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Correlated Rotation in Bis(9-triptycyl)methanes and Bis(9-triptycyl) Ethers. Separation and Interconversion of the Phase Isomers of Labeled Bevel Gears[1]

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Abstract: Several bis(9-triptycyl)methanes and bis(9-triptycyl) ethers have been prepared by the addition of benzynes to bis(9-anthryl)methane and by the thermolysis of 9-triptycyl 9-triptyceneperoxycarboxylates, respectively. The internal rotation in these bevel-gear-shaped molecules was found to be very rapid on the NMR time scale in solution, while the ^{13}C NMR spectra of the ether taken by the CPMAS technique showed the splitting of the bridgehead carbons attached to the oxygen atom, suggesting a frozen conformation with C_s symmetry. Labeling of one of the benzene rings on each triptycene unit in these bis(triptycyl) compounds by introduction of a chlorine atom at the 2- or 3-position gave *dl* and meso isomers in which only the phase relationship of the labeled cogs of the rapidly rotating bevel gear was different. In the *dl* isomer, the labeled cogs can bite each other during each 360° rotation, and every conformer is chiral. In the meso isomer, the labeled teeth are one phase apart and never come next to each other. Its conformers have either a symmetry plane or are *dl* pairs and therefore are achiral. Isolation of the "phase isomers" served as a clue to the high degree of correlation and ruled out the possibility of a noncorrelated pathway in the rapidly geared rotation in these molecules. At elevated temperatures, molecular vibrations become vigorous, and uncorrelated rotation starts to intervene. As a result, interconversion took place between the phase isomers. The rate of the isomerization was determined at 100–350 °C to give the activation parameters for the gear stripping. The ether series offered a bevel gear tighter than the methanes by ca. 10 kcal mol^{-1}. The results are interpreted in terms of a shorter C–O bond length and larger C–O stretching and C–O–C deformation force constants as compared to those of the C–C–C moiety.

Perturbation incurred in a part of a molecule by nonbonded or electrostatic interactions is eventually dispersed throughout the molecule to minimize the unfavorably increased potential energy of the system. As the appropriately coined term "conformational transmission" suggests,[2] the substituents can affect the reactivity of a remote site through progressive structural relaxation within the molecular framework. In some enzymic reactions, structural changes of protein molecules initiated by an inhibitor, an accelerator, or a substrate play an important role (called the induced-fit theory and the allosteric effect)[3] in determining the resultant reactivity. In many of these cases, torsional motion around single bonds is one of the most effective modes of transmitting structural relaxation. It is generally accepted that as a molecule gets overcrowded, the torsional motions are apt to be hindered. Typical examples may be found in the stable atropisomers of biaryls and bridgehead-substituted triptycenes.[4]

The idea of coupled or geared (=disrotatory correlation) rotation has been put forward to explain unexpectedly rapid internal rotaion in the apparently congested molecules.[5] Coupled rotation of two or more parts of a molecule often becomes energetically more feasible than independent rotation of a single group. Cogwheel motions of the rotation of the methyl groups in hexamethylbenzene may provide an intuitively straightforward example.[6] The most probable mode of rotations would be a concerted one with one methyl group rotating clockwise, the neighboring two methyl groups rotating counterclockwise, the methyl groups meta to the first one moving clockwise, and, finally, the para methyl group rotating clockwise. In many cases studied, however, the coupling is not necessarily so favorable as to preclude uncorrelated motion. If we continue the analogy of a gear, stable conformers are usually gear meshed (static gear effect), but their interconversion occurs by gear-clashing (gear-slipping) as well as gear-meshed paths. There is one case of the molecular propellers of the type Ar_3Z for which the need for correlated rotation of the aryl group was conclusively demonstrated by the observation of residual stereoisomers.[7] There are also many cases in which the coupling of more than two rotation was discussed in some detail.[8]

One of the theoretically simplest cases other than molecular propellers is the top–top coupling problem of internal rotation of two methyl groups in two-top molecules. In the potential function for propane[9] and dimethyl ether,[10] for example, 6-fold potentials

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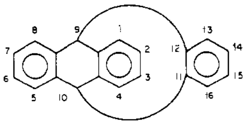
[1] For a preliminary communications, see: (a) Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547. (b) Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1981**, *103*, 958. (c) Kawada, Y.; Iwamura, H. *Tetrahedron Lett.* **1981**, *22*, 1533. Note that numbering of the triptycene skeleton in the present paper is consistent with the 9,10-dihydro-9,10-*o*-benzenoanthracene nomenclature in Chemical Abstracts and different from that in our previous publications.[1]



[2] Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965; p 345.

[3] (a) Monod, J.; Wyman, J.; Changeux, J. P. *J. Mol. Biol.* **1965**, *12*, 88. (b) Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; Chapter 5. (c) Koshland, D. E., Jr. In "The Enzymes"; Boyer, P., Ed.; Academic Press: New York, 1970; Vol. 1, p 341.

[4] Ōki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 87.

[5] (a) Shabacky, M. J.; Johnson, S. M.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1969**, *91*, 7542. (b) Roussel, C.; Chanon, M.; Metzger, J. *Tetrahedron Lett.* **1971**, 1861. (c) Liden, A.; Roussel, C.; Chanon, M.; Metzger, J.; Sandstrom, J. *Ibid.* **1974**, 3629. (d) Roussel, C.; Liden, A.; Chanon, M.; Metzger, J.; Sandstrom, J. *J. Am. Chem. Soc.* **1976**, *98*, 2847. (e) Berg, U.; Roussel, C. *Ibid.* **1980**, *102*, 7848. (f) Hounshell, W. D.; Iroff, L. D.; Iverson, D. J.; Wroczynski, R. J.; Mislow, K. *Isr. J. Chem.* **1980**, *20*, 65. (g) Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 481.

[6] Iroff, L. D. *J. Comput. Chem.* **1980**, *1*, 76 and references cited therein.

[7] (a) Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 3198, 3205. (b) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (c) Glaser, R.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2777.

[8] (a) Gust, D. *J. Am. Chem. Soc.* **19778** *99*, 6980. (b) Wroczynski, R. J.; Iroff, L. D.; Mislow, K. *J. Org. Chem.* **1978**, *43*, 4236. (c) Hounshell, W. D.; Iroff, L. D.; Wroczynski, R. J.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 5212. (d) Wroczynski, R. J.; Mislow, K. *Ibid.* **1979**, *101*, 3980 and references cited therein. (e) Biali, S. E.; Rappoport, Z. *Ibid.* **1981**, *103*, 7350. (f) Nachbar, R. B., Jr.; Johnson, C. A.; Mislow, K., private communication.

