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Transmission of Internal Rotations: Correlated, Uncorrelated, and Localized Disrotatory Rotations in Propeller Chains

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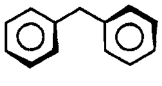
The stereochemistry of the propeller chain systems **5** and **6** is analyzed. These systems possessing two or three partially overlapping diarylmethyl moieties, respectively, exist in several conformations arising from the different possible helicities and chain arrangements. System **5** was prepared by acid-catalyzed reaction of pentamethylbenzyl acetate with durene. The ^1H NMR spectrum of **5** indicates, even at 150 K, that there is a rapid rotation of the rings on the NMR time scale. The relative energies of the conformations and the barriers for the internal rotation of the systems were calculated using molecular mechanics, and the results were compared with the parent system decamethyldiphenylmethane (**4**). The rotational mechanism of lowest activational energy of **5** and **6** is a localized disrotation in which only two neighboring rings in the chain rotate in unison. This results in a helicity reversal of the two rings and a change in the conformation of the chain. Enantiomerization of any conformation of **6** is achieved by at least three successive localized disrotatory rotations. The calculations show that the longer the propeller chain, the larger the energy barrier for a correlated rotation pathway involving all rings and this results in a smaller energetic preference of the correlated over uncorrelated (180°) rotations. This poses a limitation on the transmission of internal rotation of coupled rotors along a chain. Only systems with tightly meshed rotors and with a large energy gap between correlated and uncorrelated rotations may have efficient transmission of correlated rotations.

Introduction

Diarylmethyl (**1**) and triarylmethyl (**2**) systems can exist in a conformation in which all the rings have an identical sense of twist with regard to an arbitrary reference plane and therefore are dubbed “molecular propellers”.[1] The propeller conformation is chiral and if all the rings are identical and possess local C_2 axes, the systems exist in two enantiomeric arrangements. These arrangements can be viewed as differing in the sense of twist of the rings (the “helicity”).



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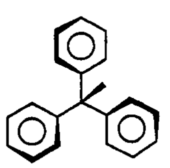

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An outstanding property of these molecular propellers is that they can display correlated rotations of the rings, in which all the rings rotate in unison along the Ar–C axes.[1-4] Correlated rotation in molecular propellers is usually analyzed in terms of “flip” mechanisms.[2,5] A “flip” is defined as the rotation of a ring through the normal to an arbitrary defined reference plane (for **1** this plane is defined by the central methylene and the two ipso aromatic carbons, for **2** this plane is defined by the three ipso aromatic carbons) while the nonflipping rings rotate through the reference plane. Another rotational pathway possible for the systems is a 180° rotation of one or more rings. In contrast to the flip mechanisms which necessarily involve all rings, the 180° mechanism does not require correlated rotation: a single ring can rotate by 180° while the remaining rings remain unchanged. All the 180° pathways result in retention of the starting helicity.[2] For molecular propellers, the rotational mechanism of the lowest activational energy (threshold mechanism) involves helicity reversal by correlated rotation of the rings.[1] Correlated rotation resembles, at a molecular level, the coupling of rotations in moving parts of mechanical devices (such as the present in cogwheels) and therefore it may be of importance in the future design of nanoscale molecular machinery.[3] Systems composed of three serially meshed triptycyl systems were studied by Iwamura and co-workers.[6,7] It has been shown experimentally in these systems that the tight intermeshing of the three triptycyl rotors results in their correlated rotation.[6] In principle, macromolecular chains properly substituted by rotors may undergo correlated rotation so that there may be a transfer of information from one end of the molecule to the other.[3,8] To the best of our knowledge, the correlated rotation in molecular chains composed of coupled propeller units have never been investigated. We therefore decided to study computationally the “propeller chains” derivatives of system **1**. These propeller chains represented by **3** are composed of *n* rings ($n > 2$) pairwise linked by ($n - 1$)

[•] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

[1] For reviews on the static and dynamic stereochemistry of molecular propellers see: Mislow, K.; Gust, D.; Finnocchiaro, P.; Boettcher, R. J. *Fortschr. Chem. Forsch.* 1974, *47*, 1. Mislow, K. *Acc. Chem. Res.* 1976, *9*, 26. Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* 1985, *127*, 1. Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. *Advances in Dynamic Stereochemistry*; Gielen, M., Ed.; Academic Press: New York, 1985; Vol. 1, p 207.

(2) Gust, D.; Mislow, K. *J. Am. Chem. Soc.* 1973, *95*, 1535.

(3) Mislow, K. *Chemtracts, Org. Chem.* 1989, *2*, 151.

(4) For recent examples of studies of correlated rotation in molecular propellers see: Howell, J. A. S.; Palin, M. G., Yates, P. C.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D. *J. Chem. Soc. Perkin Trans. 2* 1992, 1769. Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* 1992, *44*, 6669.

(5) Kurland, R. J.; Schuster, I. I., Colter, A. K. *J. Am. Chem. Soc.* 1965, *87*, 2279.

(6) Koga, N.; Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* 1983, *105*, 5498. Koga, N.; Kawada, Y.; Iwamura, H. *Tetrahedron* 1986, *42*, 1679.

(7) For a review on the dynamic stereochemistry of di- and tritriptycyl systems see: Iwamura, H.; Mislow, K. *Acc. Chem. Res.* 1988, *21*, 175.

(8) Iwamura, H. *J. Mol. Struct.* 1985, *126*, 401.

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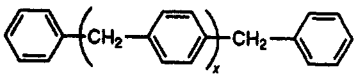

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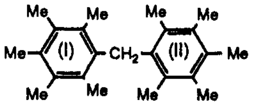
methyleneunits and may be considered as being formed by several partially overlapping (i.e., sharing a common ring) diaryl propeller subunits. These systems are therefore ideally suitable for the study of the feasibility of the coupling of correlated rotations of the rings along the chain. The goal of the present work was to answer computationally to the question whether indeed in the lowest energy rotational pathway of the systems there is a transmission of the rotation from end to end by correlated rotation of all rings.

Results and Discussion

Structural Considerations in Choosing the Systems. The parent compound diphenylmethane exists in the crystal in a propeller conformation of approximate C_2 symmetry.[9] However, according to molecular mechanics and semiempirical calculations, the propeller and a nonpropeller conformation ("gable") of C_{2v} symmetry (i.e., with both rings perpendicular to the reference plane) are of similar energies.[9] These results influenced our decision to study systems polysubstituted by methyl groups. The methyl substituents in the propeller are expected to deepen the torsional energy minimum and to increase the energy gap between propeller and nonpropeller conformations. As the subjects for the present study we chose the systems 4–6.[10,11] All compounds are hydrocarbons and therefore their conformation and rotational barriers can be reliably calculated by molecular mechanics. A comparison of the dynamic behavior of 4–6 may shed light on the effect of the increase in chain length on the transmission of the correlated rotation.



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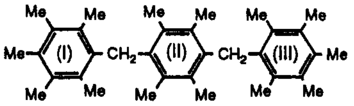

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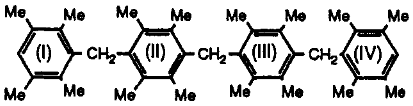

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Figure 1. Arbitrary convention for describing the (+) and (–) helicity of a diarylmethyl moiety. The methylene and the two ipso carbons attached to it are located in the plane of the paper.

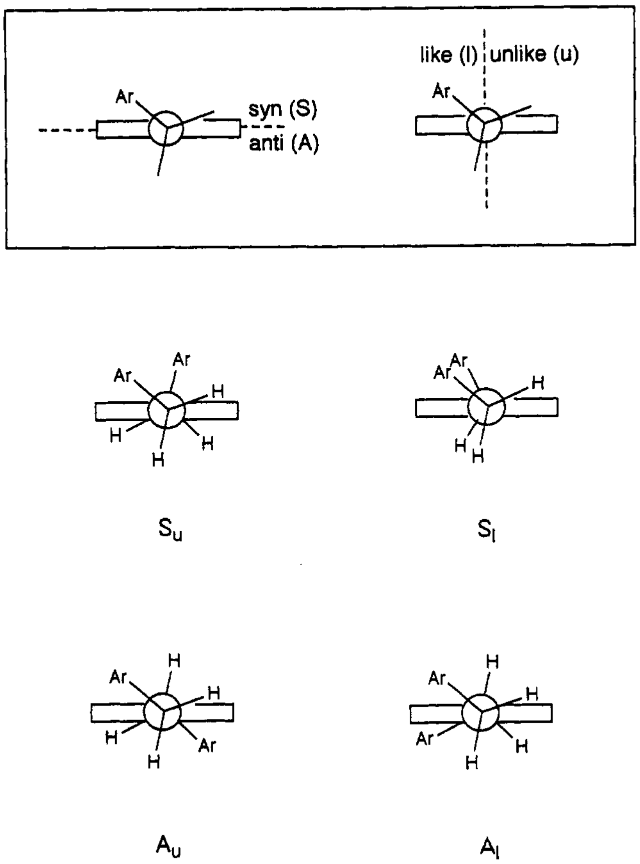

Figure 2. Top: The stereochemical convention for the description of the relative orientation of two Ar–CH$_2$ bonds attached to a given internal ring. The molecule is viewed along the CH$_2$–C$_6$R$_4$–CH$_2$ axis of a given internal ring. The plane of the internal ring (drawn horizontally) divides the space into two sectors. If the two Ar–CH$_2$ units are in the same subsectors, the conformation is called syn (S), otherwise it is called anti (A). A plane perpendicular to the reference plane further divides the space into two sections. If the groups are located in the same subsection, they are denoted "like" (l) and "unlike" (u). The conformation of the molecule is described by a combination of both descriptors. Bottom: examples of the S$_u$, S$_l$, A$_u$ and A$_l$ conformations.

Stereochemical Description of the Conformations. Compound 4 should exist in two helical conformations. We will describe the two possible helicities of a given diaryl moiety as "(+)" and "(–)" using the arbitrary convention shown in Figure 1. In the case of the propeller chain possessing n rings, $n - 1$ reference planes can be defined by each of the methylene carbons and the two ipso carbons attached to them. The helicity description of each diarylmethyl moiety can be given using the convention of Figure 1. For systems 5 and 6, the descriptors of the helicities of the diarylmethyl units take the form (+/–, +/–) and (+/–, +/–, +/–), respectively, in which the first descriptor describes the helicity of the diarylmethyl unit formed by rings I and II (cf. 5 and 6), the second by rings II and III and the third by rings III and IV. However, in contrast to 4 whose stereochemistry is dictated only by the twist angle of the rings, the stereochemistry of 5 and 6 is also a function of the arrangement of the main chain, i.e., the dihedral angle of the two Ar–CH$_2$ bonds attached to a given internal ring. For nomenclature purposes and in order to describe unambiguously each of the conformations possible, we will define two planes: the plane of an internal ring and a plane perpendicular to it. This divides the space around the internal rings into four quadrants (Figure 2). The relative orientations of the two rings attached to a given internal ring will be given using the following nomenclature: (i) If the two CH$_2$–Ar bonds

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[9] Barnes, J. C.; Paton, J. D.; Damewood, J. R., Jr.; Mislow, K. *J. Org. Chem.* **1981**, *46*, 4975.

[10] System 6 is not substituted at the para positions of the terminal rings in order to remain within the atom limit (100 atoms) of the BIGSTRN-3 program.

[11] The stereochemistry of systems possessing three and four benzene rings joined by vinyl groups (such as a (Z,Z,Z)-4,4′-bis(styryl)stilbene derivative) has been recently studied: Håkansson, M.; Jagner, S.; Sundahl, M.; Wennerström, O. *Acta Chem. Scand.* **1992**, *46*, 1160.

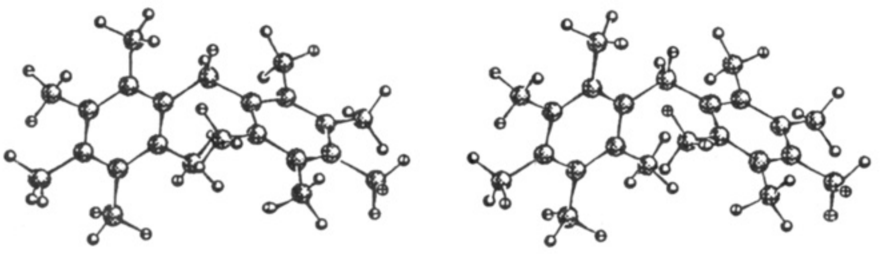


Figure 3. Stereoscopic view of the calculated conformation of 4.

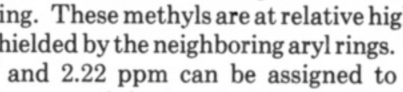
are located on the same or opposite faces of a given internal ring, these orientations will be called syn (S) and anti (A), respectively. (ii) If the CH$_2$–Ar bonds are on the same or opposite sides of the perpendicular plane, their orientation will be described as like (l) or unlike (u), respectively (Figure 2).[12] This nomenclature is useful for the description of conformations in which each diphenylmethyl unit exists in a propeller conformation. Note that in a propeller conformation the two Ar–CH$_2$ bonds attached to a given internal ring cannot be coplanar or perpendicular to the internal ring plane since this will represent torsion angles of 0° and 90°, i.e., nonpropeller conformations. Two ArCH$_2$ units in an "anti" and "unlike" relationship will be described by A$_u$. The complete conformational description therefore includes the chain arrangement (e.g., A$_u$) and the helicities of the two propeller subunits. Since either of the two terminal rings can be chosen as ring I, there may be two different descriptors for the same conformation (e.g., A$_u$(+,–) and A$_u$(–,+)). The nomenclature is demonstrated in Figure 2.

Molecular Mechanics Calculations. For the calculations we used the MM2 force field as implemented in the program BIGSTRN-3.[13] Input geometries having different combinations of coplanar, perpendicular, and twisted conformations of the rings with regards to the reference planes were based on standard bond lengths and angles. Geometry optimizations were concluded with the full matrix Newton Raphson method. The final convergence criteria for the Newton Raphson stage: root mean square gradient less than 10^{-6} kcal mol^{-1} and root mean square atom movement less than 10^{-6} Å.

Preparation of 5. Compound 4 has been described in the literature[14] and its chemistry upon dissolution in trifluoroacetic acid has been the subject of some controversy,[15] while compounds 5 and 6 are unknown. For the synthesis of 5 we reacted pentamethylbenzyl acetate (prepared by Pb(OAc)$_4$ oxidation of hexamethylbenzene)[16] with durene in the presence of triflic acid.[17] The double benzylation of durene proceeded smoothly and 5 was isolated in 57% yield.

Provided that 5 exists in a preferred propeller conformation in solution, as suggested by the molecular mechanics calculations (see below), the two protons of a given methylene group should be diastereotopic. Compound 5 displays in the ^{1}H NMR spectrum (CDCl$_3$, 400 MHz) four singlets at δ 1.99, 2.01, 2.17, and 2.22 ppm (in a 2:2:2:1 ratio) for the methyl groups and a singlet for the methylene protons. We assign the peaks at δ 1.99 and 2.01 ppm to the *o*-methyls of the terminal rings and the methyls of the internal ring. These methyls are at relative high field since they are shielded by the neighboring aryl rings. The signals at δ 2.17 and 2.22 ppm can be assigned to the *m* and *p*-methyl groups of the terminal rings. The equivalence of pairs of methyl groups in ortho and meta positions and the appearance of the methylene protons as a singlet indicates that, precluding accidental isochrony, fast aryl rotation occurs on the NMR time scale. Cooling a solution of 5 in CDCl$_2$F[18] down to 150 K resulted in an appreciable broadening of the methylene signals, but no decoalescence could be observed. Assuming that under slow exchange conditions the chemical shift difference between the two protons is less than 20 Hz and that the coalescence temperature is equal or lower than 150 K, a higher limit of 7.4 kcal mol^{-1} can be calculated for the rotational barrier of the system.

Static Stereochemistry of 4. We performed first molecular mechanics calculations on the parent molecule 4. According to the calculations, 4 exists in a propeller conformation of C_2 symmetry, in which both rings are twisted by 46° and all methyl hydrogens are arranged in an alternant "up-down" conformation (7).[19] A stereoscopic view of the calculated conformation of 4 is shown in Figure 3. The "gable" conformation in which both rings are perpendicular to the reference plane is a maximum energy form lying 27.6 kcal mol^{-1} above the propeller conformation. The substantial increase in steric energy of the gable form is probably due to the repulsion between pairs of *o*-methyl groups above and below the reference plane.



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Static Stereochemistry of 5. System 5 can be thought as formed by two diarylmethyl moieties (defined by the ring pairs I, II and II, III) sharing a common ring (the

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[12] The dihedral angle between the two Ar–CH$_2$ bonds attached to an internal ring can be in principle specified by the descriptors sp, ap, sc, and ac (Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 251). However, in order to describe the conformation in our system it is necessary to specify the relative orientation of the internal ring. We therefore use a nomenclature which borrows freely the descriptors "like" and "unlike" proposed by Prelog and Helmchen for the description of stereochemical pairs (Prelog, V.; Helmchen, G. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 567).

[13] Nachbar, R. B., Jr.; Mislow, K. QCPE No. 514. Nachbar, R. B., Jr.; Mislow, K. *QCPE Bull.* **1986**, *6*, 96.

[14] Welch, C. M.; Smith, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 4392.

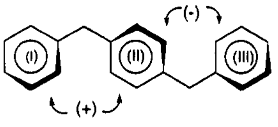
[15] Sankararaman, S.; Lau, W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1991**, 396. Eberson, L.; Radner, F. *Acta Chem. Scand.* **1992**, *46*, 630.

[16] Magnusson, C.; Olofson, B.; Nyberg, K. *Chem. Scr.* **1971**, *1*, 57.

[17] It has been shown by Nyberg that alkyl-substituted benzenes can undergo CF$_3$SO$_3$H-catalyzed Friedel–Crafts reaction with pentamethylbenzyl acetate: Nyberg, K. *Chem. Scr.* **1973**, *4*, 143.

[18] Siegel, J.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

[19] Molecular mechanics calculations (Iroff, L. D. *J. Comput. Chem.* **1980**, *1*, 76) indicate that in hexamethylbenzene the conformation with alternant "up-down" arrangements of the methyl hydrogens (of D_{3d} symmetry) is favored over the conformation with eclipsed methyl groups arranged in an homodirectional[21] fashion. For a review on the conformation of alkyl groups see: Berg, U.; Sandstrom, J. *Adv. Phys. Org. Chem.* **1989**, *25*, 1.



A_u (+,-)

Figure 4. The A_u(+,–) conformation of **5**. Note that when viewed from the right reference plane the internal ring has a (+) sense of twist, while the same ring has a (–) sense of twist when viewed from the left reference plane.

Table I. Calculated Relative Steric Energies and Symmetries of the Different Conformers of 5

descriptor	symmetry[a]	relative steric energy (kcal mol^{-1})
A_u(+,–)	C_i	0
Al(+,+)/(–,–)[b]	C_2	0.1
S_u(+,+)/(–,–)[b]	C_2	0.4
S_l(+,–)	C_1	1.3

[a] Symmetry of the calculated conformations. [b] Enantiomeric conformations.

internal ring II). In principle, the different conformations of the system result from the two possible helicities of the moieties ((+) or (–)) and the arrangement of the main chain (S or A, l or u) with regards to the single internal ring. Interestingly, for a given orientation of the main chain *not all the helicity combinations are possible.* For example, whereas (+,–) or (–,+) combinations of helicities are possible for the A_u conformation, (+,+) or (–,–) arrangements are impossible. This is a direct result of the overlapping nature of the two diaryl propeller subunits. As shown in Figure 4, for the A_u conformation a (+) arrangement of the internal ring with regards to a given reference plane corresponds to a (–) arrangement with regards to the second reference plane, provided that each diarylmethyl unit exists in a propeller conformation, i.e., both rings are twisted in the same sense. Clearly, the only conformation possible in which both diarylmethyl subunits exist in a propeller conformation is (+,–) or its equivalent (–,+). Similarly one can conclude that whereas the A_u and S_l arrangements require opposite helicities of the subunits ((+,–) or (–,+)), for the A_l and S_u conformations only (–,–) or (+,+) helicity combinations are possible. Interestingly, in contrast to system **1**, achiral conformations of **5** in which each diarylmethyl unit exists in a propeller conformation are possible. This is due to the fact that **5** has an even number of $ArCH_2Ar$ propeller subunits. If the two subunits have opposite helicities the molecule may adopt an achiral conformation. In general, a propeller chain like **3** containing an odd number of rings, in which each diarylmethyl subunit exists in a propeller conformation, may exist in an achiral conformation, while in a system with an even number of rings, all propeller conformations must exclusively exist in chiral conformations. In the case of **5**, achiral conformations can be obtained only if the chain conformation allows opposite helicities in the diarylmethyl units, and this can only be accomplished in the S_l and A_u conformations.

In order to estimate the energies of the different conformations of **5**, we again performed molecular mechanics calculations. For the A_l and S_u conformations, (–,–) and (+,+) helicities correspond to enantiomeric conformations. In these as in other chiral systems only one enantiomer was calculated. The calculated relative energies and symmetries of the different conformers of **5** are collected in Table I. According to the calculations, the A_u and A_l conformers have similar steric energies which are lower than the energies of the S_u and S_l forms. This indicates, as intuitively expected, that when the two terminal rings are in spatial proximity (as in the S_l arrangement) the steric energy becomes larger. Stereoscopic views of the A_u and A_l conformations are displayed in Figure 5. As in the case of **4** all methyl hydrogens exist in a "up-down" arrangement. In the achiral A_u(+,–) conformation the twist angle of the rings is 46°. The dihedral angle between the two Ar–CH_2 bonds is exactly 180°. For the A_l(+,+) form the twist angle of the rings is 47° (for the terminal rings) and 46° (for the internal ring), while the dihedral angle between the two Ar–CH_2 bonds is 94°.

Table II. Calculated Related Steric Energies and Symmetries of the Different Conformers of 6

conformation	descriptor	symmetry	relative steric energy (kcal mol^{-1})
a/$\bar{a}$	A_lA_l(+,+,+)/(–,–,–)	C_2	0.2
b/$\bar{b}$	A_uA_l(+,–,–)/(–,+,+)	C_1	0.1
c/$\bar{c}$	A_uA_u(+,–,+)/(–,+,–)	C_2	0.0
d/$\bar{d}$	S_uA_l(+,+,+)/(–,–,–)	C_1	0.4
e/$\bar{e}$	S_uA_u(–,–,+)/(+,+,–)	C_1	0.4
f/$\bar{f}$	S_lA_l(–,+,+)/(+,–,–)	C_1	1.4
g/$\bar{g}$	S_lA_u(+,–,+)/(–,+,–)	C_1	1.2
h/$\bar{h}$	S_uS_u(+,+,+)/(–,–,–)	C_2	0.9
i/$\bar{i}$	S_uS_l(+,+,–)/(–,–,+)	C_1	1.4
j/$\bar{j}$	S_lS_l(+,–,+)/(–,+,–)	C_2	2.8

Static Stereochemistry of 6. System **6** is much more complex than **5**. In order to analyze the stereochemistry of **6** and for designation of the forms it is convenient to consider **6** as being formed by two partially overlapping triaryl subunits (defined by the rings I, II, III and II, III, IV). The conformational description that we will use has the general form A_bC_d(*,*,*) where A_b describes the conformation (e.g., A_u) of the triaryl subunit I, II, III; C_d describes the conformation of the (II,III,IV) subunit, and each asterisk describes the helicity ((+) or (–)) of a diaryl propeller subunit, the first asterisk corresponding to the diaryl subunit defined by the rings I and II, the second asterisk by the rings II and III, and the third asterisk by the rings III and IV. The choosing of one of the two terminal rings as ring I is arbitrary, and two descriptors exist for each conformation of C_1 symmetry. For example both S_uA_u(–,–,+) and A_uS_u(+,–,–) describe identical conformations.

Assuming that in the low-energy conformation the rings in a given diarylmethyl unit adopt a propeller conformation it can be easily shown, as in the case of **5**, that not all helicity combinations are possible for a given arrangement of the chain. For example, for the A_uA_u or S_lS_l conformations only combinations of helicities of alternating signs are possible (i.e., (+,–,+) or (–,+,–)) while for the S_uS_u or A_lA_l conformations only (+,+,+) or (–,–,–) arrangements are possible. On the basis of these considerations, only 20 different "allowed" combinations exist, which represent 10 different enantiomeric pairs. Pairs of conformers which relate as enantiomers can be easily recognized since they must have an identical arrangement of the main chain but opposite set of helicities. For example, the pairs of conformers S_uA_l(–,–,+) and S_uA_l(+,+,–) represent enantiomers. The list of possible conformers, together with their symmetries and calculated steric energies are collected in Table II. According to the calculations, the lowest energy conformer is the A_uA_u(+,–,+), but the A_uA_l(+,–,–), and A_lA_l(+,+,+) forms have nearly identical steric energies (0.1 and 0.2 kcal mol^{-1}). The A_uA_u(+,–,+) conformer has

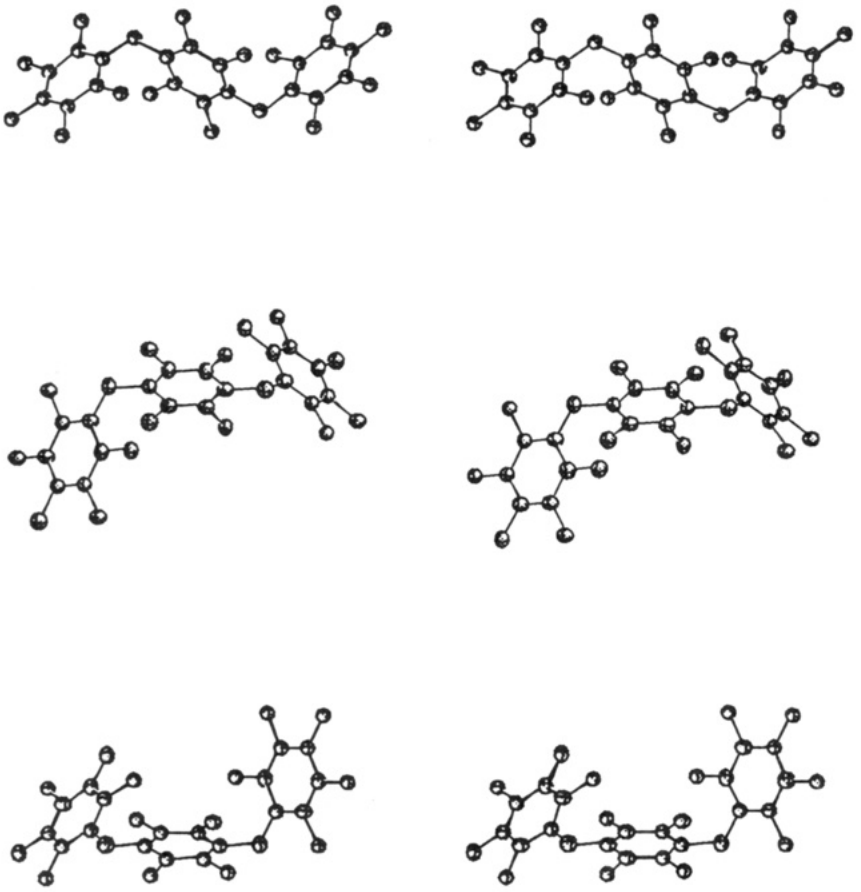


Figure 5. Stereoscopic drawings of the calculated conformations A_u, A_l, and S_u of **5**.

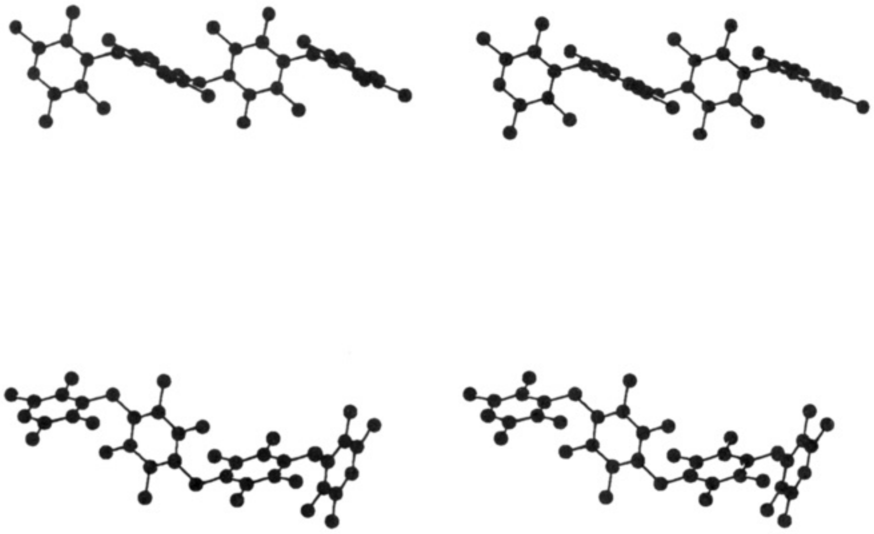


Figure 6. Stereoscopic drawings of the calculated conformations $A_uA_u(+,-,+)$ and $A_uA_l(+,-,-)$ of **6**.

a calculated C_2 symmetry, and the twist angles of the rings are 46° (for the terminal rings) and 36° (for the internal rings). From the results of Table II it can be seen that in general *anti* arrangements of the chain are somewhat favored over the *syn*, each S_u and S_l arrangement increasing the steric energy by ca. 0.4 and 1.4 kcal mol^{-1}, respectively, over the A_u form. Stereoviews of the calculated geometries of the $A_uA_u(+,-,+)$ and $A_uA_l(+,-,-)$ conformers are shown in Figure 6.

Dynamic Stereochemistry of the Parent System 4. According to the calculations the "perpendicular" and "gable" conformations corresponding to the transition states of the one- and two-ring flips lie 1.6 and 27.6 kcal mol^{-1} above the ground state conformation. In order to calculate the barrier for uncorrelated rotation we attempted to rotate one ring by 180° by "driving" it, i.e., by increasing or decreasing its torsional angle by 10° steps. In both cases, the process resulted in helicity reversal, i.e., in a correlated rotation of the rings by a one-ring flip mechanism. We decided therefore to calculate the conformational map of 4, i.e., to map the steric energy as a function of the torsional angles of the rings. The calculations were performed by increasing or decreasing the torsional angles of the rings by 10° steps. The results (in

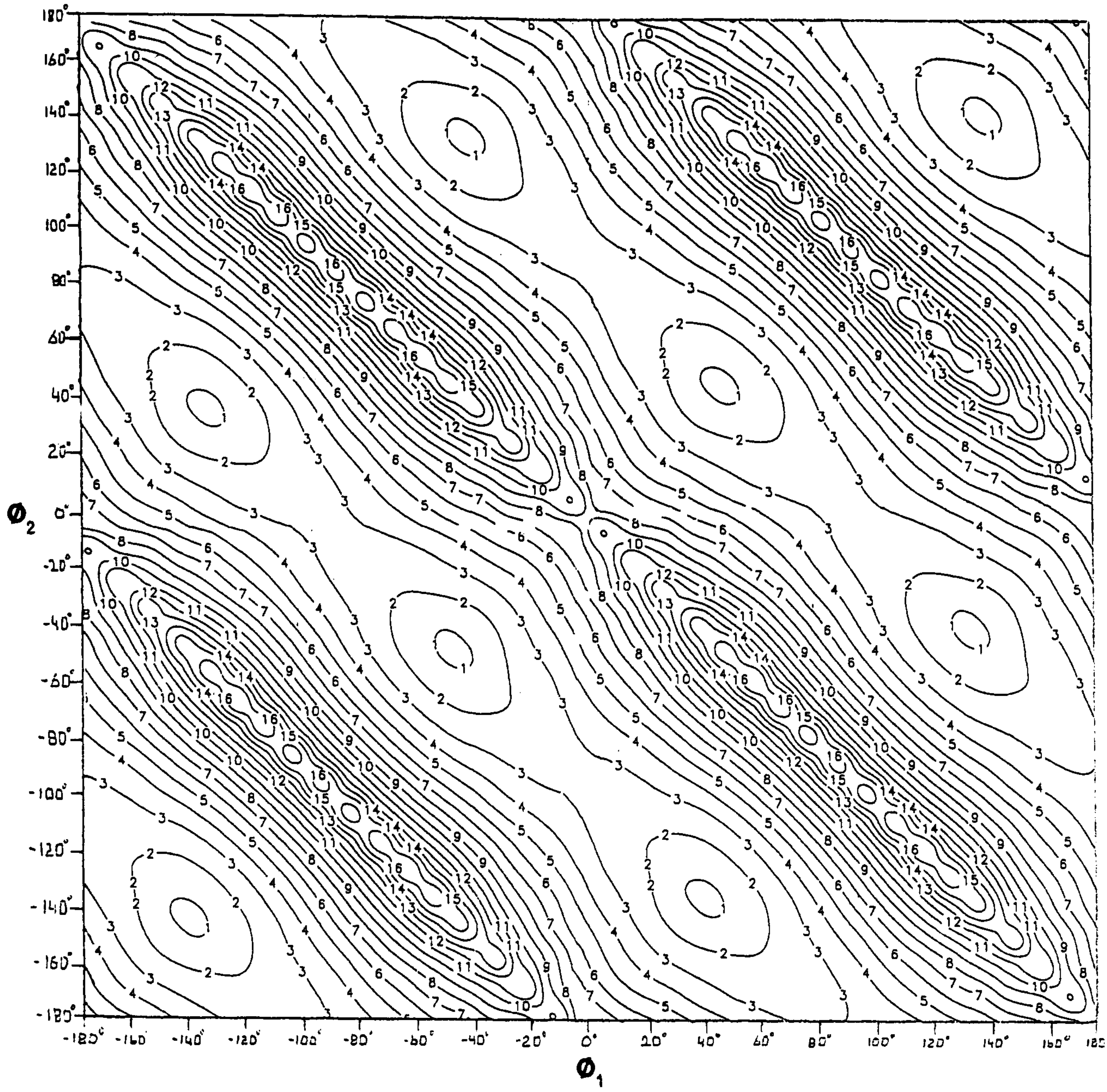


Figure 7. Conformational map for decamethyldiphenylmethane (4). The first and second contours represent steric energies of 0.15 and 1.6 kcal mol^{-1} above the global minimum. All other contours represent an increase in steric energy of 2 kcal mol^{-1}.

the form of a topographic map) are displayed in Figure 7. Starting from a given minima, the correlated rotations correspond to pathways which connect minima of opposite helicities (e.g., from (+46°, +46°) to (−46°, −46°)) which run parallel either to the [(0°,0°), (90°,90°)] or the [(0°,90°),(90°,0)] diagonals, while the uncorrelated rotations correspond to pathways which link two minima of identical helicities (e.g., from (+46°, +46°) to (−134°, −134°)) and which run parallel either to the x or y axis of the map. Based on the calculated conformational map it can be concluded that the uncorrelated rotation has a barrier of 25.6 kcal mol^{-1} and therefore lies 24 kcal mol^{-1} above the threshold mechanism, i.e., the correlated rotation by a one-ring flip process.[20] According to the calculations in the transition state of the one-ring flip there is a difference in the conformation of the methyl groups of the two rings. In the ring perpendicular to the reference plane the hydrogen atoms are arranged in an "up-down" manner, whereas in the coplanar ring, one of the hydrogens of each methyl is eclipsed to the aryl ring, with all methyls arranged in an homodirectional[21] manner.

Rotational Barriers of 5. The internal rotation of the rings by flip mechanisms should change the helicities of the two diarylmethyl subunits (+⇄−) but it should not change the conformation of the chain, i.e., its syn or anti arrangement. The flip mechanisms will result therefore in homomerization of the achiral conformers (A_u(+,−) and S_l(+,−)) and enantiomerization of the chiral ones.

In order to estimate the barrier for the different flip processes in **5** we constrained the dihedral angles of the

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[20] A one-ring flip is the usual threshold rotational mechanism of diarylmethyl propellers. See for example: Weissensteiner, W.; Scharf, J.; Schlögl, K. *J. Org. Chem.* **1987**, *52*, 1210.

[21] Mislow, K. *Chimia* **1986**, *40*, 395. Biali, S. E.; Buda, A. B.; Mislow, K. *J. Org. Chem.* **1988**, *53*, 1289.

Table III. Calculated Relative Steric Energies (in kcal mol^{-1}) for the Ideal Transition State of the Flip Processes of 5 in the Anti (A) and Syn (S) Chain Conformations

process[a]	A[b]	S[b]
zero-ring flip	86	86
(I/III)-one ring flip[c]	46	45
(II)-one-ring flip	7.2	7.2
(I),(II)/(II),(III)-two ring flip[c]	25	21
(I),(III)-two ring flip	6.9	7.1
(I),(II),(III)-three ring flip	39	39

[a] Roman numbers in parentheses denote the flipping rings. [b] Calculated relative steric energy (steric energy of the transition state less the steric energy of the conformer $\mathrm{A_u}$ (+,–) or $\mathrm{S_l}$(+,+)). [c] Two symmetry equivalent processes.

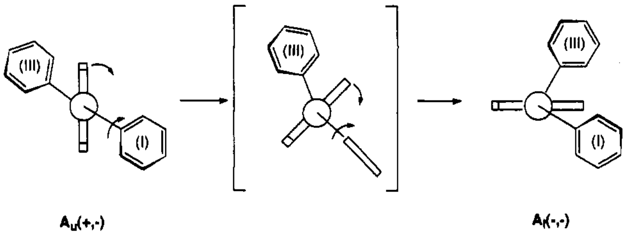

Figure 8. A localized disrotatory motion in 5 as viewed along the $\mathrm{CH_2ArCH_2}$ axis. Hydrogen atoms of the methylene units were omitted for clarity. Rings I and II rotate disrotatorily, and in the ideal transition state they are coplanar and perpendicular, respectively, to their common reference plane. Although ring III does not change its torsional angle with regards to its own reference plane, it rigidly accompanies the motion of ring II and therefore the steric relationship between the two Ar–$\mathrm{CH_2}$ bonds changes. The net process results in conversion of the $\mathrm{A_u}$(+,–) form into the $\mathrm{A_l}$(–,–).

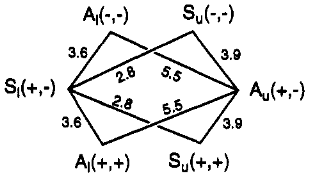

Figure 9. Interconversion graph of the six isomers of 5. Each vertex represents an isomer and each edge a mutual interconversion pathway by a localized disrotation. Calculated energy barriers (in kcal mol^{-1}) for the different processes are shown on the edges of the graph.

rings to all different combinations of 0° and/or 90°. The results obtained for the A and S chain arrangements are collected in Table III. In the following discussion, the rings which flip will be shown in parentheses while the mechanisms will be denoted as zero-, one-, two-, or three-ring flips depending on the number of rings which flip. For example, a flip mechanism involving correlated rotation of the three rings in which the two terminal rings pass through the normal of their respective reference planes will be denoted as a "(I,III)-two-ring flip". As shown in Table III the relative energies of the flip mechanisms are nearly independent of the chain conformation. Flip mechanisms in which two vicinal rings rotate conrotatorily and both rings "flip" (pass through a normal to the reference plane) or "nonflip" are of considerably higher steric energy than mechanisms in which the two rings rotate disrotatorily. The flip mechanism of lowest activation energy corresponds to a (I, III)-two-ring flip with a barrier of 6.9 kcal/mol with the (II)-one-ring flip lying only 0.3 kcal mol^{-1} above it. Clearly, the calculated barrier of the threshold flip process is higher for 5 than for 4.

Driving of one of the terminal rings gave an unexpected result: the process resulted in a change in the torsional angle of the driven ring and the disrotatory motion of the internal ring. The other terminal ring did not rotate (i.e., its torsional angle with its reference plane did not change) and moved attached as a rigid body to the rotating internal ring. We will call this process in which only two rings undergo a disrotation a "localized disrotatory rotation" in order to stress that, in the process, only two rings in the propeller chain rotate. In contrast to the classical correlated rotation, this process must result in a change of the conformation of the chain, from *syn* to *anti* and/or from *like* to *unlike* and vice versa (Figure 8). Starting from the $\mathrm{A_u}$(+,–) conformer, this process results in its conversion to the $\mathrm{A_l}$(–,–)/$\mathrm{A_l}$(+,+) and $\mathrm{S_u}$(+,+)/$\mathrm{S_u}$(–,–) conformers with barriers of 5.5 and 3.9 kcal mol^{-1}, respectively. The localized disrotation therefore may have a lower barrier than the lowest calculated flip mechanism. The calculated barrier for the localized disrotation is higher than the barrier calculated for the one-ring flip of 4. The energy difference between the two barriers probably arises due to conformational effects (see below).

Since a single localized disrotatory motion cannot result in enantiomerization (or homomerization), we constructed the interconversion graph for the process. In this graph each vertex represents a different conformer, and an edge represents a localized disrotatory motion of the rings (Figure 9). As shown in Figure 9 the connectivity of the achiral isomers is twice as large as the connectivity of the chiral ones. This is the result of the higher symmetry number of the chiral isomers (C_2 symmetry, $\sigma = 2$) as compared with the achiral ones (C_s and C_i symmetry, $\sigma = 1$). As seen from Figure 9, a localized disrotation results in a conformational change in the chain, either from syn to anti (S ⇄ A) or from "like" to "unlike" (l ⇄ u). Concomitantly, the helicity of one of the propeller subunits must change. Starting for example from the $\mathrm{S_l}$(+,–), a single localized disrotation may result in a S → A change (the $\mathrm{A_l}$(+,+) or $\mathrm{A_l}$(–,–) conformers) or l → u change (i.e., the $\mathrm{S_u}$(+,+) or $\mathrm{S_u}$(–,–) conformers). One can deduct from the graph that an even number (at least two) of localized disrotations is needed for the enantiomerization of a chiral conformation. The calculated barriers for all possible interconversions by localized disrotations between the conformers of 5 are also displayed in Figure 9. The calculated barrier for the mutual interconversion between all the conformers of 5 (3.9 kcal mol^{-1}) is in agreement with the higher limit estimated by NMR (<7.4 kcal mol^{-1}).

Interestingly, the calculated barrier for the interconversion between the $\mathrm{A_u}$(+,–) and $\mathrm{A_l}$(+,+) forms (5.5 kcal mol^{-1}) is significantly higher than the barrier for the $\mathrm{S_l}$(+,–) ⇄ $\mathrm{S_u}$(–,–) interconversion (2.8 kcal mol^{-1}). It is difficult to pinpoint the exact reason for this energy difference, but examination of the calculated transition states geometries seems to indicate that it arises from conformational effects of the methyl groups in the internal ring.[22] In the transition state for the $\mathrm{S_l}$(+,–) ⇄ $\mathrm{S_u}$(–,–) interconversion the methyl groups of the internal ring (perpendicular to the reference plane) are relatively unhindered and are arranged in an "up-down" fashion, similar to the arrangement found for the perpendicular ring in the transition state of the one-ring flip of 4. In contrast, in

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[22] According to the calculations, the higher steric energy in the barrier for the $\mathrm{A_u}$(+,–) ⇄ $\mathrm{A_l}$(+,+) interconversion is due to angle and van der Waals strain in the internal ring.

Table IV. Calculated Relative Steric Energies (kcal mol^{-1}) for the Ideal Transition State of the Flip Processes of the AA, AS, and SS Chain Arrangements of 6

process^a	AA^b	AS^b	SS^b
zero-ring flip	130	122	126
(I)/(IV)-one ring flip^c	90	88	85
(II)/(III)-one ring flip^c	30	49	47
(I),(II)/(III),(IV)-two ring flip^c	54	64	62
(I),(III)/(II),(IV)-two ring flip^c	10	10	10
(I),(IV)-two ring flip	51	49	47
(II),(III)-two ring flip	30	26	20
(I),(II),(III)/(II),(III),(IV)-three ring flip^c	44	44	38
(I),(II),(IV)/(I),(III),(IV)-three ring flip^c	29	25	25
(I),(II),(III),(IV)-four ring flip	59	59	59

^{a} Roman numbers in parentheses denote the flipping rings. ^{b} Calculated relative steric energy (steric energy of the transition state less the steric energy of the conformer A_u $A_u(+,-,+)$, $A_uS_l(+,-,+)$ or $S_lS_l(+,-,+)$. ^{c} Two symmetry equivalent processes.

the transition state of the $A_u(+,-) \rightleftarrows A_l(+,+)$ interconversion two methyl groups (in a para relationship) of the internal ring are not arranged in an "up-down" but in an eclipsed conformation. Examination of CPK molecular models shows that in the transition state of the $A_u(+,-) \rightleftarrows A_l(+,+)$ interconversion an all "up-down" arrangement of the methyl groups of the internal ring should result in repulsive steric interactions. These interactions are only partially avoided by twisting two methyl groups, which results in a higher steric energy.

Dynamic Stereochemistry of 6. Similarly to the case of 5, the flip mechanisms should result in helicity reversal of the diarylmethyl moieties without concomitant change in the chain conformation. Since all the "propeller" conformers of 6 are chiral, each flip mechanism results in enantiomerization (e.g., $A_uA_u(+,-,+) \rightleftarrows A_uA_u(-,+,-)$). The transition states for the different flip mechanisms of 6, starting from an AA chain conformation were calculated by freezing the rings at all combinations of 90° and/or 0°. The calculated barriers are collected in Table IV. As in the case of 5, the lowest energy flip mechanism corresponds to a process in which the rings are alternately perpendicular and coplanar to the reference planes, i.e., a (I,III) (or its equivalent (II,IV)) two-ring flip. Starting from the lowest energy conformation (A_uA_u), this process has a relative barrier of 10 kcal mol^{-1} (Table III). The calculations were repeated for the AS and SS chain arrangements with the same results: in the lowest energy flip mechanism the rings are alternately perpendicular and coplanar with the double bond. On the basis of the calculated barriers for 4–6, it can be concluded that the lowest energy mechanism of correlated rotation is a flip mechanism in which, in the ideal transition state, the rings are alternately arranged in a perpendicular and coplanar fashion to the reference planes. The calculated barrier for the process increases with the increase in length of the propeller chain (1.6 kcal mol^{-1} for 4, 6.9 kcal mol^{-1} for 5, 10 kcal mol^{-1} for 6).

We studied also the rotational processes of 6 by driving a terminal ring by 10° steps. As in the case of 5 the process resulted in a localized disrotation of the driven ring and its neighbor. In order to describe completely the dynamic behavior or 6 it is necessary, as in the case of 5, to build the interconversion graph between conformers. This graph, should consist of 20 vertices, representing the 10 enantiomeric pairs, interconnected by edges representing interconversion by localized disrotations. These processes should exchange between S and A or between l and u arrangements of two Ar–CH$_2$ bonds connected to the rotating internal ring, while the remaining chain arrangement conformation should be unchanged. Starting for example from the $A_uA_u(+,-,+)$ (designated c in Table II), a localized disrotation of rings I and II (or III and IV) should result in the $A_lA_u(-,-,+)$ (b) or the $S_uA_u(-,-,+)$ form (e). Disrotation of the rings II and III reverses the helicity of the central diarylmethyl unit and results in a change in the chain conformation of the two partially overlapping triaryl subunits. The disrotation involves rotation of the rings in different directions, and therefore each subunit will change differently: i.e., if one subunit changes from A_u to S_u, the second will change from A_u to A_l. Based on these considerations, one can conclude that a correlated disrotation of the central diaryl ring must interconvert the $A_uA_u(+,-,+)$ with the $S_uA_l(+,+,+)$ isomer. In the case of the $A_uA_u(+,-,+)$ conformer the two terminal and internal rings are pairwise symmetry equivalent, but for conformers of C_1 symmetry six different processes are possible. The complete interconversion graph including the calculated barriers is shown in Figure 10.[23] According to the graph, all isomers mutually interconvert by localized disrotations, and at least three localized disrotations are necessary to achieve enantiomerization of a given conformation.[23] For example, for the $A_uA_u(+,-,+)$ form (c), this can be accomplished for example by the $c \rightarrow e \rightarrow \bar{b} \rightarrow \bar{c}$ pathway. In the localized disrotatory motion the molecule never achieves an achiral conformation and therefore all the enantiomerization pathways are chiral. For each pathway a second route (enantiomeric to it) must also be present (e.g., $c \rightarrow b \rightarrow \bar{e} \rightarrow \bar{c}$) which is related to the first by the inversion center in the graph. Each enantiomerization pathway must involve three localized disrotations of the ring pairs (I,II), (II,III), and (III,IV) (in any order) with

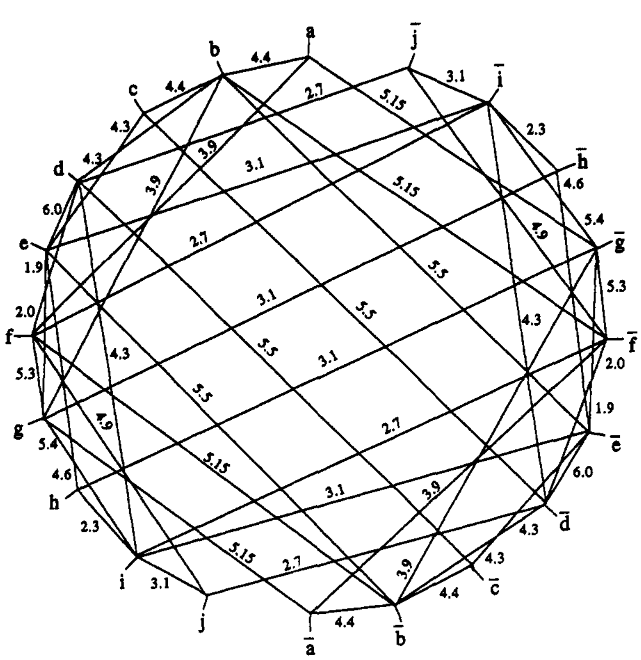

Figure 10. Interconversion graph for the 20 isomers of 6. The vertices represent the different isomers and the edges interconversion pathways by localized disrotatory rotations. The isomers are represented by letters (see Table II). Two identical letters with and without an overbar represent an enantiomeric pair. Calculated energy barriers (in kcal mol^{-1}) for the different processes are shown on the edges of the graph. All energies are relative to the conformer c.

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[23] In the case of 6 the barriers for the localized disrotations were calculated by freezing the torsional angles of the two rotating rings at 0° and 90°.

the net result that the helicities of the three diarylmethyl moieties are reversed. According to the calculations, the $\bar{c} \rightarrow \bar{b} \rightarrow e \rightarrow c$ interconversions have barriers (relative to the steric energy of c) of 4.4, 5.5, and 4.3 kcal mol^{-1}, respectively, and therefore the enantiomerization barrier by this pathway is 5.5 kcal mol^{-1}.[24] In principle other enantiomerization pathways of c may have a lower barrier. The minimum energy pathway of enantiomerization of each conformer was found by examination of the graph. Localized disrotations with barriers equal or lower than 3.1 kcal mol^{-1} interconvert between the $\bar{d}$, $\bar{e}$, $\bar{f}$, $\bar{g}$, h, i, and j conformers (or their enantiomers d, e, f, g, $\bar{h}$, $\bar{i}$, and $\bar{j}$). Interconversion of the conformers $\bar{a}$ and $\bar{b}$ (or a and b) with the previous sets has a barrier of 3.9 kcal mol^{-1}. Interconversion of c (or $\bar{c}$) with the complete set of conformers requires a barrier of 4.3 kcal mol^{-1} but two pathways which connect the two sets ($i \rightleftarrows d$ and $\bar{i} \rightleftarrows \bar{d}$) have also a barrier of 4.3 kcal mol^{-1}. This barrier therefore represents the enantiomerization barrier by the minimum energy pathway for each conformer of the system. For example, enantiomerization of c can be achieved by the following route $c \rightarrow e \rightarrow \bar{i} \rightarrow \bar{d} \rightarrow j \rightarrow i \rightarrow \bar{e} \rightarrow \bar{c}$ with a general barrier of 4.3 kcal mol^{-1}. The enantiomerization barrier is substantially lower than the barrier of the flip mechanism of lowest activation energy (10 kcal mol^{-1}), indicating that there is a large energy preference of localized disrotations over correlated rotations.

Transmission of Rotations in Propeller Chains. From the calculations it can be concluded that the threshold rotational mechanism of the propeller chains 5 and 6 differs from the corresponding parent molecular propeller 4. To a first approximation the barrier for uncorrelated (180°) rotation of a terminal ring should be independent of the length of the system, since this barrier is mainly dictated by the steric interactions between the rotating ring and its closest neighbor. Provided the system exists in an extended conformation (A_u), these barriers should be roughly similar for all the members of the family. On the other hand, the calculations show that the barrier of the correlated rotation by a flip mechanism of lowest activation energy *increases* with the length of the propeller chain. This can be rationalized, since any flip mechanism involves all rings, and the larger the number of rings that rotate, the larger the number of repulsive interactions present in the transition state. It can be concluded therefore that the longer the propeller chain, the smaller the energetic preference of correlated ("flip") over uncorrelated (180°) rotations. This poses a limitation on the transmission of internal rotation of coupled rotors along a chain. Only systems with tightly meshed rotors (such as a polytriptycyl chain) and with a large energy gap between correlated and uncorrelated rotations may have efficient transmission of correlated rotations. For the propeller chains studied in the present work, the threshold rotational mechanism is a correlated disrotation which involves only two rings at a time. This localized rotation is energetically preferred over the flip pathways since, by performing localized disrotations in succession (and not in correlated fashion), the molecules localize the steric interactions, therefore avoiding the situation in which repulsive steric interactions exist in all rings.

Experimental Section

Preparation of 5. To a cooled solution of pentamethylbenzyl acetate (166 mg) and durene (73 mg) in 1.2 mL of CH_2Cl_2 was added, under stirring, 5 μL of triflic acid. After 5 min the reaction was quenched by addition of 3 mL of an aqueous solution of $NaHCO_3$. The phases were separated, and the organic phase was evaporated. The residue was recrystallized from CH_2Cl_2/EtOH yielding 98 mg (57%) of 5: mp 291 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.99 (s, 12 H, *o*-Me), 2.01 (s, 12H, *o*-Me), 2.17 (s, 12 H, *m*-Me), 2.21 (s, 6H, *p*-Me), 4.17 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.96, 16.98, 17.16, 17.21, 33.66, 132.05, 132.27, 132.35, 132.62, 136.60, 137.07; MS (EI) *m*/*z* 454 (M).

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[24] The barrier heights of the different localized disrotations is in agreement with the behavior observed for 5. In general, barriers which involve mutual interconversion between A_u and A_l subunits are higher than barriers which interconvert S_l and S_u subunits.