, $J = 7.5$ Hz), 2.13 (1 H, d, $J = 7.5$ Hz); MS m/e (rel intensity) 280 (M^+ , 34), 140 (64), 59 (100). Anal. Calcd for $\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4\text{Cl}$: C, 51.35; H, 3.23; N, 9.98. Found: C, 51.72; H, 3.16; N, 9.90.

The Cyclopropanes (21) from 2a and 1-Hexene. A solution of the diazo ester (**1a**, 50 mg) in 1-hexene (3 mL) in a Pyrex tube was irradiated as described above and the reaction mixture was separated by preparative TLC (CHCl_3 - n -hexane = 1:4) to give 1-(methoxycarbonyl)-1-(4-nitrophenyl)-2-butylcyclopropanes (**21**). (Syn- CO_2Me)-**21**: 20 mg (31.8%); NMR (δ , CDCl_3) 8.10 (2 H, d, $J = 8.0$ Hz), 7.45 (2 H, d, $J = 8.0$ Hz), 3.62 (3 H, s), 1.63-0.92 (12 H, m); MS m/e (rel intensity) 277 (M^+ , 37), 208 (100), 176 (62), 148 (89). (Anti- CO_2Me)-**21**: 12 mg (18.8%); NMR (δ , CDCl_3) 8.15 (2 H, d, $J = 8.0$ Hz), 7.40 (2 H, d, $J = 8.0$ Hz), 3.60 (3 H, s), 1.82-0.80 (12 H, m); MS m/e (rel intensity) 277 (M^+ , 37), 208 (100), 176 (62), 148 (89).

The Cyclopropanes (23) from 2 and Substituted Styrenes (22). A

solution of **1a** and **1c** (50 mg) in substituted styrenes (**22**, 200 mg) and benzene (0.2 mL) was irradiated as described above and the reaction mixture was separated by preparative TLC (CHCl_3 - n -hexane = 2:3) to give isomeric pure 1,2-diaryl-1-(methoxycarbonyl)cyclopropanes (**23**). The isomer ratio was roughly 1:1 and overall yields were about 80-90% in each run. The NMR and mass spectra of each isomer are given in Table XI together with the melting points.

Anal. **23** (Y = 4-Me) Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.67; H, 5.47; N, 4.41.

Anal. **23** (Y = H) Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.88; H, 5.06; N, 4.53.

Anal. **23** (Y = 4-Cl) Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_4\text{Cl}$: C, 61.55; H, 4.25; N, 4.22. Found: C, 61.04; H, 4.12; N, 4.04.

Anal. **23** (Y = 4-Br) Calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_4\text{Br}$: C, 54.28; H, 3.75; N, 3.72. Found: C, 54.95; H, 3.53; N, 3.53.

Anal. **23** (Y = 4-CN) Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_4$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.05; H, 4.29; N, 8.65.

Anal. **23** (Y = 4- NO_2) Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_6$: C, 59.65; H, 4.12; N, 8.18. Found: C, 59.90; H, 4.10; N, 8.11.

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Triangulanes: Stereoisomerism and General Method of Synthesis

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Abstract: The class of spirocondensed cyclopropanes, triangulanes, is defined and stereochemical problems of unbranched triangulanes (UTs) are considered from an algebraic-combinatorial point of view. The general method of triangulane synthesis that consists of the addition of chloromethylcarbene to methylenecyclopropanes with subsequent dehydrochlorination and final cyclopropanation of the resulting methylenetriangulanes is suggested and realized for [5]- and [6]-members of the family.

In the period of just over 90 years since spiro-pentane (**1**) was prepared¹ the spirocondensed three-membered ring systems, with their destabilization energy over of 65 kcal/mol,^{2,3} have been the subject of numerous theoretical²⁻⁵ investigations. We define

(1) Gustavson, G. J. *Prakt. Chem.* **1896**, *54*, 104.

(2) (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. (b) Ioffe, A. I.; Svyatkin, V. A.; Nefedov, O. M. *Structures of cyclopropane derivatives* Nauka: Moscow, 1986; in Russian.

(3) (a) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. P. *J. Am. Chem. Soc.* **1970**, *92*, 2377. (b) Würthwein, E. U.; Chandrasekar, J. J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 843.

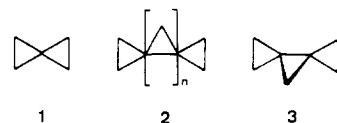
(4) (a) Zilberg, S. P.; Ioffe, A. I.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 261. (b) Baird, N. C.; Dewar, M. J. C. *J. Am. Chem. Soc.* **1967**, *89*, 3966. (c) Dewar, M. J. C.; Worley, S. D. *J. Chem. Phys.* **1969**, *50*, 654. (d) Yonezawa, T.; Shimizu, K.; Kato, H. *Bull. Soc. Chem. Jpn.* **1968**, *41*, 2336. (e) Randić, M.; Maksić, Z. *Theor. Chim. Acta* **1965**, *3*, 59. (f) Randić, M.; Jerkunica, J. M.; Stefanovic, D. *Croat. Chem. Acta* **1966**, *38*, 49.

(5) de Meijere, A. *Angew. Chem.* **1979**, *91*, 867. (b) Gleiter, R.; Haider, R.; Conia, J.-M.; Barrier, J.-P.; de Meijere, A.; Weber, W. *J. Chem. Soc., Chem. Commun.* **1979**, 130.

(6) Fitjer, L.; Conia, J.-M. *Angew. Chem.* **1973**, *85*, 832, 349.

(7) (a) Fitjer, L. *Chem. Ber.* **1982**, *115*, 1035. (b) Fitjer, L. *Angew. Chem.* **1976**, *88*, 803. (c) Zefirov, N. S.; Lukin, K. A.; Kozhushkov, S. I.; Kuznetsova, T. S.; Domarev, A. M.; Sosonkin, I. M. *Zh. Org. Khim.* **1989**, *25*, 312. (d) Denis, J. M.; Girard, C.; Conia, J.-M. *Synthesis* **1972**, 549. (e) Weber, W.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2450.

"triangulanes" as the class of hydrocarbons whose skeleton is constructed exclusively from spiro-attached three-membered rings. The simplest subclass, that of unbranched triangulanes (UTs), may be represented with general formula **2**.⁹ The parent hydrocarbon **1** (or [2]-triangulane),¹⁻³ as well as the [3]-,^{6,7d} and [4]-^{6,7c} members of the family, have been synthesized up to date.