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due to the crossed rotational terms are found from the analysis of the microwave spectra to be less than a few percent of the 3-fold barrier for independent rotation. In the course of our elaboration of these two-top molecules in order to design a system in which coupled rotation could be more significant than independent rotation, it occurred to us that the bis(9-triptycyl)-X type molecule has a close structural resemblance to a mechanical bevel gear with three cogs on each wheel. We noted that a rather thin blade of the benzeno groups might be more suited to tight meshing of the gear than more or less spherical groups such as methyl or *tert*-butyl hitherto studied.[8c,d,f] As we see in the next paragraph, the stereochemical consequence of dynamic gearing is dependent on the number of cogs on each wheel and how to label them. A bis(9-triptycyl)-X system with a single label on each triptycene moiety is the simplest case with unique phase isomerism.[11] Quite independently from ours, Mislow and co-workers have developed the problem of the geared system. After counting the number of possible isomers systematically on the basis of group theoretical considerations, they succeeded in separating the *dl* and meso isomers of bis(2,3-dimethyl-9-triptycyl)methane, which were observed to undergo interconversion with the barrier $\Delta G^{\ddagger} = 34.1$ kcal mol^{-1}.[12] We report here very rapid fully coupled rotation around the two C–X bonds in bis(9-triptycyl)-X compounds (X = CH_2 and O), chromatographic separation of the resultant phase isomers of suitably labeled derivatives, and, finally, the high activation energy barrier to interconversion (gear slippage) between the isomers, which shows a marked dependence on the central atom X.

Molecular Design of a System Showing Dynamic Gearing

Bis(9-triptycyl)-X compounds seem to be ideally suited for realizing perfectly geared rotation. Dynamic gearing reveals itself primarily as equivalence of the six benzene rings of the two triptycene units. The equivalence is, however, not a necessary condition for dynamic gearing, because rapid uncorrelated rotation may also explain the same phenomenon. In order to differentiate between the two possibilities, we are compelled to have recourse to the stereochemical consequence of labeling of the benzene ring. We note that when there is high correlation in the torsional motion of the two neighboring C–X bonds, a unique phase relationship should be established between the teeth labeled one each on the triptycene wheels, however fast the rotation may be. In one of the previous papers we showed that the single labeling of a cog in each wheel of a bevel gear made of *m*- and *n*-toothed wheels gives rise to one meso and $(N-1)/2$ *dl* isomers when the greatest common divisor N of numbers m and n is odd (including one) and $N/2$ *dl* isomers when N is even.[1c,13] In the case of our bis(9-triptycyl)-X compounds, $N = 3$, and therefore labeling of one of the benzene rings of each triptycene unit symmetrically should lead to one meso and one *dl* isomer. They are shown perspectively in Figure 1. In one isomer, the labeled cogs bite each other once in a full cycle of rotation, while in the other they are one phase apart and never come next to each other. The former contains three doubly degenerate conformers: a = b, c = f, and d = e. They are all chiral, and the isomer made of these conformers should consist of a *dl* pair. The other isomer contains a doubly degenerate conformer (g = j) with a plane of symmetry and a *dl* pair of conformers both doubly degenerate (h = i and k = l) and therefore should be achiral. We call this isomer meso.

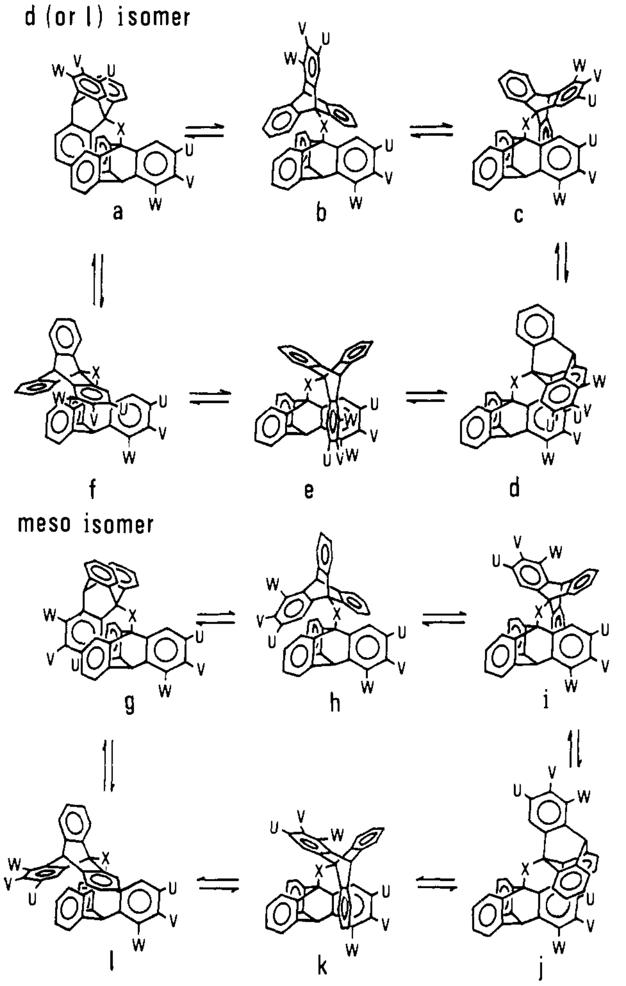

Figure 1. Phase isomers *dl* (a–f) and meso (g–l) of the labeled bis(9-triptycyl)-X compounds. The geared rotation can be very fast, and yet they do not interconvert unless rotation around the two C–X bonds becomes out of gear.

Inspection of molecular models reveals that the labels should preferably be put either at the 3- or 4-position of the benzene ring so as to avoid possible steric interference to the coupled rotation. If the rotation is trapped, there is a chance of generating further isomerism from each phase isomer and making the stereochemical problem more complex.[14] For example, if the substituents at the 1- and 1′-positions destabilize conformers g = j and the rotation passing through these conformers becomes hindered, the meso isomer will now turn into the pair of *dl* isomers h = i and k = l. From the standpoint of a preparative work, however, labeling either of 1- and 4- or of 2- and 3-positions seems to be easier, as there is no need to separate positional isomers of a label in any stage of the synthetic route. Also, the choice of the labeling atoms or groups must be important. Ideally, the substituent effect should be minimal in an electrostatic as well as steric sense. At the same time, the labels have to provide a means of separation of isomers both in the intermediate and final stages. Combining the considerations given above, we decided to make 4,4′-dimethyl derivatives as one of the least perturbed bevel gears and 3,3′-dichloro compounds as a slightly more perturbed one but having a good chance of separation of the resulting isomers. For evaluation of

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(9) Hirota, E.; Matsumura, C.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1124.

(10) (a) Durig, J. R.; Li, Y. S.; Groner, P. *J. Mol. Spectrosc.* **1976**, *62*, 159. (b) Hayashi, M.; Imachi, M. *Chem. Lett.* **1975**, 1249.

(11) We would like to adopt the term "phase isomerism" to describe the phenomenon giving birth to stereoisomers in which only the phase relationship between the labeled cogs is different in the rapidly rotating molecular gears. The term corresponds to "residual stereoisomerism" previously proposed to describe a similar phenomenon due to correlated rotation in molecular propellers.[7]

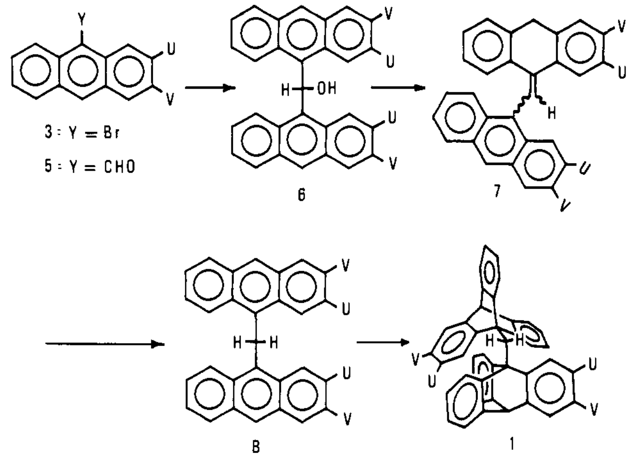
(12) (a) Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961. (b) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957.

(13) Table I in ref 1c should be

the greatest common divisor of m and n		number of isomers	
		meso	*dl*
N	odd (including 1)	1	$(N-1)/2$
N	even	0	$N/2$

(14) The 1-methyl substituent appears not to be enough for effecting further isomerism at ambient temperatures. However, it is enough to restrict gearing on the NMR time scale. See: Johnson, C. A.; Guenzi, A.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6240.

Scheme I



a: U = H, V = H

c: U = Cl, V = H

d: U = H, V = Cl

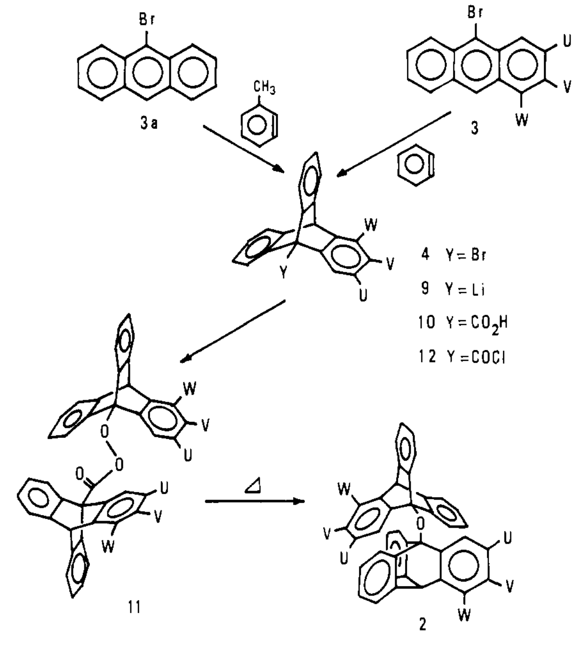
the steric effect to the geared rotation, 2,2'-dichloro compounds were also included.

Bis(9-anthryl)methane (**8a**) has been known for some time,[15] and addition of 2 mol of benzyne to **8a** is a rational approach to bis(9-triptycyl)methane (**1a**). On the other hand, synthesis of bis(9-triptycyl) ether (**2a**) is not so straightforward. 9-Hydroxytriptycene is readily available, but the absence of S_N2 reactivity at the bridgehead position of triptycene derivatives excludes a conventional method for preparing **2a**. It proved impossible to get any reasonable amount of bis(9-anthryl) ether according to the method described in the literature.[16] Several attempts to prepare the ether from 9-bromoanthracene and anthrone under Ullmann conditions have been unsuccessful in our hands. Thus the idea of obtaining **2a** by a method similar to **1a** had to be abandoned at an early stage of our project. A literature search revealed that some ethers had been obtained by decarboxylation of the corresponding peroxyesters in moderate yields.[17] Thermolysis of 9-triptycyl 9-triptyceneperoxycarboxylate (**11a**) to effect cage recombination was thought to provide a reasonable access to **2a**.

Results and Discussion

Synthesis. Bis(9-triptycyl)methanes **1a**, **1c**, and **1d** and bis(9-triptycyl) ethers **2a–d** were prepared according to Schemes I and II, respectively. Separation of positional isomers due to the labeling was performed at the stage of the 9-bromoanthracenes (**3**) for the methane series and 9-bromotriptycenes (**4**) for the ether series by using gel permeation liquid chromatography (GPLC) in most cases.[18]

Scheme II



a: U = H, V = H, W = H

b: U = H, V = H, W = CH_3

c: U = Cl, V = H, W = H

d: U = H, V = Cl, W = H

Addition of 2 mol of benzyne to bis(9-anthryl)methanes (**8**) was carried out by using 7–15 equiv of anthranilic acid to give, first, the corresponding monoadduct as a main product. Employing a further 30 equiv of the benzyne precursor gave the bisadduct **1** together with a small amount of 1,4,9',10'-bisadduct.

The unexpected difficulty encountered in the carbonation of triptycyllithium (**9–10**) has already been reported.[19] As long as a rapid stream of carbon dioxide gas was employed at low temperatures, the reaction course was quite normal, giving a high yield of carboxylic acids **10**. The yields of peroxyesters **11** were not necessarily high, since side reactions leading to the corresponding triptycenes and 9-hydroxytriptycenes always accompanied the formation of the hydroperoxides. Although 1 equiv of acid chloride **12** was used, no 9-triptycyl 9-triptycenecarboxylate was obtained. The amount of **12** could be reduced to 0.4 equiv without affecting the yield. The result may be ascribed to the lower steric demand and higher nucleophilicity of 9-triptyceneperoxy- than 9-triptycyloxylithium.

Decarboxylation of **11** as carried out by thermolysis of a suspension in perfluorodecalin was unexpectedly successful. Especially in the case of unsubstituted **11a**, the yield of **2a** was almost quantitative. So far, the highest yield of an ether product reported in the literature was 75% in the photolysis of *tert*-butyl peroxyacetate in mineral oil.[17] Decarboxylation in our case provides by far the highest yield recorded of the ether from the corresponding peroxyester. There are a number of reasons conceivable for the success of the cage-recombination reaction. First, the peroxyester was so insoluble in perfluorodecalin that decomposition is considered to have taken place in the solid, where diffusion of radical pairs may be neglected. Second, even when some part of the peroxyester was in solution, the translational and/or overall rotational escape from the solvent cage must have been hampered by the steric bulk of 9-triptycyl and 9-triptycyloxy radicals to give efficient recombination between this pair of radicals. The loss of radicals by hydrogen abstraction from solvent molecules was also minimized by using the perfluorinated solvent. Third, a bridgehead cation is inherently unstable, and any degree of polar character, which is often present in the transition state for the decomposition of peroxyesters and can be responsible for the

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[15] Applequist, D. E.; Swart, D. J. *J. Org. Chem.* **1975**, *40*, 1800.

[16] Cooke, W. H.; Heilbron, I. M.; Walker, G. H. *J. Chem. Soc.* **1925**, *127*, 2250.

[17] Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 5175.

[18] Structural assignment was made by ^{1}H NMR. Two 9-bromo-*x*-chloroanthracenes **3c**, melting point 139–140 °C, and **3d**, melting point 134–135 °C, obtained by bromination of 2-chloroanthracene, showed the d_o + d_od_m pattern in the δ 7.9–8.0 and 8.3–8.6 regions, respectively (subscripts o and m denote splitting due to ortho (ca. 8 Hz) and meta (ca. 1 Hz) hydrogens, respectively). When the bromine atom was replaced by the formyl group, **5c** from **3c** showed a d_od_m at δ 8.75 and a d_m at δ 8.95. Thus the assignment is based on the effect of the peri bromine atom and formyl group on the downfield shifts of the nearby hydrogens. Identification of **4c** and **4d** was similarly made on the basis of the multiplet pattern of 1- (δ ~7.8) and 4-protons (δ ~7.4). Whereas **4c** showed gross d_o + d_od_m pattern in the δ 7.4 region, **4d** gave a similar pattern in the δ 7.8 region. The addition of benzyne to **3c** gave **4c**. While the bridgehead protons of **4a**, **4b'**, and **4c** appear at δ 5.4, that of **4b** is shifted downfield (δ 5.66) presumably due to a van der Waals shift caused by proximity of the methyl group. In ref 1b the assignments opposite to the above were erroneously made. Therefore, Figure 2 in ref 1b should be for **2c** instead of **2b**.

[19] Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1981**, *46*, 3357.

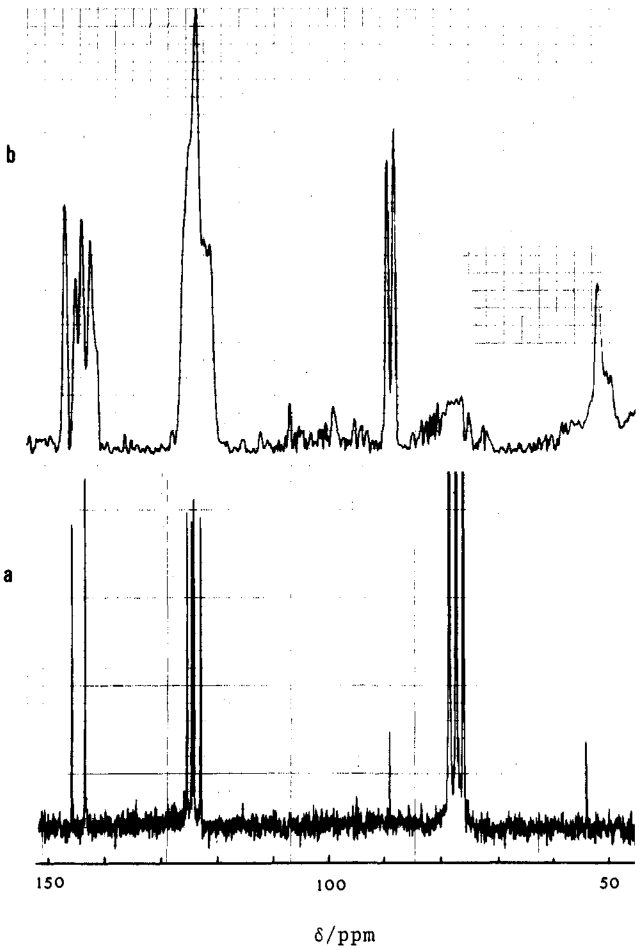
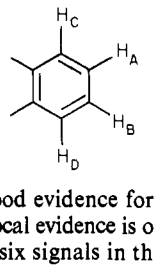


Figure 2. $^{13}C\{^1H\}$ NMR spectra of **2a**: (a) in $CDCl_3$ (25.1 MHz) and (b) as powder (75.46 MHz). The extra signals in the latter are due to imperfect cancellation of the side-band signals.

complication of the reaction by rearrangement in the cation moiety, should be absent here. Triptycyl radicals themselves have no tendency toward rearrangement.[20]

Barrier Height for the Coupled Rotation. ^1H NMR spectra of **1a** and **2a** are very characteristic and are composed of two d_od_m patterns in the δ 7.3–7.9 region for 1- and 4-H and two t_od_m in the δ 6.9–7.2 region, which are assigned to 2- and 3-H having almost equal nuclear spin–spin coupling constants for the two ortho hydrogens, namely, $J_{AB} = J_{AC} = J_{BD} = J_o$, $J_{AD} = J_{BC} = J_m$, and $J_{CD} = J_p \simeq 0$ in the ABCD spin system. Although the simplicity of the NMR spectra is good evidence for the equivalence of the six benzene rings, unequivocal evidence is obtained from ^{13}C NMR spectra that showed only six signals in the aromatic region (See Figure 2).

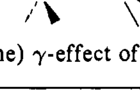


The ground-state conformation is considered to have either C_s or effectively C_s symmetry (vide infra) or C_2 symmetry and to be degenerate 6-fold.[21] Since in each preferred conformation there are four (for C_s) and three (for C_2) different environments for the benzene ring, their apparent equivalence is rationalized more reasonably in terms of rapid interconversion among the degenerate conformers on the NMR time scale than of fortuitous coincidence of chemical shifts for the geometrically different sites. The six-peak ^{13}C spectrum showed essentially no temperature dependence down to −94 °C on dichloromethane-d_2.[1a] Since the unique benzene ring on one triptycene unit that is flanked by two benzene rings of the other triptycene unit should have a considerably different magnetic environment compared with other benzene rings, we can reasonably expect that there may be a 1–3 ppm chemical shift difference present between the unique and outside benzene rings as judged from the ring-current model of Johnson and Bovey.[22] The observed ^{13}C NMR result, showing that the chemical shift difference of this magnitude could possibly be still averaged out at −94 °C, indicates that the barrier height, if present,[12,14] should not be greater than ca. 8 kcal mol^{-1} as calculated by the Eyring equation.

The low barrier should be taken as quite a contrast to the usually high barrier associated with triptycenes carrying more or less axially symmetric substituents at the bridgehead.[4,23] Note that interaction between the opposing peri substituents is so significant that there is a substantial barrier even in 1,2-bis(1-methyl-9-triptycyl)acetylene.[24] It is interesting that once the linear alignment is lost and correlated motion becomes possible, the barrier can get extremely low. Also responsible for the low barrier is the 6-fold degeneracy of the ground state, which inevitably leads to the small difference in free energy between the ground and transition states.

Supposing that the barrier for the geared rotation in these bis(9-triptycyl)-X compounds **1** and **2** may be as low as predicted by the moleular mechanical calculations,[11,13] we then became interested in the ^{13}C NMR spectra of these compounds in the solid state. It is well-known that when a molecule is present in several conformations that differ only by no more than a few kilocalories per mole in internal energy, crystal-packing forces often play a decisive role in determining molecular geometry and allow one particular conformer to dominate others. It is claimed recently that very fast reactions, e.g., chemical-exchange processes in metal complexes and valence tautomerization that involves almost no gross structural change, may be considerably retarded in the solid phase relative to those in fluid solution.[25]

^{13}C NMR spectra of **1a** and **1b** taken by the CPMAS technique on powdered samples revealed splitting of the ^{13}C signals obtained in solution into two or more lines. The spectrum of **2a** is reproduced in Figure 2b. The splitting in the aromatic region amounts to ca. 3 ppm, supporting our previous assumption used for estimating the geared rotational barrier. Notice that the two carbon atoms attached to the oxygen (δ 89.08 in $CDCl_3$) are now nonequivalent (Δδ = 1.3). The observation of the split signals leads to two conclusions. Firstly, if the chemical shifts are governed by internal stereoelectronic factors, the benzene ring carbons should split into 18 and 24 signals depending on the C_2 and C_s symmetry conformations, respectively, although the signal resolution is not that high. The unequivalent bridgehead carbon attached to the oxygen seems to indicate that the frozen conformation has C_s rather than C_2 symmetry. Notice that the unsubstituted bridgehead carbons appear not to split further. The origin of the observed chemical shift nonequivalence is not clear at the moment. Either the different conformational disposition of C-9's with respect to the lone pair of electrons on oxygen, the different (cis and gauche) γ-effect of the other triptycene unit,



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(20) (a) Bartlett, P. D.; Lewis, E. S. *J. Am. Chem. Soc.* **1950**, *72* 1005. (b) Bartlett, P. D.; Greene, F. D. *Ibid.* **1954**, *76*, 1088.

(21) The molecular structure of **1a** has been shown by X-ray crystallography and the empirical force field method to have C_2 symmetry (Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerström, O.; Mislow, K. *J. Am. Chem. Soc.* **1982**, *104*, 5163). Our solid-state NMR data suggest the C_s conformation of **2a** (see text).

(22) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(23) (a) Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1973**, 232. (b) Schwartz, L. H.; Koukotas, C.; Yu, C. *J. Am. Chem. Soc.* **1977**, *99*, 7710. (c) Otsuka, S.; Mitsuhashi, T.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3663.

(24) Mew, P. K. T.; Vogtle, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 159.

(25) (a) Lyerla, J. R.; Fyfe, C. A.; Yannoni, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 1351. (b) Miller, R. D.; Yannoni, C. S. *Ibid.* **1980**, *102*, 7396 and references cited therein.

or the differential anisotropy of the benzene rings may be reponsible for the observed chemical shift difference in the frozen system.[26]

In principle, however, the symmetry of a molecule in a crystal is defined by the set of symmetry operations of the space group rather than symmetry within the molecule. Unless a molecule lies on a crystallographic symmetry element, it is asymmetric. Even C_2 symmetry could show nonequivalent C-9 and C′-9. Therefore, the foregoing statement should be taken with reservation until the latter possibility is ruled out by the observation of a coalescence phenomenon in a variable-temperature NMR study on the solid sample.[25a]

Separation of the Phase Isomers. Molecular models suggest that the barrier height for the gear slippage cannot be as low as 8 kcal mol^{-1}. As already pointed out, however, the averaged NMR signals could be explained also by such a process. Lack of gear slippage at all should be demonstrated unequivocally by separation of the phase isomers. A barrier height to the gear slippage high enough to separate the isomers was guaranteed by the conventional DNMR technique applied to **2b**.

The ^{13}C NMR spectrum of **2b** is composed of a closely spaced 1:2 doublet, 1:1:1 triplet, or of their superposition and clearly shows the presence of the meso and *dl* isomers in a nearly statistical 1:2 ratio. The measurement was made at 25 MHz and at ambient temperatures. When subjected to higher temperature measurements in 1,1,2,2-tetrachloroethane-d_2 solution, a pair of the corresponding signals separated by a chemical shift as small as 1.4 Hz (for the carbons bearing the methyl substituent) showed no sign of coalescence at all even at 150 °C. Thus we can easily estimate the barrier height as larger than 25 kcal mol^{-1} on the basis of the Eyring equation.

Separation of the isomers of **2b** has, however, not been achieved yet in spite of our thorough attempts, which included fractional crystallization, HPLC on both normal- and reversed-phase columns (3 × 1 ft standard columns in both cases), and chromatograph on silica gel impregnated with 20% silver nitrate. Apparently the small difference in physical properties between the meso and *dl* isomers produced by the methyl group at the 4-position of the bis(triptycyl) skeleton may not be large enough to make their separation possible. In this regard, it is quite surprising that the meso and *dl* isomers of the 2,2′,3,3′-tetramethyl derivative of **1** are easily separated by column chromatography on silica of small particle size.[10b] Substituents at the 2- and/or 3-positions seem to help separation even when they are nonpolar alkyl groups. Whereas the 4-substituent is situated in the periphery of the bis(triptycyl) molecule, the 2-substituent seems to be particularly subject to the environmental change from one conformation to another and may be responsible for bigger difference in the macroscopic properties of the molecules.

Indeed 2- and 3-chloro-substituted derivatives **1c**, **1d**, **2c**, and **2d** were easily separated by normal-phase HPLC. Isolation of the pure *dl* isomer, which was usually present in 1.6- to 2-fold excess over the meso isomer as predicted statistically, was possible by mere recrystallization in the case of **2d**. As judged from the retention volumes of HPLC, the polarity of the compounds appears to be in the order *dl* isomers > meso isomers, 2-chloro derivatives > 3-chloro derivatives and methanes **1** > ethers **2**. The trend can be partly rationalized by considering the mutual orientation of the C–Cl and C–O bond dipoles (ca. 1.5 and 0.8 D, respectively)[27] in each conformation. For example, the angle of the two C–Cl bonds in the *dl* isomers is considered to be smaller than that in the meso isomers for most of the conformers. Comparison of the 2- and 3-chloro derivatives on the basis of molecular models provides a similar rationale (vide infra).

The ^{13}C NMR data for the isolated isomers are collected in Table I. Although ethers **2** showed normal melting behavior, namely, no isomerization in the solid phase up to the melting point, the methane isomers had practically common melting points starting from either of the two isomers. Isomerization before melting of the crystals seems to have taken place here, suggesting lower barrier for gear slippage (vide infra).

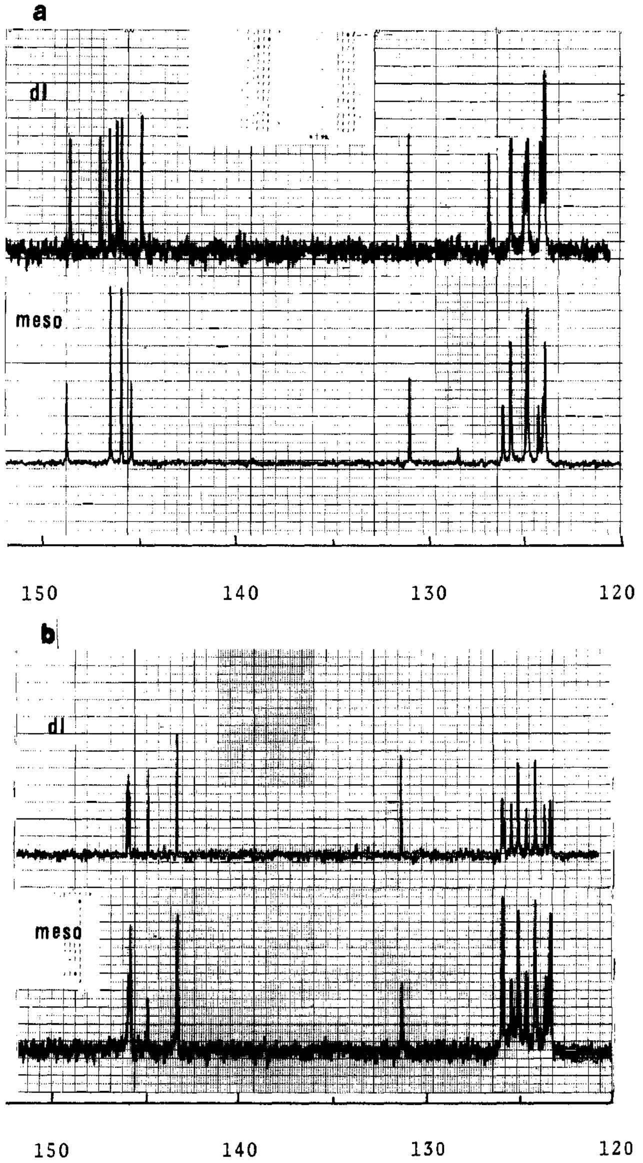

Figure 3. 25.1-MHz ^{13}C NMR spectra of (a) **1d** and (b) **2d** in CDCl$_3$ (the aromatic regions only).

NMR Spectral Assignments. Nearly two-to-one product ratios of the isolated isomers are fully indicative of the *dl* and meso forms for the more abundant and less abundant products, respectively. More rigorous structural assignments of the isomers are obtained by their NMR spectra. While the two unsubstituted benzene rings of a meso isomer are magnetically equivalent, those of a *dl* isomer are diastereotopic. Accordingly, a meso isomer should give 12 ^{13}C signals in the aromatic region, among which 6 will have a unit intensity while the other 6 will be twice as strong. The *dl* isomer should show 18 signals of equal intensity. In Figure 3 are given the ^{13}C spectra of **1d** and **2d** for both isomers. While the signals due to the substituted and unsubstituted benzene rings are easily distinguished from the intensity consideration for the meso isomers, it does not hold for the *dl* isomers.

Assignments were carried out on the basis of selective and off-resonance decouplings, undecoupled measurements, substituent effects of the methyl group and chlorine atom shielding the para and deshielding the ortho and meta positions,[28] and comparison

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(26) (a) Cremer, D.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 6900. (b) Epiotis, N. D.; Yates, R. L. *Ibid.* **1976**, *98*, 461.

(27) Smyth, C. P. "Dielectric Behavior and Structure"; McGraw-Hill: New York, 1955.

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Table I. ^{13}C NMR Chemical Shifts (ppm from Internal Me_4Si) for Triptycene Derivatives

compound	isomer	C-1 C-8 C-13	C-2 C-7 C-14	C-3 C-6 C-15	C-4 C-5 C-16	C-4a C-10a C-11	C-9a C-8a C-12	C-9	C-10	others
triptycene		123.79	125.31	125.31	123.79	145.51	145.51	53.57	53.57	
9-methyltriptycene		121.01	125.09	125.19	123.51	146.67	147.44	49.34	54.27	13.22 (CH_3)
1a		125.07	124.57	125.42	123.71	146.67	146.95	55.35	55.12	25.78 (CH_2)
2-chlorotriptycene		124.24	130.68	124.74	125.07	144.12	147.46	53.57	53.85	
		123.79	125.56	125.51	123.91	145.09	144.74			
1c	meso	125.91	130.21	125.04	124.53	145.54	148.41	54.72	54.63	25.55 (CH_2)
		124.91	124.97	125.91	123.92	146.09	146.27			
1c	*dl*	124.76	130.56	125.64	124.97	145.41	149.29	54.98	54.67	25.55 (CH_2)
		125.84	124.61	125.35	123.71	146.25	145.44			
		124.97	124.97	125.91	123.92	146.05	146.34			
1d	meso	126.20	124.24	131.02	124.09	148.74	145.40	54.86	54.72	25.80 (CH_2)
		124.91	124.96	125.78	123.99	145.91	146.47			
1d	*dl*	126.91	124.23	131.06	124.05	148.56	144.83	54.86	54.72	25.76 (CH_2)
		124.16	125.06	125.75	124.03	146.12	146.98			
		124.88	124.95	125.80	124.01	145.81	146.51			
9-hydroxytriptycene		118.94	125.00	125.35	123.12	143.61	145.72	80.73	52.67	
2a		124.23	124.62	125.46	123.00	143.79	146.14	89.08	53.67	
9-hydroxy-4-methyltriptycene		116.91	124.92	127.26	131.69	142.07	146.17	80.97	49.10	18.44 (CH_3)
		119.22	125.31	125.88	123.99	143.75	146.36			
2b	meso	122.45	124.42	127.26	131.27	142.17	146.72	89.39	49.91	18.66 (CH_3)
		124.66	124.85	125.59	123.24	143.91	146.69			
2b	*dl*	122.07	124.54	127.26	131.30	142.24	147.01	89.41	49.88	18.71 (CH_3)
		125.04	124.73	125.59	123.24	143.85	146.36			
		124.66	124.85	125.59	123.24	143.88	146.72			
2-chloro-9-hydroxytriptycene		120.31	131.21	125.44	124.49	142.52	148.24	80.73	52.67	
		119.29	125.51	125.93	123.51	143.61	145.44			
2c	meso	124.91	130.68	125.55	124.28	142.79	147.79	88.96	53.12	
		124.28	125.14	126.09	123.35	143.51	145.62			
2c	*dl*	123.59	131.23	125.69	124.38	142.75	149.31	89.06	53.10	
		125.64	124.58	125.93	123.28	143.67	144.16			
		124.28	125.21	126.10	123.34	143.44	145.78			
3-chloro-9-hydroxytriptycene		120.58	125.11	131.17	123.86	145.78	144.80	80.62	52.50	
		119.14	125.54	125.89	123.59	143.28	145.66			
2d	meso	125.51	124.71	131.23	123.69	145.94	144.90	88.98	53.30	
		124.24	125.13	125.99	123.44	143.30	145.82			
		124.21	125.14	131.36	123.71	145.86	144.80	88.98	53.28	
2d	*dl*	125.50	124.68	125.95	123.39	143.26	145.96			
		124.21	125.14	125.98	123.42	143.28	145.82			

of chemical shifts with those of reference compounds. For ethers **2**, assignments of the ^{13}C signals were more straightforward since selective decoupling was effectively applied to more widely separated ^{1}H NMR signals. The bridging oxygen was also helpful in effecting larger chemical shift differences between the two bridgehead carbons.

Of the two lowest field signals for the quaternary ring carbons of **2a**, the higher field one at δ 143.8 was affected more by selective irradiation at the bridgehead proton. Therefore the carbon signals at ca. δ 143 were always assigned to carbon 4a. The assignment was supported independently by the presence of long-range coupling (ca. 0.8 Hz)[29] with the 4-methyl protons. The ortho carbons of toluene show such a long-range coupling. The ring substituent effects are also compatible with this assignment of the bridgehead carbons. For example, a 2-chlorine atom induces a 1.0 ppm upfield and a 1.7 ppm downfield shift of the 4a-carbon (para to Cl) and the 9a-carbon (meta to Cl), respectively, in the meso isomer of **2c**.

It was the two quaternary ring carbons of the methane series that were most difficult to distinguish. They are usually separated into two groups, one of which has a less complicated pattern in the undecoupled spectra and is more affected by the irradiation of the bridgehead proton than the other. By analogy with the ethers, the former was tentatively assigned to the 4a-carbons.

By inspection of molecular models, the ring-current effects of the neighboring benzene rings are estimated to be shielding when the benzene ring under consideration is flanked by two benzene rings of the other triptycene unit. The shielding effects will be in the order: 1- > 2- > 3- > 4-carbons. The positions 4a and 9a are estimated not to be influenced very much. The 1-, 2-, and 3-carbons of the two flanking benzene rings are also situated in the shielding zone. The 4a- and 9a-positions are now in the deshielding zone. The benzene rings in the other disposition seem to suffer deshielding effects that are stronger on the 1-, 2-, and 9a-carbons than on the 3-, 4-, and 4a-carbons. The observed shifts of each carbon are the weighted average of the six possible conformations.

When ^{13}C chemical shift values of **1a** and **2a** are compared with those of 9-methyl- and 9-hydroxytriptycenes, respectively, we find that the above estimation works in a number of cases. However, a large downfield shift ($\Delta\delta$ 4.1 and 5.3 for **1a** and **2a**, respectively) found for position 1 and the equivalent carbons is considerably more than is explicable in terms of the anisotropy. A van der Waals shift due to severe congestion may be contributing to the downfield shift of the carbons at these positions.

The difference in chemical shifts among positional isomers of the substitutent and between the meso and *dl* isomers is considered to be due to differential effects of anisotropy of the benzene rings caused by deviation of the population of each conformer from the statistical $^1/_6$. When the unsubstituted benzene rings are compared, we note that the chemical shifts for the carbons of the outer 5-, 6-, 10a-, 11-, 15-, and 16-positions are reasonably constant. In order to make the trends in chemical shifts clearer, we give in Figure 4 chemical shift differences ($\Delta\delta$) between the meso and *dl* isomers and the magnetic nonequivalence of the two unsubstituted benzene rings of the *dl* isomers, respectively. Apart from the 3-chloro-substituted methane (**1c**), $\Delta\delta$ values are mostly within ±0.2 ppm for 3-, 4-, 4a-, and their equivalent positions. **1c** seems to have a considerably biased population as judged from larger $\Delta\delta$ values even for the outer carbons. The equilibrated isomer ratio *dl*/meso for this compound is abnormal (vide infra). For the inner carbons (1, 2, 9a, and their equivalents), a difference

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[29] The aromatic hydrogens were selectively decoupled.

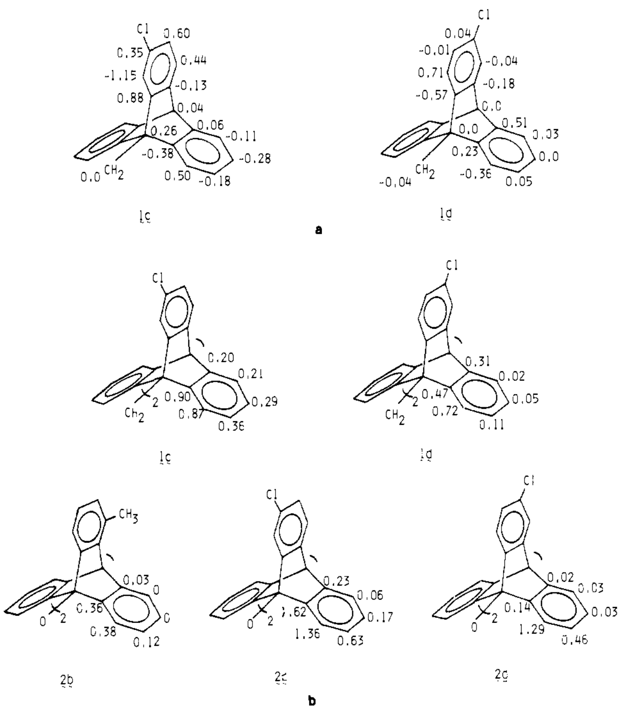

Figure 4. ^{13}C NMR chemical shift differences ($\Delta\delta$) between the meso and *dl* isomers (the mean values are used for the diastereotopic positions of the latter) in **1c** and **1d** (a) and the magnetic nonequivalence of the two diastereotopic unsubstituted benzene rings of the *dl* isomers (b).

up to 1.6 ppm was found. These values are largest in **1c** and **2c** and smallest in **2b** and, therefore, show the largest substituent effect for the 2-chloro and the smallest for the 4-methyl groups. Correlation between $\Delta\delta$ and magnetic nonequivalence is quite clear.

As one (ring a) of the two unsubstituted benzene rings of the *dl* isomers occupies a magnetic environment similar to that of the substituted benzene ring and the other (ring b) that of the unsubstituted benzene ring of the corresponding meso isomer, ring a is considered to have similar $\Delta\delta$ values to the substituted benzene ring while ring b should show smaller $\Delta\delta$ values as long as populational deviation of each conformer from $^1/_6$ remains small. This is found to be the case, and the values on the second and third rows in Table I for the *dl* isomers are arranged this way, the second row having $\Delta\delta$ values similar to those of the substituted benzene ring.

Interconversion of the Meso and *dl* Isomers. When the rate of geared rotation is increased by raising the temperature, there should be a certain temperature at which the molecular vibrations become so vigorous that the torsional motion gets easily out of gear. This gear slippage should be observed as interconversion of the meso and *dl* isomers. The isomerization rates were determined on diphenylmethane solutions of **2c** and **2d** and *o*-dichlorobenzene solutions of **1c** and **1d**. We achieved higher accuracy by starting from a pure sample of the meso isomer in each case. Convenient temperature ranges for the measurements proved to be 200–330 °C for the ethers and 110–210 °C for the methanes. A possible mechamism of the isomerization involving a homolysis–recombination pathway was ruled out by the observation that no trace of the corresponding triptycene was detected after the isomerization experiments, even in a good hydrogen-donating solvent like diphenylmethane. The high reactivity of the triptycyl radical ensures that, when it is formed, triptycene results.

The results of the kinetic studies and the Arrhenius plots of the rate constants at several temperatures (Figure 5) are summarized in Table II. We first note that the activation energy values of the ethers are higher than those of the correspondingly substituted methanes by about 10 kcal mol^{-1}. Relative rates of isomerization compared at 200 °C (Table III) differ by a factor of 10^4. Prior to this study, we had thought intuitively and incorrectly that a possible inversion at the divalent oxygen[30] might give rise to a looser gear for the ethers. The markedly higher barriers observed for the ethers are now consistent with the Mulliken–Walsh diagram[31] and are ascribed to a combined structural effect of the shorter C–X bond length (1.410 Å of $(CH_3)_2O$[32] vs. 1.526 Å of $(CH_3)_2CH_2$,[33] for example), the larger C–X stretching force constant (4.38 mdyn $Å^{-1}$ for $(CH_3CH_2)_2O$ vs. 3.7 mdyn $Å^{-1}$ for $(CH_3CH_2)_2CH_2$[34]), and to the larger C–X–C bending force constant (0.30 dyne $Å^{-1}$ for $(CH_3CH_2)_2O$ vs. 0.20 mdyn $Å^{-1}$ for $(CH_3CH_2)_2CH_2$[34]) for the ethers as compared to the methanes. Accordingly, bis(9-triptycyl)silanes or sulfides in which the central atom X of our bis(triptycyl)-X system is a silicon or sulfur atom are expected to show less strict dynamic gearing, since the relevant bond lengths are longer and the force constants for the deformation are smaller here. Our preliminary results on bis(3-chloro-9-triptycyl)silane support the prediction.[35]

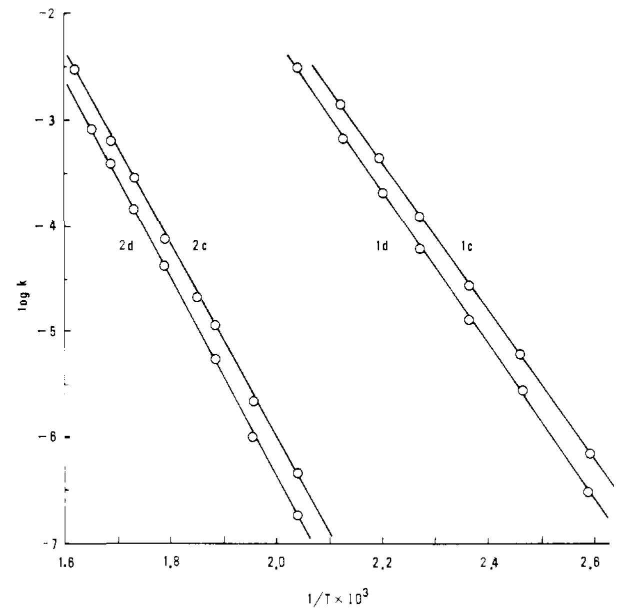

Figure 5. Arrhenius plots of the rates of interconversion of the phase isomers due to gear slippage in **1c**, **1d**, **2c**, and **2d**.

Table II. Activation Parameters for Throwing the Bis(9-triptycyl)-X Molecules Out of Gear

	X	U	V	W	E_a, kcal mol^{-1}	log A	K (*dl*/meso)
1c[a]	CH_2	Cl	H	H	32.2 ± 0.1	12.1 ± 0.1	1.65 ± 0.01
1d[a]	CH_2	H	Cl	H	33.1 ± 0.2	12.2 ± 0.1	1.86 ± 0.01
2c[b]	O	Cl	H	H	42.0 ± 0.5	12.3 ± 0.2	1.90 ± 0.03
2d[b]	O	H	Cl	H	43.2 ± 0.3	12.5 ± 0.1	1.89 ± 0.01

[a] In *o*-dichlorobenzene. [b] In diphenylmethane.

Table III. Relative Rates for the Gear Slippage of the Bis(9-triptycyl)-X Compounds at 200 °C

	X	U	V	W	k_{rel} (200 °C)
1c	CH_2	Cl	H	H	4.60×10^4
1d	CH_2	H	Cl	H	2.48×10^4
2c	O	Cl	H	H	2.41
2d	O	H	Cl	H	1

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(30) Gordon, A. J.; Gallagher, J. P. *Tetrahedron Lett.* **1970**, 2541.

(31) Buenker, R. J.; Peyerimhoff, S. D. *Chem. Rev.* **1974**, *74*, 127.

(32) (a) Kasai, P. H.; