Tetrahedron Vol. 42, No. 6, pp. 1679 to 1686, 1986
Printed in Great Britain.

0040–4020/86 $3.00+.00

SYNTHESIS OF 9,10-BIS(9-TRIPTYCYLOXY)TRIPTYCENES

MOLECULAR DESIGN OF A SYSTEM WITH DOUBLY CORRELATED INTERNAL ROTATION

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(*Received in USA* 30 *April* 1985)

Abstract—Torsional motions around the two C—C and C—O bonds in di(9-triptycyl)methanes, Tp_2CH_2, and di(9-triptycyl) ethers, Tp_2O, respectively, have a high barrier to uncorrelated rotation and a very low barrier to coupled disrotation. As a result, new stereoisomerism is generated due to different phase relationships between appropriately labeled benzene rings, at least one on each Tp unit. To extend the concept and further demonstrate the high correlation in the torsional motions for these systems, a doubly geared molecule, 9,10-bis(3-chlorotriptycyloxy)triptycene (1), was conceived and constructed. Bis(3-chloro-9-triptycyl) 9,10-triptycenebis(peroxycarboxylate) was prepared. The *meso* and *dl* isomers of 1 were separated by HPLC on microsilica. The structures were confirmed by high resolution ^{13}C-NMR spectra which revealed an interesting stereochemical feature: one benzene ring of the middle unsubstituted triptycene moiety is diastereotopic to the other two. The rates of isomerization were measured in diphenylmethane solution to give the activation parameters for the gear slipping process: $\Delta H^{\ddagger} = 42.1 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.2 \pm 2.3$ e.u. The significance of these findings as an extreme case for the dynamics of molecular chains is discussed.

Background and purpose

Whereas torsional degrees of freedom are often hindered by non-bonded interactions between the rotors in overcrowded molecules, sometimes torsional motions in some congested molecules are not as much hindered as one might expect. Correlated internal rotation is the concept introduced in dynamic stereochemistry to account for these phenomena.[1] When two or more torsional motions take place in concert the barrier can become lower than those for the independent rotations. The di(9-triptycyl)methane, Tp_2CH_2,[2,3] and di(9-triptycyl) ether, Tp_2O, are bevel gear-shaped molecules[2] which provide dramatic examples in which potential energy barriers to rotation around the two C—C and the two C—O bonds (for methane and for ether, respectively) differ considerably between uncorrelated and correlated torsional motions. Thus, the disrotatorily coupled internal rotation is predicted to show a barrier no higher than 1 kcal mol^{-1} by empirical force field calculation.[2h,3f] An indirect kinetic study by means of exciplex fluorescence dynamics gives a value for this barrier of 4.2–4.8 kcal mol^{-1} in ether.[2i,2j] The barrier to the uncorrelated process is measured from the rate of the gear-slipping process as 32–33 kcal mol^{-1} for the methanes and 42–43 kcal mol^{-1} for the ethers.[2,3] These high barriers to uncorrelated rotation and very low barriers to coupled disrotation give rise to new stereoisomerism due to a different phase relationship of the appropriately labeled benzene rings, at least one on each triptycene unit. In the simplest case when only two benzene rings are labeled, one on each Tp group, a phase relationship is established between the labeled benzene rings. This relationship is kept constant irrespective of the rate of the coupled rotation. There are two such phase relations in Tp_2CH_2 and Tp_2O (Fig. 1). In one labeling pattern, the labeled benzene rings "bite" each other during the course of the geared rotation circuit and the conformers produced are all chiral. In the other, the labeled rings never come next to one another and the conformers either have a symmetry plane or consist of an enantiomeric pair. These two different labeling patterns show as two different chemical entities: two distinct stereoisomers are produced. Such stereoisomerism pertaining to the torsional degree of freedom is unique in that it is independent of the rate of internal rotation. As long as the two torsional motions are coupled, rotation may take place very rapidly. In one example of a di(9-triptycyl) ether,[2j] the rate constant is estimated as 9.0×10^8 s^{-1} at 10°.

With this background in mind, we became interested in finding out if the phase relationship between the labels can be detected even when the two "wheels" are separated further. As an extension of our earlier work, we introduced an additional triptycene framework between the two wheels to generate a doubly connected bevel gear system. More specifically, 9,10-(9-triptycyloxy)triptycene (1) in which only the outer two Tp units are labeled became the target, both for our synthetic work and for the separation of the diastereomers.

Synthesis and separation of phase isomers

Historically, the triptycene skeleton was constructed for the first time by chemical modification of the 2-cyclohexene-1,4-dione ring into a benzene ring in the Diels–Alder adduct of anthracene with *p*-benzoquinone.[4] Since its advent, nearly all triptycene derivatives have been made by addition of benzyne to anthracenes.[5] Di- and poly(9-triptycyl) derivatives are not exceptions. Two choices were open to us: to construct the corresponding di- and polyanthracenes first, and then proceed with the Diels–Alder reaction, or to connect triptycene units already prepared. 9,9′-Bitriptycyl, Tp_2,[6] di(9-triptycyl)methanes, $(Tp_2)_2CH_2$,[2,3] and 1,2-di(9-triptycyl)ethane, $(TpCH_2)_2$,[7] are examples prepared by the first method. When the corresponding anthracenes are difficult to make, the alternative method of connecting the two triptycyl units has to be employed. Di(9-

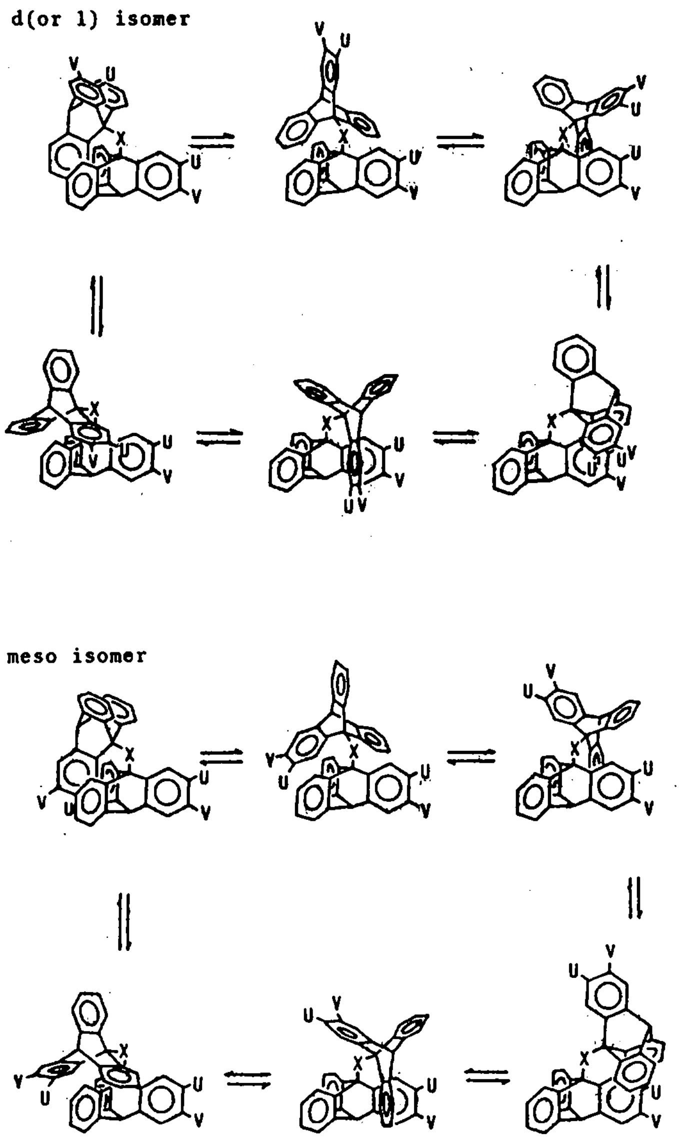


Fig. 1. Conformational gearing circuits for the *dl* and *meso* isomers of the labeled Tp_2X ($X = CH_2$, O, etc.).

triptycyl)mercury, Tp_2Hg,[8] and di(9-triptycyl)silanes, Tp_2SiH_2,[2d] are prepared by electrophilic reaction at the bridgehead of 9-triptycyllithium with mercury(II) chloride and chlorosilanes, respectively.

It proved impossible to get any reasonable amount of di(9-anthryl) ether according to the method described in the literature.[9] This eliminated the first approach. Coupling routes to the di(9-triptycyl) ether, Tp_2O, are subject to another difficulty. Since the 9-triptycyl carbonium ion is very unstable, nucleophilic substitution at the bridgehead is not feasible.[10] Fortunately, the 9-triptycyl radicals are not so unstable,[11] although they are avid hydrogen abstractors. There are some free radical substitution reactions known in the literature.[12] Therefore, recourse was made to the cage recombination reaction of the 9-triptycyl–9-triptycyloxy radical pair. For this purpose our thermolysis of 9-triptycyl 9-triptyceneperoxycarboxylate, $TpCO_3Tp$, was adopted (Scheme 1).[2d]

Of the three possible diperoxyesters,

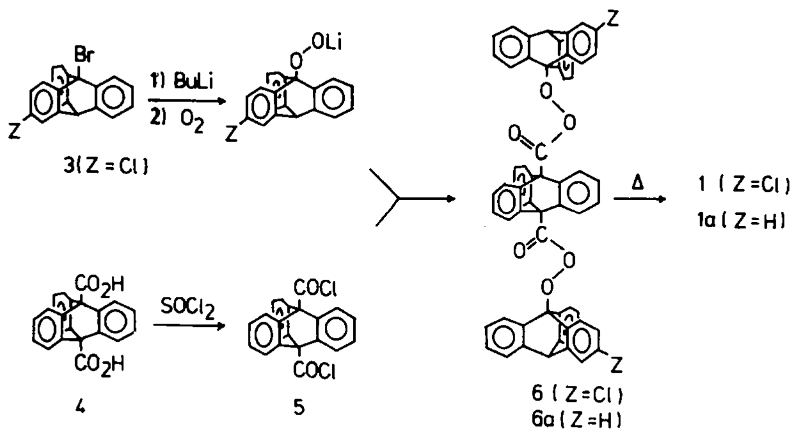
$$Tp—COO_2—Tp'—O_2COTp,$$

$$Tp—COO_2—Tp'—COO_2Tp$$

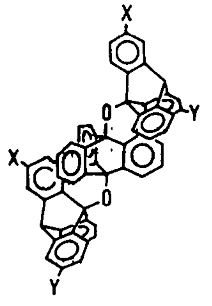
and

$$Tp—O_2CO—Tp'—COO_2Tp,$$

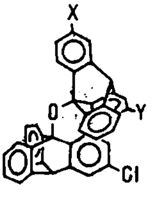
we chose the latter combination **6a** as the intermediate for the doubly geared diether **1**. A preliminary experiment with the unsubstituted diether **1a** proved satisfactory. For the labeled compound **1** (Scheme 1), a diethyl ether solution of the lithium salt of 3-chloro-9-hydroperoxytriptycene was prepared by the reaction of 9-bromo-3-chlorotriptycene (**3**)[2d] with butyllithium followed by reaction with oxygen in ether at −78°. The solution was allowed to react with triptycene-9,10-dicarbonyl dichloride (**5**) to give the bisperoxyester (**6**), m.p. 110–160° (dec.) in 10% yield. Thermal de-



Scheme 1.



1a (X = Y = H)
1, meso (X = Cl, Y = H)
1, d(or l) (X = H, Y = Cl)



2, meso (X = Cl, Y = H)
2, d(or l) (X = H, Y = Cl)

composition in perfluorodecalin at 150° gave diether 1 in 32% yield as a white powder.†

The product was subjected to HPLC on microsilica with elution by 4% CH_2Cl_2 in n-hexane. A typical chromatogram shows (Fig. 2) that the first fraction was the statistically more abundant *dl* isomer and the second, more polar, fraction was the less abundant *meso* isomer. The isomers of the corresponding monoether, bis(3-chloro-9-triptycyl) ether 2, showed the opposite chromatographic behavior; the *meso* isomer was eluted first under similar conditions.[24] The effective polarity of the *meso* vs *dl* isomers must be reversed on going from the monoethers 2 to the diethers 1. This can be roughly understood by considering the average angles between the two C—Cl bond dipoles in the two isomeric molecules. In monoether 2, the chloro-substituted benzene rings never come next to each other in the conformational gearing circuit of the *meso* isomer (Fig. 1) and therefore the two C—Cl bonds are on average in opposite directions, thus reducing the effective polarity of the compound relative to the *dl* compound. In the *meso* isomer of the diether, two terminal triptycene units can rotate with the two chloro-substituted benzene rings in phase. These two benzene rings can get into the same notch of the middle triptycene wheel only in the case of the *meso* isomer. Therefore the two C—Cl bond dipoles tend to be oriented in the same direction, which makes this *meso* isomer more polar than its *dl* isomer.

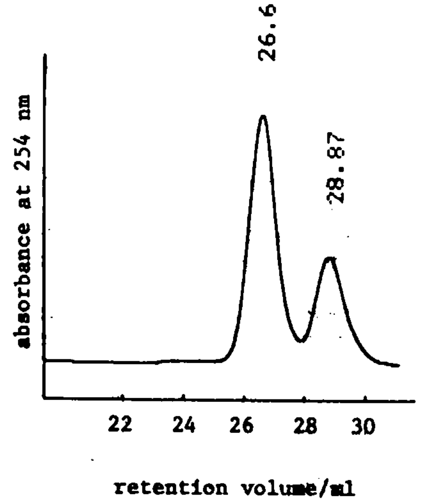


Fig. 2. Analytical HPLC separation of the *dl* (fraction 1) and *meso* (fraction 2) isomers of diether 1.

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† Some comments on this procedure are appropriate. Organolithium compounds are known to give the lithium hydroperoxide according to Eq. (1). Since the latter can still react with an organolithium compound (Eq. (2))

$$RLi + O_2 \longrightarrow RO_2Li \quad (1)$$

$$RO_2Li + RLi \longrightarrow 2ROLi \quad (2)$$

we recommend the reverse addition of the suspension of RLi to ether saturated with dry O_2 in order to avoid a high stationary concentration of the lithium reagent. Formation of the alkoxide according to Eq. (2) could not be fully excluded. However, the reactivity of the hydroperoxide was decidedly higher than that of the alkoxide towards the acyl chloride, at least as far as 9-triptycyls were concerned, and therefore the peroxyacetate in Nujol at 30°.[13] Di(9-triptycyl) ether, Tp_2O, precedents for the formation of ether products from the decomposition of the corresponding peroxy esters. The highest yield, to our knowledge, had been 75% for the formation of t-butyl methyl ether by the photolysis of t-butyl peroxyacetate in Nujol at 30°.[13] Di(9-triptycyl) ether, Tp_2O, was obtained almost in quantitative yield when the decomposition of the peroxyester was carried out in perfluorodecalin at 150°.[24] Generation of the bulky 9-triptycyl and 9-triptycyloxy radicals face to face with each other is considered to be one of the reasons for the success of the cage-recombination reaction.

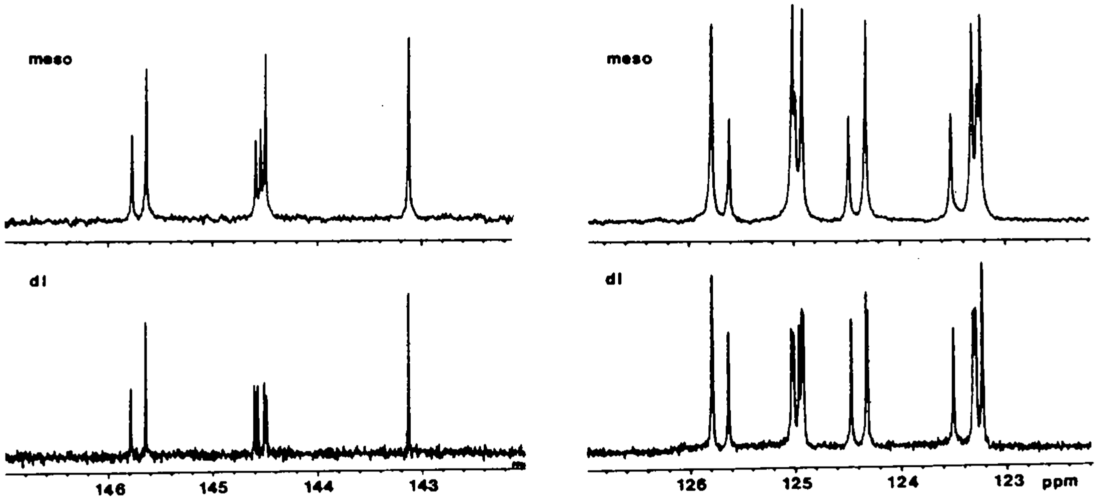
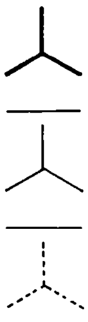


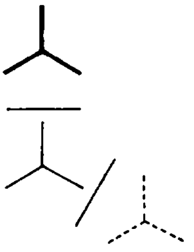
Fig. 3. 100.40 MHz ^{13}C-NMR spectra of the *meso* and *dl* isomers in CDCl$_3$ (the aromatic regions only).

Stereochemical properties of the isomers

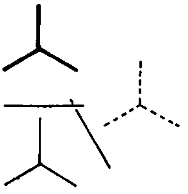
^{13}C-NMR spectra obtained at 100.40 MHz were instrumental in verifying the structural assignment (Fig. 3). The unsubstituted diether **1a** showed six tertiary and three quaternary aromatic carbon signals, demonstrating the presence of only one kind of benzene ring each for the inner and outer triptycene units. This observation also confirmed the rapidity of internal rotation around the C—O bonds in these molecules on the NMR time scale. If the structure had been frozen in a manner like that found in the crystals of Tp$_2$O,^{2h} namely in the C$_s$ conformation for each bevel gear, there would be four conformations A, B, C and D possible.



A



B



C

D

They could have given 6(2:2:2:1:1:1), 4(4:2:2:1), 9(1:1:1:1:1:1:1:1:1) and 4(4:2:2:1) kinds of benzene rings in different environments, respectively. Only two kinds of benzene rings in a 6:3 ratio were observed.

The second HPLC fraction, m.p. 505°, gave a simpler ^{13}C-NMR spectrum than the first fraction and therefore should be assigned to the more highly symmetric *meso* isomer. We had naively thought that the three benzene rings in the middle triptycene unit would be equivalent. Accordingly, the quaternary benzene ring carbons attached to the bridgehead carbons should have appeared as a quintet in 6:4:4:2:2 intensity ratios. The spectrum obtained under high resolution showed six lines in 4:4:4:2:2:2 ratios instead. Comparison with the ^{13}C-NMR spectra of isomeric monoethers **2** and of unsubstituted diether **1a** revealed that the signal corresponding to the apparently equivalent six quaternary ring carbons of the middle triptycene moiety was now split into a 4:2 doublet at δ 144.49 and 144.54 (or 144.59). Since the molecular framework of the diether is flexible and because the torsional motions are perfectly correlated, the *meso* isomer belongs effectively to the C$_{2v}$ point group with the C$_2$ axis lying in the plane of one benzene ring (a) and passing through the center of the middle triptycene unit (Fig. 4(a)).† Therefore, the other two benzene rings (b and c) are equivalent, while ring a is unique in that it never comes next to the labeled rings of the outer triptycene units. Thus assignment of the *meso* isomer was confirmed.

The first HPLC fraction of **1**, m.p. 509°, showing a more complicated ^{13}C-NMR spectrum, should be the racemic compound. The quaternary benzenoid carbons attached to the bridgehead carbons are

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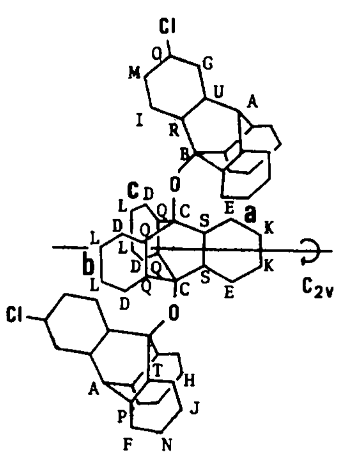
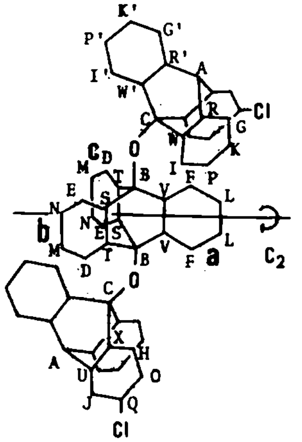
† In **1**, conformation of the molecular skeleton is not necessarily fixed as shown in A, but additional comformers B–D are also conceivable. Non-equivalence of the unsubstituted benzene rings in the middle triptycene unit will be more readily understood if the molecules are assumed to have the comformation frozen as in D.



A	53.32
B or C	87.17
C or B	89.49
D	123.23
E	123.26
F	123.32
G	123.51
H	124.32
I	124.48
J or N	124.92
K	124.99
L	125.01
M	125.61
N or J	125.79
O	131.16
P	143.12
Q	144.49
R or S	144.54
S or R	144.59
T	145.63
U	145.77

(a)



A	53.71		M or N	125.01
B or C	87.52		N or M	125.04
C or B	89.19		O	125.64
D	123.23		P and P'	125.79
E	123.23		Q	131.17
F	123.29		R and R'	143.13
G and G'	123.30,	123.32	S or T	144.49
H	123.51		T or S	144.52
I and I'	124.31,	124.33	U and U' or V	144.58
J	124.47		V or U and U'	144.61
K and K'	124.92,	124.94	W and W'	145.65
L	124.97		X	145.79

(b)

Fig. 4. Symmetry properties of the isomeric diether 1 and ^{13}C chemical shift data.

composed of seven lines with the intensity ratio of 4:2:2:2:2:4:2. Inspection of molecular models reveals that the middle triptycene unit has local C_2 symmetry with the C_2 axis lying in the plane of one (a) of the benzene rings as above. Thus ring a is diastereotopic to the other two (b and c) rings. Rings b and c are equivalent in such a way that the upper carbons in ring b are equivalent to the bottom ones in ring c and *vice versa* (Fig. 4(b)). As a result, the quaternary benzenoid carbons of the unsubstituted triptycene unit show as a 2:2:2 triplet (three of the four peaks at δ 144.49, 144.52, 144.58 and 144.61) in the ^{13}C-NMR spectrum.

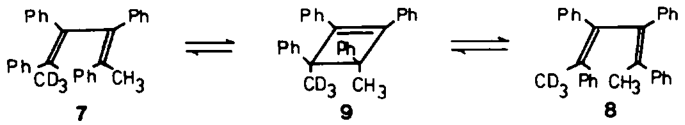
It is expected that, at higher temperatures, librational motions of the tritriptycyl molecules become very vigorous, the gears become loose, and, as a result, gear-clashing processes will interfere with gear-meshing. This feature would show as the interconversion of the stereoisomers obtained above. The rates of isomerization from the *dl* to *meso* isomers were measured in diphenylmethane solutions in the temperature range 238–332°. Arrhenius plots of the results (Table 1) gave the activation energy parameters: $\Delta H^{\ddagger} = 42.1 \pm 1.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -3.2 \pm 2.3$ e.u., $E_a = 43.2 \pm 1.3$ kcal mol^{-1}, $\log A = 12.8 \pm 0.5$, and $K(dl/meso) = 2.05 \pm 0.07$. These values are, within experimental errors, the same as those for the monoether 2[12a] except that the *A*-value is about twice as much in the diether. The same gear slippage process must be operative in both ethers, and this is taken to indicate that the two gears in diether 1 are independent.

We note that the entropy of activation is not highly negative. Jackman *et al.* proposed that a large negative $\Delta S^{\ddagger}$ value (-7 to -20 e.u.) may be used as a criterion for correlated internal rotations.[14] This seems to apply aptly when the difference in $\Delta H^{\ddagger}$ between the correlated and uncorrelated pathways is small. When the uncorrelated route requires a prohibitively high barrier, $\Delta S^\ddagger$ may not necessarily assume a large negative value.

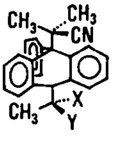
REWARDS

We have been able to demonstrate that, in bis- and tris(9-triptycyl) derivatives, the torsional motions take place in strict disrotation. Whereas "disrotatory" motions are the technical expression popular in orbital symmetry-controlled reactions, steric effects can also be responsible for such motions, as our work shows. Let us compare these two sorts of disrotatory motions.

As a persuasive demonstration of the strict conservation of orbital symmetry in electrocyclic reactions, the highly substituted butadienes 7 and 8 have been taken as examples.[15] They undergo equilibration through intermediacy of the cyclobutene 9. After 51 days at 124°, each cyclobutene molecule had faultlessly undergone 2.6×10^6 conrotatory openings, and a disrotatory mistake had yet to appear.[16] In the present case, of non-bonded interaction-controlled motions in the dichloro ethers, each gear undergoes disrotation 3.4×10^{16} times and only one in 50,000 wheels is computed to miss gearing at 124° in 51 days. The symmetry allowed conrotatory opening of the cyclobutene ring is estimated to be favored by a minimum of 7.3 kcal mol^{-1} over the symmetry forbidden disrotatory opening mode.[16] The disrotatory motion is favored by 30–40 kcal mol^{-1} over the other modes in di(9-triptycyl) derivatives.



Previously we reported recognition of the conformational relationship between the two CMe_2CN substituents across the bridgeheads of a triptycene molecule, since torsion of the pivot bonds was fully restricted as in 10 to give the *meso* and *dl* isomers.[17] The present results extend this stereochemical notion in that the two substituents may rotate rapidly as long as they are correlated.



10, meso (X = CH_3, Y = CN)

10, d(or l)(X = CN, Y = CH_3)

Another conclusion from this research, based in particular upon the low potential energy value for the correlated internal rotation, is that cooperativity in torsional motions can be very important in chain dynamics of large and congested molecular chains.

EXPERIMENTAL

General methods. M.ps were determined by differential scanning calorimetry on a du Pont 990 Thermal Analyzer. ^{1}H- and ^{13}C-NMR spectra were taken on a Varian EM390 and JEOL GX400 spectrometer with the δ values given in ppm downfield from TMS. High resolution mass analyses were performed at the Analytical Center of the Institute for Basic Biology in Okazaki National Research Institutes. IR spectra were recorded on a Hitachi 295 IR spectrometer. Lobar column (Merck) equipped with a Duramat pump and an Altex UV detector was used for preparative column chromatography. HPLC was performed on a Waters model ALC/GPC 244 apparatus with μ-Porasil columns. The analytical and preparative runs were carried out on 1/4 in × 1 ft and 3/8 in × 1 ft columns with flow rates of 1 and 6 ml min^{-1}, respectively, and with elution by 4% of CH_2Cl_2 in n-hexane. A recorder was replaced with a Shimadzu CR1-A data processor for the kinetic analyses.

All chemicals were used as received except for drying when necessary. Starting materials, 3[24] and triptycene 9,10-dicarboxylic acid[18] were prepared according to the literature.

Triptycene-9,10-*dicarbonyl dichloride* (5)[18]

Compound 4 (1.0 g) and $SOCl_2$ (5 ml) were heated to reflux until the suspension became clear. Excess $SOCl_2$ was removed completely under reduced pressure. The residue was dissolved in benzene and used for the synthesis of peroxyester without purification.

Di(9-*triptycyl*) *triptycene*-9,10-*diperoxycarboxylate* (6a)

To a cold (−78° or below) soln of the Li salt of triptycene-9-hydroperoxide prepared as described previously[24] from 930 mg (2.8 mmol) of 9-bromotriptycene was added with a syringe 265 mg (0.7 mmol) of 5 dissolved in benzene (20 ml). After the addition, the cold bath was removed and stirring was continued overnight. Following usual aqueous workup, the crude product mixture was chromatographed on silica gel employing n-hexane–dichloromethane (1 : 1–0 : 1) as eluent. The bis(peroxyester) (6a) was obtained as colorless flakes (2nd band, 115 mg, 19%) along with triptycene (1st band, 225 mg, 31%) and 9-hydroxytriptycene (3rd band, 320 mg, 42%): ^{1}H-NMR (99.6 MHz, $CDCl_3$) δ 5.44 (s, 2H), 6.96–7.24 (m, 18H), 7.44–7.64 (m, 6H), 7.72–7.88 (m, 6H), 7.88–8.08 (dd, 6H); IR (KBr) 1775 (C=O), 1460, 1110, 995, 755, 645 cm^{-1}.

9,10-*Bis*(9-*triptycyloxy*)*triptycene* (1a)

Peroxyester 6a (115 mg, 0.13 mmol) was suspended in perfluorodecalin (5 ml), gradually heated to 160° over a 1 hr period, and maintained at that temp for 30 min. Following evaporation of the solvent, the brown residue was successively purified by column chromatography on silica gel and GPC to give 1a: colorless solid (40 mg, 39%); m.p. (DSC) 567°; ^{1}H-NMR (99.6 MHz, $CDCl_3$) δ 5.53 (s, 2H), 6.72–7.20 (m, 18H), 7.40–7.60 (m, 6H), 7.68–7.96 (m, 12H); ^{13}C-NMR (100 MHz, $CDCl_2CDCl_2$) δ 58.39, 87.41, 89.25, 123.17, 123.21, 124.26, 124.61, 124.80, 125.48, 143.63, 144.50, 145.86; IR (KBr) 1440, 1215, 1195, 1065, 740, 640 cm^{-1}. (Found: C, 91.39; H, 4.93. Calc for $C_{60}H_{38}O_2$: C, 91.11; H, 4.84%.)

9,10 - *Bis*(3 - *chloro* - 9 - *triptycyl*) *triptycene* - 9,10 - *diperoxycarboxylate* (6)

To 3 (2.08 g, 6 mmol) dissolved in benzene/diethyl ether (120 ml/240 ml) was added BuLi (7.2 mmol) at −50°. The soln was stirred for 30 min and then another 30 min at room temp. The resulting suspension of 3-chloro-9-triptycyllithium was slowly (*ca* 5 hr) added through a double ended needle to dry diethyl ether (200 ml) saturated with O_2 at −70°. The dry O_2 was kept bubbling into the soln. After complete addition, 5 in benzene (60 ml) was added by syringe to the ether soln of the peroxide over 5 min. The cold bath was removed and the mixture was kept stirred overnight. The resulting ppt of LiCl was removed by filtration and the filtrate was reduced to dryness under

Table 1. Kinetic and thermodynamic parameters for the isomerization of labeled diether 1

Temperature (°)	k (s^{-1})	K (*meso*/*dl*)	$\Delta G^{\ddagger}$ (kcal mol^{-1})
238	2.02×10^{-6}	0.48	43.7
258	1.01×10^{-5}	0.51	43.8
281	4.55×10^{-5}	0.48	44.1
305	3.13×10^{-4}	0.47	43.8
317	6.56×10^{-4}	0.51	44.5
332	1.33×10^{-3}	0.48	44.2

reduced pressure without heating to avoid thermal decomposition. The residue was chromatographed on silica gel with a mixture of CH_2Cl_2–n-hexane (1 : 1) to give **6** as a white powder. After recrystallization from chloroform and cyclohexane, 102 mg (10% yield based on **5**) of **6** was obtained: m.p. 110–160° (dec.); IR (KBr) 1770 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.28 (s, 2H), 6.80–7.10 (m, 16H), 7.30–7.50 (m, 6H), 7.60–7.88 (m, 12H).

9,10 - *Bis*(3 - *chloro* - 9 - *triptycyloxy*)*triptycene* (**1**)

Peroxyester **6** (94 mg) was suspended in perfluorodecalin (1 ml) gradually heated to 150° over a period of 1 hr and maintained at that temp for 30 min. After evaporation of the solvent completely, a brown residue was purified by a Lobar column and recrystallization from CH_2Cl_2–MeOH to give a colorless powder in 32% yield: IR (KBr) 1220 cm^{-1}. The obtained isomeric mixture of **1** was separated by means of HPLC on μ-Porasil semipreparative column with 4% CH_2Cl_2 in n-hexane elution: *dl* isomer; m.p. 509°; ^{1}H-NMR ($CDCl_3$) δ 5.48 (s, 2H), 6.76–7.16 (m, 16H), 7.40–7.62 (m, 6H), 7.62–7.92 (m, 12H); HR-MS spectrum for $C_{60}H_{36}O_2{}^{35}Cl_2$, *m*/*e* (calc) 858.2092, *m*/*e* (obsd) 858.2091: meso isomer; m.p. 505°; the same ^{1}H-NMR spectrum as the *dl* isomer.

Kinetic measurements

The rates of isomerization were measured in the temp range 238–332° for solns of the *dl* isomer of **1** in diphenylmethane (*ca* 1.2 mM). Sealed glass capillary tubes (1.0 × 80 mm) containing the soln were immersed in a hot bath.[2d] After a given period of time (a few minutes to several days), samples were taken out of the bath and cooled in ice–water to stop the isomerization reaction. The *dl*/*meso* isomer ratios were obtained by analytical HPLC and analyzed according to Eqs (3) and (4):

$$dl \underset{Kk}{\overset{k}{\rightleftharpoons}} meso \qquad (3)$$

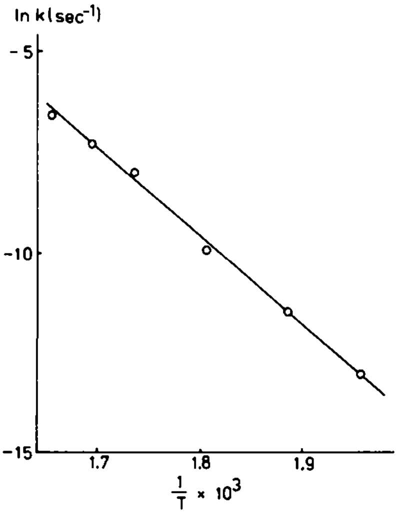


Fig. 5. Arrhenius plots of the rates of interconversion (*dl* → *meso*) of the isomeric diether 1.

$$k(K+1)t = \ln (x_\infty(1+x)/(x_\infty - x)) \qquad (4)$$

where k, K and $x = A_{dl}/A_{meso}$ are the rate constants for isomerization from the *dl* to *meso* isomers, the equilibrium constant defined as C_{dl}/C_{meso}, and the observed ratio of absorbance of the two isomers at 254 nm, respectively. The ratio of molar absorptivity of the two isomers at the same wavelength was unity. In order to obtain x_∞, the samples were heated for several half-lives in the temp range of rapid isomerization. In the case of slow isomerization, they were first equilibrated at higher temp and then heated at a given temp for a few half-lives to save time. Results are given in Table 1 and Fig. 5.

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