In this paper we shall deal exclusively with UTs and address ourselves to two specific topics: (i) enumeration problems and stereoisomerism of UTs and (ii) general synthetic method of UTs.

Stereochemical Problems of Unbranched Triangulanes. Three-membered rings of spiro-pentane (**1**) occupy two mutually

(8) Arora, S.; Binger, P. *Synthesis* **1974**, 801.

(9) (a) Branched and cyclic triangulanes are other theoretically possible subclasses. Note that in monocyclic triangulanes all bonds of a central cycle must belong to exactly one cyclopropane ring; for this reason only [3]-rotane^{9b} (but not other rotanes) can be accepted as triangulane structure. (b) Pascard, C.; Prange, T.; de Meijere, A.; Weber, W.; Barnier, J.; Conia, J.-M. *J. Chem. Soc., Chem. Commun.* **1979**, 425.

Chart I

$$N_1 = \frac{1}{2} \sum_{i=1}^2 X(\delta_i) = \begin{cases} 1/2 (2^{n-3} + 2 \cdot 2^{(n-4)/2}) = 2^{n-4} + 2^{(n-4)/2}, & n - \text{even} \\ 1/2 (2^{n-3} + 2^{(n-3)/2}) = 2^{n-4} + 2^{(n-5)/2}, & n - \text{odd} \end{cases} \quad (1)$$

$$N_2 = \frac{1}{4} \sum_{i=1}^4 X(\delta_i) = \begin{cases} 1/4 (2^{n-3} + 2 \cdot 2^{(n-4)/2} + 0 + 0) = 2^{n-5} + 2^{(n-6)/2}, & n - \text{even} \\ 1/4 (2^{n-3} + 2^{(n-3)/2} + 0 + 2^{(n-3)/2}) = 2^{n-5} + 2^{(n-5)/2}, & n - \text{odd} \end{cases} \quad (2)$$

$$N_3 = N_1 - N_2 = \begin{cases} 2^{n-4} + 2^{(n-4)/2} - 2^{n-5} - 2^{(n-6)/2} = 2^{n-5} + 2^{(n-6)/2}, & n - \text{even} \\ 2^{n-4} - 2^{n-5} = 2^{n-5}, & n - \text{odd} \end{cases} \quad (3)$$

$$N_4 = N_2 - N_3 = \begin{cases} 0, & n - \text{even} \\ 2^{(n-5)/2}, & n - \text{odd} \end{cases} \quad (4)$$

perpendicular planes. Hence, the [3]-triangulane molecule, 3, being achiral itself, has two enantiotopic positions a and b and, in turn, may lead to two enantiomeric [4]-triangulanes due to attachment of the fourth cyclopropane ring either in positions a and b of 3. Clearly, the problem of UT stereochemistry is quite complicated for higher members of the family and needs general consideration.

Two intriguing problems may be stated here: (i) enumeration of possible stereoisomeric UTs and (ii) construction of the generation tree to represent the interrelations between the stereoisomers of UTs and their key synthetic precursors. The solution of both problems can be easily reached on the basis of the *abstract configuration theory*.¹⁰⁻¹³ The notion of abstract configuration completely ignores metrical characteristics of molecular shapes and this makes it possible to employ it directly for various enumeration and constructive enumeration problems of organic chemistry. This notion makes it also possible to elaborate new classes of characteristics of spatial models of molecules. Two investigated classes of configurational-topological indices (i.e. chain^{13a,b} and metric^{13b} ones) express not only the graph structures of organic molecules but the molecular shapes as well.

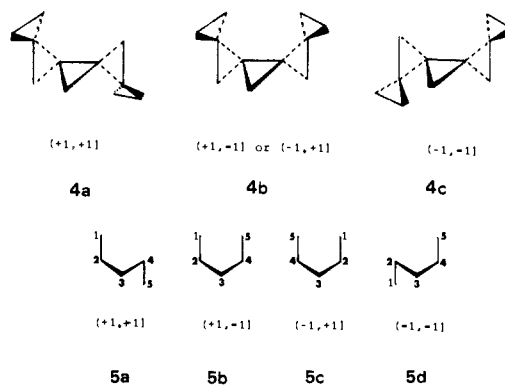
In the case of triangulanes the analysis of 3-dimensional (3D) chain configurations¹² must be performed. First of all, every [n]-triangulane stereoisomer may be associated with a unique spatial graph with n nodes.¹⁴ Each node of this graph is located

Table I. The Numbers of Stereoisomeric Unbranched [n]-Triangulanes

n	N ₁	N ₂	N ₃	N ₄
2*	1	1	0	1
3*	1	1	0	1
4	2	1	1	0
5	3	2	1	1
6	6	3	3	0
7	10	6	4	2
8	20	10	10	0
9	36	20	16	4
10	72	36	36	0

* The obvious values of N₁ - N₄ cannot be obtained by means of Burnside's Lemma because no 4-tuples can be constructed in these cases.

in the center of the corresponding cyclopropane ring is located in the center of the corresponding cyclopropane ring and two nodes are connected by a line if the two rings have a common atom. The spatial graphs relating to the stereoisomeric [5]-triangulanes 4a-c are shown pictorially (5a-d).



One may see that four sequentially connected nodes of such graphs can never lie in a plane: the corresponding dihedral angles are always equal to 90°. For this reason the relative spatial arrangement of graph nodes is to be characterized by *binary* 3D configurations,¹⁶ the examples of configurational codes [consisting of images of 4-tuples (1,3,4) and (2,3,4,3), see ref 10] are presented

(15) (a) Balaban, A. T.; Haryar, F. *Tetrahedron* **1968**, *24*, 2505. (b) Balaban, A. T. *Match (Mülheim)* **1976**, *2*, 51. (c) Balaban, A. T. *Rev. Roum. Chim.* **1976**, *21*, 1049.

(16) (a) This is a difference between triangulane spatial graphs and spatial graphs representing n-alkane skeleton rotamers,^{15b,c} see also ref 16b. The latter graphs must be characterized by ternary 3D chain configurations. (b) Randić, M. *Int. J. Quant. Chem., Quant. Boil. Symp.* **1980**, *7*, 187.

(10) The abstract configuration may be briefly defined as an equivalency class of mappings from the set of ordered m-tuples (m = 3 for 2D and m = 4 for 3D cases) into the set [-1,0,+1].¹¹ In the spatial case the image φ of 4-tuple (i,j,k,l) equal to -1 or +1 means that the point (or atom) l is located behind or before the plane in which three other points (atoms) i,j,k are arranged clockwise; the zero value of φ means all four points (atoms) to lie in one plane. It should be stressed however that the image φ of every 4-tuple depends not only on points i,j,k,l being chosen but also on their relative order. Even permutations of points do not affect the image while odd permutations change its sign; thus φ(i,j,k,l) = -φ(j,i,k,l) = -φ(k,j,i,l) = φ(l,k,j,i), etc.

(11) (a) Tratch, S. S.; Zefirov, N. S. In *Principles of Symmetry and Systemology in Chemistry*; Stepanov, N. F., Ed.; Moscow State University Publ.: Moscow, 1987; p 54. (b) Klin, M. H.; Tratch, S. S.; Zefirov, N. S. *Rep. Mole. Theor.*, in press.

(12) The molecular chain configuration is a special kind of partial configuration. It is defined as mapping φ from the set of ordered 3- or 4-tuples (consisting of three or four sequentially connected atoms) into the set [-1,+1] in binary or into the set [-1,0,+1] in ternary case.¹³ The complete set of all possible n-atomic chain configurations Φ = {φ} consists of 2^{n-d} or 3^{n-d} mappings (d is dimensionality, that is d = 2 or d = 3). The partition of the set Φ into equivalency classes (abstract chain configurations) depends on the action of a certain induced group; the solution of enumeration problems is especially simple just for chain molecular species.

(13) (a) Tratch, S. S.; Devdariani, R. O.; Zefirov, N. S. *Zh. Org. Khim.*, in press. (b) Zefirov, N. S.; Tratch, S. S. *Proceedings of 8th USSR conference on Application of Computers in Molecular Spectroscopy and Chemical studies*. Theses, Novosibirsk, 1989, p 139.

(14) Similar graphs (called characteristic or dualist graphs) were introduced by Balaban^{15a,b} for the characterization of polybenzenoid hydrocarbons.

beneath graphs 5a-d. It is important for configurational codes to be transformed into their "right-to-left" counterparts if the nodes of the chain graph are renumbered (cf. codes of spatial graphs 5b and c). These codes are independent of node numbering only if the corresponding $[n]$ -triangulane molecule possesses a C_2 axis of symmetry (4a,c and 5a,d).

The enumeration of unbranched $[n]$ -triangulanes needs two permutation groups to be considered.¹⁷ The first one consists of two permutations converting the spatial graph into itself¹⁸ while the second group consists of four permutations converting this graph either to itself or to its mirror image.¹⁹ The application of the first group makes it possible to calculate the total number, N_1 , of individual $[n]$ -triangulane enantiomers together with achiral structures. The second group produces the number, N_2 , of corresponding pairs of enantiomers also together with achiral structures. The known values of N_1 and N_2 allow the counting of the number of racemic pairs, $N_3 = N_1 - N_2$, as well as of achiral, $N_4 = N_2 - N_3$, unbranched triangulanes.

The counting of N_1 and N_2 is an exercise using the well-known Burnside's Lemma.^{20,21} The results obtained²² depend on the

(17) (a) A more detailed mathematical treatment is needed to understand the action of these groups. Let W be a set of 4-tuples $(1,2,3,4), (2,3,4,5), \dots, (n-3, n-2, n-1, n)$ and M be a set of labels -1 and $+1$. The complete set $\Phi = \{\varphi\}$ of binary 3D chain configurations evidently consists of 2^{n-3} mappings from W to M . Let G be a group consisting of two permutations

$$g_0 = \begin{pmatrix} (1,2,3,4) & (2,3,4,5) & \dots & (n-3, n-2, n-1, n) \\ (1,2,3,4) & (2,3,4,5) & \dots & (n-3, n-2, n-1, n) \end{pmatrix}$$

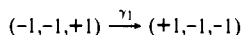
$$g_1 = \begin{pmatrix} (1,2,3,4) & (2,3,4,5) & \dots & (n-3, n-2, n-1, n) \\ (n, n-1, n-2, n-3) & (n-1, n-2, n-3, n-4) & \dots & (4, 3, 2, 1) \end{pmatrix}$$

with g_0 being the identity permutation and g_1 being a permutation which converts 1st, 2nd, 3rd, ... 4-tuple into $(n-3)$ th, $(n-4)$ th, $(n-5)$ th and so on. Note that g_1 corresponds to renumbering of spatial graph nodes and does not affect the image of every 4-tuple $\{\varphi(i,k,j,l) = \varphi(i,j,k,l)\}$. The second group H consisting of permutations

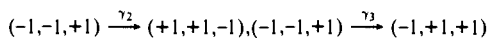
$$h_0 = \begin{pmatrix} -1 & +1 \\ -1 & +1 \end{pmatrix} \quad \text{and} \quad h_1 = \begin{pmatrix} -1 & +1 \\ +1 & -1 \end{pmatrix}$$

acts on the set M ; note that identity group $E = \{h_0\}$ may be thought to be a subgroup of H . From the groups G and H (or G and E) a new permutation group acting on the set Φ may be constructed; this group was investigated by Harary and Palmer^{17b} and is known as a power group. In the general case the power group Γ is the action of a direct product $G \times H$ of G and H ; it consists of $|G| \cdot |H|$ ordered pairs (g_i, h_j) , $g_i \in G, h_j \in H$. (b) Harary, F.; Palmer, E. M. *J. Combinatorial Theory*, 1966, 1, 157.

(18) This group $\Gamma_1 = E^G$, consisting of two permutations $\gamma_0 = (g_0, h_0)$ and $\gamma_1 = (g_1, h_0)$, partitions the set Φ into disjoint subsets (equivalence classes or orbits); all the mappings φ belonging to the same orbit of Γ_1 represent a single spatial graph of corresponding UT stereoisomer (the enantiomers are also distinguished). Note that γ_0 converts each configurational code into itself and γ_1 converts each code to its "right-to-left" counterpart



(19) This groups $\Gamma_2 = H^G$ consists of four permutations $\gamma_0, \gamma_1, \gamma_2 = (g_0, h_1)$ and $\gamma_3 = (g_1, h_1)$. The action of Γ_2 also partitions the set Φ into disjoint subsets; in this case the mappings φ corresponding to two enantiomers of chiral $[n]$ -triangulane are collected into one equivalency class. Note that the action of γ_2 and γ_3 results in the change of the sign in all components of configurational code

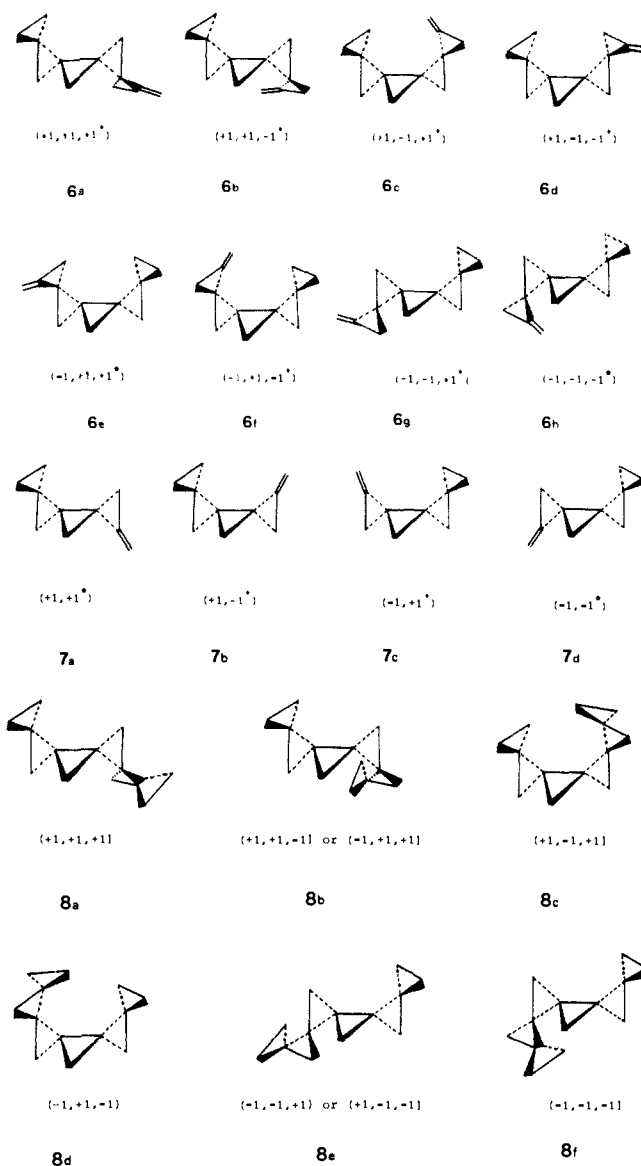


(20) (a) The Burnside's Lemma makes it possible to calculate the number N of orbits for arbitrary permutation group $\Pi = \{\pi_i\}$ acting on the set $X = \{x_i\}$. For this purpose the number $\chi(\pi_i)$ of elements $x_i \in X$ which are converted into itself must be known for every permutation

$$N = 1/|\Pi| \sum_{\pi_i \in \Pi} \chi(\pi_i)$$

The application of Burnside's Lemma to two other problems (enumeration of 2D chain configurations and of processes with linear electron transfer) is described elsewhere with more details.^{13,20b} (b) Tratch, S. S.; Gamziani, G. A.; Zefirov, N. S. *Zh. Org. Khim.* 1987, 23, 2488.

Chart II



parity of n [see eqs 1, 2 (Chart I)]. For this reason the values for chiral and achiral $[n]$ -triangulanes also depend on the parity of the number of cyclopropane units [see eqs 3, 4 (Chart I)]. The numbers of stereoisomeric triangulanes with 2-10 cyclopropane rings are collected in Table I. The values of N_4 in Table I (and eq 4) show that there exists only one achiral triangulane with an even number of three-membered rings; that is spiropentane ([2]-triangulane) molecule (1).

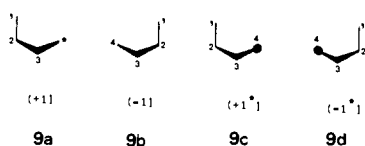
For the construction of the triangulane generation tree the interrelations between stereoisomeric UTs and their synthetic precursors must be carefully analyzed. Of the two types of precursors, namely chloromethyltriangulanes and methylene-triangulanes (vide infra), the latter are considered to be key precursors.²³

(21) Klin, M. C.; Pöschel, R.; Rosenbaum, K. *Angewandte Algebra für Mathematiker und Informatiker*, VEB Deutscher Verlag der Wissenschaften: Berlin, 1988; S. 54.

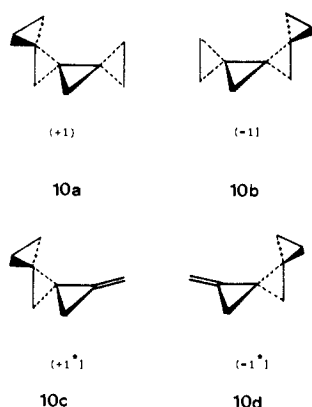
(22) The calculation of the values $\chi(\gamma_k)$, $k = 0, 1, 2, 3$ is based on pure combinatorial considerations. The permutation $\gamma_0 = (g_0, h_0)$ converts all configurational codes into themselves, thus $\chi(\gamma_0) = 2^{n-3}$. The permutation $\gamma_1 = (g_1, h_0)$ converts into themselves only "symmetrical" codes with the first component identical with $(n-3)$ th, second component identical with $(n-2)$ th, etc [the code $(-1, +1, +1, -1)$ may serve as an example]. The number of such codes $\chi(\gamma_1)$ is evidently equal to $2 \cdot 2^{(n-4)/2}$ (if n is even) or to $2^{(n-3)/2}$ (if n is odd). The permutation $\gamma_2 = (g_0, h_1)$ does not convert any code into itself, for this reason $\chi(\gamma_2) = 0$. The last permutation $\gamma_3 = (g_1, h_1)$ converts into themselves only "antisymmetrical" codes [similar to code $(-1, +1, -1, +1)$]. The number of such codes is zero if n is even (and $n-3$ is odd) and is equal to $2^{(n-3)/2}$ if n is odd (and $n-3$ is even).

First, it should be noted that for each $[n]$ -UT structure two or four stereoisomeric methylene- $[n]$ -triangulanes can be formally related. The methylene- $[5]$ -triangulanes (**6**) (Chart II) related to the $[5]$ -triangulanes **4** may serve as examples. On the other hand, each methylene- $[n]$ -triangulane can really produce (vide infra) exactly two methylene- $[n + 1]$ -triangulane stereoisomers; for instance, methylene- $[5]$ -triangulanes **6a,b**; **6c,d**; **6e,h** can be obtained from the stereoisomeric methylene- $[4]$ -triangulanes **7a**, **7b**, **7c**, and **7d**, respectively. The reaction of each methylene- $[n]$ -UT with methylene leads finally to a single $[n + 1]$ -UT structure: **6h** \rightarrow **8a**, **6b** \rightarrow **8b**, **6c** \rightarrow **8c**, **6d** \rightarrow **8e**, **6e** \rightarrow **8b**, **6f** \rightarrow **8d**, **6g** \rightarrow **8e**, and **6h** \rightarrow **8f** (note that two different methylene- $[5]$ -UTs can produce however just the same $[6]$ -triangulane stereoisomer).

The careful analysis of interrelations between UTs and their methylene derivatives needs the spatial graphs for the latter to be constructed. The unique characterization of methylene-UT stereoisomers may be achieved by means of *labeled* spatial graphs which are similar to those of the triangulanes but contain an additional $(n + 1)$ th labeled node corresponding to the methylene group. The differences between labeled and unlabeled spatial graphs are exemplified by graphs **9a,b** (relating to $[4]$ -triangulanes **10a,b**) and **9c,d** (relating to methylene $[3]$ -triangulanes **10c,d**).



It should be noted that the nodes of methylene- $[n]$ -UT spatial graphs *cannot be renumbered*. For that reason the codes of corresponding chain configurations are nonequivalent to their "right-to-left" counterparts; this is marked by an asterisk after the last component of codes in **9c,d** (see also methylenetriangulane codes **6**, **7**, **10c,d**).



It is easy to see that all labeled graphs similar to those of **9c,d** are chiral; this means that all methylene- $[n]$ -UTs (except the simplest "no code" methylenespiropentane) are also chiral and form enantiomeric pairs (**10c,d**; **7a,d**; **7b,c**; **6a,h**; **6b,g**; **6c,f**; and **6d,e**). This fact makes it possible to easily find the relations between the values of N_1' (total number of methylene-UTs), N_2' (number of racemic pairs plus achiral structures), N_3' (number of racemic pairs), and N_4' (number of achiral structures). Obviously $N_1' = 2N_2'$; $N_2 = N_3'$; and $N_4 = 0$. The calculation of N_1' and N_2 may also be performed by using Burnside's Lemma;²⁴ the results obtained do not depend on the parity of n : $N_1' = 2^{n-2}$; $N_2 = N_3' = 2^{n-3}$.

(23) Chloromethyl-substituted triangulanes **12** have an additional stereogenic center which complicates the configurational relationships; this center disappears however after dehydrochlorination.

(24) The formal proof is as follows. For methylene- $[n]$ -triangulanes the set Φ consists of 2^{n-2} mappings, $G' = \{g_0\}$, $H' = \{h_0, h_1\}$, $\Gamma_1' = \{\gamma_0'\} = \{(g_0, h_0)\}$, and $\Gamma_2' = \{\gamma_0', \gamma_1'\} = \{(g_0, h_0), (g_0, h_1)\}$. The application of Burnside's Lemma produces $\chi(\gamma_0') = 2^{n-2}$, $\chi(\gamma_1') = 0$, and $N_1' = \chi(\gamma_0')/1 = 2^{n-2}$, $N_2' = (\chi(\gamma_0') + \chi(\gamma_1'))/2 = 2^{n-3}$.

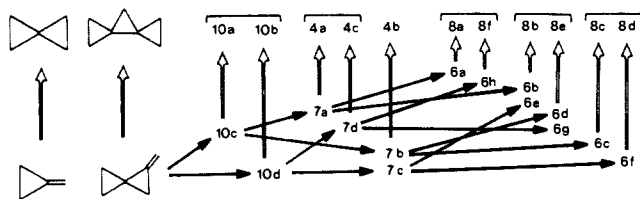


Figure 1. Triangulane generation tree.

The above consideration permits the formulation of four simple rules for the construction of generation trees: (1) each methylene- $[n]$ -UT configurational code may be transformed into the methylene- $[n + 1]$ -UT configurational code by inserting of $+1$ or -1 between the last component and asterisk, (2) each methylene- $[n]$ -UT configurational code may be transformed to the corresponding $[n + 1]$ -UT code by erasing the asterisk, (3) two codes of $[n]$ -UTs relate to the same stereoisomer if one of them is a "right-to-left" counterpart of another code, and (4) all components of the configurational codes of enantiomeric triangulanes differ by their signs; if the change of sign in all components leads to the "right-to-left" counterpart of the code, then the corresponding triangulane molecule is achiral and belongs to C_s point symmetry group. Note that chiral UTs can belong either to C_2 or to C_1 point groups; in the former case configurational codes are always symmetrical, while in the second case they are completely unsymmetrical.²⁵

The application of the above rules (with subsequent reconstruction of perspective formulas via intermediate spatial graphs) allows the creation of the generation trees for UTs with an arbitrary number of cyclopropane units; Figure 1 depicts such a tree for $[2]$ - $[6]$ -triangulanes.²⁶ Two modes of molecular transformations involved are indicated by different arrows.

Synthesis of Unbranched $[5]$ - and $[6]$ -Triangulanes. The $[1 + 2]$ -cycloaddition reaction is the best method for the construction of three-membered ring systems due to its universality and the existence of a variety of good procedures. In particular, methylenecyclopropane and its derivatives easily undergo $[1 + 2]$ -cycloadditions to give the spiropentane structural block.^{6,7c,d,8,27-29} Taking this into account, methylene- $[n]$ -triangulanes with an exo double bond attached to a terminal three-membered ring may be employed as suitable starting materials for the synthesis of $[n + 1]$ -unbranched triangulanes.

The more important problem in the elaboration of the general synthetic method for UTs consists in the development of a standard *repetitive* reaction sequence to convert methylene- $[n]$ -triangulane into the next member of the family, methylene- $[n + 1]$ -triangulane. The $[1 + 2]$ -cycloaddition of vinylidene could be a direct solution of the problem; however, a good preparative method of vinylidene cycloaddition is still unknown and hence one needs to consider the application of vinylidene synthons.

(25) The symmetry elements I , C_2 , and σ evidently relate to permutations $\gamma_0 = (g_0, h_0)$, $\gamma_1 = (g_1, h_0)$ and $\gamma_2 = (g_1, h_1)$ respectively. For this reason the point symmetry group of triangulane molecule may be characterized by a certain subgroup of Γ which consists of permutations converting a given mapping φ into itself. This group is known as the *automorphism group*, $\text{Aut}(\varphi)$. Thus, $\text{Aut}(\varphi) = \{\gamma_0\}$ for completely unsymmetrical UTs, $\text{Aut}(\varphi) = \{\gamma_0, \gamma_1\}$ for chiral UTs with C_2 point group and $\text{Aut}(\varphi) = \{\gamma_0, \gamma_2\}$ for achiral UTs with C_s point group. The first two automorphism groups may be represented as power groups (E^E and E^C , respectively). Configurational codes make it possible to count the numbers of triangulane stereoisomers with the fixed point symmetry group. An application of Burnside's Lemma, or Polya's Theorem, or even simple combinatorial considerations allows additionally to enumerate the corresponding substituted derivatives of UTs. For example, the number of symmetrical codes corresponding to chiral C_2 $[n]$ -triangulanes is equal to $2^{(n-2)/2}$ for even values and to $2^{(n-3)/2}$ for odd values of n . For this reason the total number of corresponding monosubstituted derivatives is equal to $(n+2) \cdot 2^{(n-2)/2}$ for even n and to $(n+2) \cdot 2^{(n-3)/2}$ for odd n ; all these monosubstituted UTs are chiral and forms enantiomeric pairs.

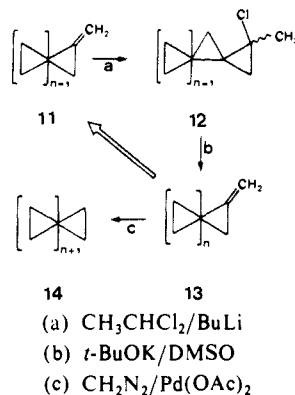
(26) Note that "generation trees" similar to that of Figure 1 do contain cycles if the arrows are changed for indirect lines. For this reason such trees may be more accurately defined as the directed graphs containing no oriented cycles.

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A promising pathway consists of the [1 + 2]-cycloaddition of chloromethylcarbene, generated from 1,1-dichloroethane, to methylene- $[n]$ -triangulane with subsequent dehydrochlorination, leading to methylene- $[n + 1]$ -triangulane. The "termination" of this sequence includes the cyclopropanation of each of the higher methylenetriangulanes. The general scheme of the method is represented by the transformations $11 \rightarrow 12 \rightarrow 13 \rightarrow 14$.



Scarce literature data seem to support this scheme: all of the steps, $11 \rightarrow 12$,^{8,27,28} $12 \rightarrow 13$,^{7c,8,28,30} and $13 \rightarrow 14$,^{7c,29} were exemplified for methylenecyclopropane derivatives. Moreover, we have shown recently, that methylene-[3]-triangulane racemate, **10c,d**, is (i) available in a gram scale and (ii) can be easily methylated to give [4]-triangulane.^{7c}

We have found that the reaction of **10c,d** with 1,1-dichloroethane in the presence of *n*-butyllithium gave a mixture of four diastereomeric chlorides **12** ($n = 3$). The dehydrochlorination of this mixture with *t*-BuOK in DMSO gave the mixture of methylene-[4]-triangulanes, **7a,d** and **7b,c**. Subsequent cyclopropanation with CH_2N_2 in the presence of $\text{Pd}(\text{OAc})_2$ ^{7c,29} produced the desired [5]-triangulanes as a mixture of two diastereomers **4a,c** and **4b** in the ratio of 3.7:1. The total yield of [5]-triangulanes based on **10c,d** was 58%.

The identification of diastereomeric **4** in the mixture was made on the basis of ¹H NMR spectra. The racemic diastereomer **4a,c** has a C_2 -group symmetry axis (vide supra) and hence the protons of the central CH_2 group appear as a singlet, while the protons of the two equivalent neighbouring CH_2 -groups show an AB-system. On the contrary, the diastereomer **4b** possesses a symmetry plane and the CH_2 -protons of all three internal cyclopropane rings appear as AB-systems.

If the above mixture **7a,d** + **7b,c** (ratio of 3.8:1) undergoes the same sequential treatment, the mixture (3:2) of two of the three possible diastereomers of [6]-triangulanes **8** were obtained with a total yield of 46%. These isomers were separated with preparative GLC, and their ¹H NMR spectra permitted the assignment of their configuration. The spectrum of a minor compound shows four AB systems of four internal CH_2 -groups and, hence, this is the unsymmetrical diastereomer **8b,e**, which has no C_2 axis. The major diastereomer shows two AB-systems for the internal CH_2 -groups and, hence, must have a C_2 axis. Thus, this compound could be either the **8a,f** or the **8c,d** diastereomer. The comparison of the ratio of [6]-triangulanes obtained with the isomeric ratio of the starting methylene-[4]-triangulanes together with the generation tree (Figure 1) leads to the conclusion that this isomer is **8a,f**.

The fact that diastereomer **8c,d** was absent in the reaction mixture can be easily explained from steric reasons. An examination of structures of **7b,c** shows the chloromethylcarbene attack (with subsequent dehydrochlorination) leading to methylene-[5]-triangulanes **6c,f** to be disfavored, owing to steric hindrances. Analogous speculation may be evidently applied in the case of higher triangulanes.

In conclusion, it is worthwhile to note that the suggested method of synthesis can be easily extended for the higher members of the

UTs family³¹ and consideration of stereochemical relationships (similar to those of Figure 1) could serve as a guide line for the experimental studies.

Experimental Section

General. ¹H NMR spectra were obtained on Tesla BS-467, Bruker WM-250, and Varian XL-400 instruments for solutions in CDCl_3 . ¹³C NMR spectra were measured by using a Bruker WM-250 instrument also for solutions in CDCl_3 . GLC analyses and separations were performed with use of silicone SE-30 or OV-225, 5% on Chromatrone N-AW-DMCS. All solvents and reagents were purified and dried by standard techniques. Extracts were dried over MgSO_4 . Methylene-[3]-triangulane, **10c,d**, was prepared by using the literature procedure^{7c} with a 75% yield, bp 45 °C (45 mm).

General Procedures for the Preparation of 1-Chloro-1-methyltriangulanes. To a well stirred solution of methylenetriangulane (75 mmol) and 1,1-dichloroethane (225 mmol) in Et_2O (25 mL) was added 1.6 M of BuLi (150 mmol) in pentane at -30 to -35 °C for 2 h. After stirring for 30 min the solution was allowed to warm to room temperature and quenched with water. The organic layer was dried, carefully concentrated, and distilled in vacuo.

1-Chloro-1-methyl-[4]-triangulanes (12**, $n = 3$).** From 3.18 g (30 mmol) of **10c,d**^{7c} 4.3 g (85%) of mixture of stereoisomeric (27:9:50:14) **12** ($n = 3$) was obtained: bp 60 °C (10 mm); n_D^{20} 1.4870; ¹H NMR δ 0.5–1.37 (10 H, m), 1.43, 1.5, 1.53, 1.63 (3 H, s). Calcd. for $\text{C}_{10}\text{H}_{13}\text{Cl}$: C, 71.22; H, 7.72; Cl, 21.07. Found: C, 68.88; H, 8.02; Cl, 20.71.

1-Chloro-1-methyl-[5]-triangulanes (12**, $n = 4$).** From 2.64 g (20 mmol) of **7** (**a,d** + **b,c**, vide infra) 2.33 g (60%) of a mixture of isomeric chlorides **12** ($n = 4$) was obtained: bp 85–86 °C (6 mm); n_D^{20} 1.5010; ¹H NMR δ 0.4–0.83 (4 H, m), 0.83–1.33 (8 H, m), 1.43, 1.53, 1.6, 1.65 (3 H, s). Calcd. for $\text{C}_{12}\text{H}_{15}\text{Cl}$: C, 74.04; H, 7.71. Found: C, 73.88; H, 8.01.

General Procedure for the Preparation of 1-Methylenetriangulanes. 1-Chloro-1-methyltriangulanes (45 mmol) was added to the stirred mixture of *t*-BuOK (70 mmol) in dry DMSO (60 mL) at 60–70 °C over an argon atmosphere. After the mixture was stirred for 20 min the workup included extraction of the cooled reaction mixture with pentane. The extract was washed with water, dried, carefully concentrated, and distilled in vacuo.

1-Methyl-[4]-triangulanes (7a,d** and **7b,c**).** From 3.37 g (20 mmol) of chloromethyl-[4]-triangulane mixture (**12**, $n = 3$), 1.98 g (75%) of the mixture of **7a,d** and **7b,c** (3.8:1) was obtained: bp 56–58 °C (23 mm); n_D^{20} 1.5010. **7a,d**: ¹H NMR δ 0.7–0.95 (m, 4 H), 1.13 (d, $J = 3.9$ Hz, 1 H), 1.27 (d, $J = 3.9$ Hz, 1 H), 1.3–1.35 (dm, $J = 8$ Hz, 1 H), 1.44 (d, $J = 3.7$ Hz, 1 H), 1.45–1.50 (dm, $J = 8$ and 2.3 Hz, 1 H), 1.52 (d, $J = 3.7$ Hz, 1 H), 5.24 (td, $J = 2.3$ and 0.9 Hz, 1 H), 5.31 (m, 1 H); ¹³C-¹H NMR δ 4.09 (t, $J = 162$ Hz), 4.81 (t, $J = 162.1$ Hz), 5.63 (s), 8.43 (t, $J = 163.5$ Hz), 12.4 (t, $J = 166.5$ Hz), 14.46 (s), 16.06 (t, $J = 162$ Hz), 17.01 (s), 99.15 (t, $J = 161.2$ Hz), 135.83 (s). **7b,c**: ¹H NMR δ 0.7–0.9 (m, 4 H), 1.07 (d, $J = 6$ Hz, 1 H), 1.21 (d, $J = 4$ Hz, 1 H), 1.34 (d, $J = 6$ Hz, 1 H), 1.34–1.43 (m, 2 H), 1.63 (d, $J = 4$ Hz, 1 H), 5.08 (td, $J = 2.3$ and 0.8 Hz), 5.31 (m, 1 H). ¹³C NMR δ 5.36, 10.08, 12.16, 14.46, 16.0, 99.65 (CH_2), 10.58, 15.07, 17.20, 135.90 (C). Calcd. for $\text{C}_{10}\text{H}_{12}$: C, 90.91; H, 9.09. Found: C, 90.59; H, 9.47.

1-Methylene-[5]-triangulanes (6**).** From 1.95 g (20 mmol) of a chloromethyl-[5]-triangulane mixture (**12**, $n = 4$), 1.29 g (82%) of a mixture of **6** (46:39:8:7) was obtained: bp 85 °C (18 mm); n_D^{20} 1.5122. **6**: ¹H NMR δ 0.5–0.95 (m, 4 H), 1–1.5 (m, 8 H), 5.12 (td, $J = 0.85$ and 2.4), 5.16 (td, $J = 0.9$ and 2.4 Hz), 5.19 (td, $J = 0.9$ and 2.4 Hz), 5.21 (td, $J = 0.9$ and 2.4 Hz) (overall 1 H), 5.29 (m), 5.31 (m), 5.24, 5.26 (m) (overall 1 H). Calcd. for $\text{C}_{12}\text{H}_{14}$: C, 91.14; H, 8.86. Found: C, 90.89; H, 8.58.

General Procedure for the Preparation of Triangulanes. To the mixture of 1-methylenetriangulane (5 mmol) and palladium diacetate (50 mg) in Et_2O (10 mL) was added the ethereal solution of diazomethane (from 15 g of nitrosomethylurea) during 20 min at -4 °C. After 15 min the mixture was allowed to warm up to room temperature, filtered

(31) There are several problems of particular interest which crucially depend on real syntheses of UTs. For instance, the heats of formation for the first members of triangulane family seem to indicate a progressive extra destabilization with an increment of 8–10 kcal/mol for every spirocenter.^{2b} This is to be verified for the higher members of the UT family. As a matter of fact, we have found that experimental ΔH_f° (g) for [3]- and [4]-UTs are 72.9 and 102.09 kcal/mol (unpublished data). MMX88 calculations of ΔH_f° gave the following results: 76.005 ([3]-UT), 107.970 ([4]-UT), 139.855 (**4b**), 139.922 (**4a,c**), 171.870 (**8a,f**), 171.755 (**8b,e**), 172.124 (**8c,d**). Thus, the thermodynamic driving force is apparently strong for UTs thermal reorganization. However, the remarkable observation in our experiments was their relative thermal stability at least at the temperatures required for distillation in vacuo and GLC separations.

through silica gel layer, carefully concentrated, and distilled in vacuo.

[5]-Triangulanes (**4a,c** and **4b**). From 1.32 g (10 mmol) of a methylene-[4]-triangulane mixture **7**, 1.33 g (91%) of a mixture of **4a,c** and **4b** (3.7:1) was obtained: bp 70 °C (2 mm); n_D^{25} 1.4925; d_4^{20} 0.916. **4a,c**: $^1\text{H NMR}$ δ 0.62–0.86 (m, 8 H), 1.30 (s, 2 H), 1.45–1.60 (AB system $\delta_A = 1.47$, $\delta_B = 1.57$, $J = 3.9$ Hz); $^{13}\text{C NMR}$, δ 4.30, 4.74, 10.95, 11.23 (CH₂), 13.81, 18.71 (C). **4b**: $^1\text{H NMR}$ δ 0.54–0.77 (m, 8 H), 1.12 (d, $J = 4.3$ Hz, 1 H), 1.13 (d, $J = 3.7$ Hz, 2 H), 1.21 (d, $J = 3.7$ Hz, 2 H), 1.24 (d, $J = 4.3$ Hz, 1 H); $^{13}\text{C NMR}$ δ 5.06, 7.13, 11.39, 12.90 (CH₂), 14.12, 19.50 (C). Calcd. for C₁₁H₁₄: C, 90.41; H, 9.59. Found: C, 89.99; H, 9.99.

[6]-Triangulanes (**8a,f** and **8b,e**). From 0.79 g (5 mmol) of a methy-

lene-[5]-triangulane mixture **6**, 0.8 g (93%) of a mixture of **8** (3:2) was obtained bp 85 °C (2 mm); n_D^{21} 1.5079. Compounds **8a,f** and **8b,e** were separated by GLC. **8a,f**: $^1\text{H NMR}$ δ 0.68–0.9 (m, 8 H), 0.95 (d, $J = 3.9$ Hz, 2 H), 1.16 (d, $J = 3.8$ Hz, 2H), 1.17 (d, $J = 3.9$ Hz, 2H), 1.19 (d, $J = 3.8$ Hz, 2 H); $^{13}\text{C-}^1\text{H NMR}$ δ 4.43 (t, $J = 161.6$ Hz), 4.85 (t, $J = 161.4$ Hz), 5.61 (s), 10.13 (t, $J = 160.1$ Hz), 11.24 (t, $J = 160.2$ Hz), 13.67 (s), 18.13 (s), 18.83 (s). **8b,e**: $^1\text{H NMR}$ δ 0.63–0.94 (m, 8 H), 0.98 (d, $J = 3.7$ Hz, 1 H), 1.01 (d, $J = 3.7$ Hz, 1 H), 1.07 (d, $J = 3.9$ Hz, 1 H), 1.12 (d, $J = 3.7$ Hz, 1 H), 1.16 (d, $J = 2.3$ Hz, 1 H), 1.18 (d, $J = 2.3$ Hz, 1 H), 1.24 (d, $J = 3.7$ Hz, 1 H), 1.29 (d, $J = 3.7$ Hz, 1 H); $^{13}\text{C NMR}$ δ 4.44, 4.85, 5.20, 7.21, 10.21, 11.93, 12.89, 13.03 (CH₂), 12.21, 13.91, 14.29, 19.96, 20.55 (C).

Fluorinated Macrocyclic Ethers as Fluoride Ion Hosts. Novel Structures and Dynamic Properties¹

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Abstract: The reaction of tris(dimethylamino)sulfonium trimethyldifluorosilicate with fluorinated macrocyclic ether **3** provides a novel fluoride ion nesting complex **4**. X-ray crystal structure analysis shows that the central fluoride is held within the chiral cavity (C₂ symmetry) by interaction with four CH₂ groups. The nearest tris(dimethylamino)sulfonium (TAS) cation serves as a lid for the complex anion. The 18-membered ring undergoes substantial conformational change to accommodate the fluoride ion guest. NMR spectra show that the central fluoride is tightly bound. Multiple pathways for enantiomerization are found, and the preferred pathway depends upon the temperature. Measured rate constants for the pair-wise exchange of diastereotopic nuclei (–95 °C to –70 °C) give activation parameters for one "normal" enantiomerization process: $\Delta G^\ddagger = 9.8$ kcal/mol, $\Delta H^\ddagger = 9.1$ kcal/mol, $\Delta S^\ddagger = -3.7$ eu. At lower temperatures, anti-Arrhenius behavior is observed for another conformational process in which the rate of exchange of geminally coupled nuclei increases as the temperature decreases. Ab initio calculations on a model of the anion complex indicate a minimum-energy geometry similar to that observed in the crystal structure of the salt.

Introduction

Noncovalent or supramolecular chemistry is an exceptionally active area of research.^{2–5} Despite this activity, synthetic anion-binding substances are rather rare,^{6–9} and studies of cooperative

binding behavior involving highly fluorinated hosts have not been reported. Whereas a variety of fluorinated, anionic complexes which might be considered in host/guest terms have been reported,^{10–14} these complexes involve predominantly covalent in-

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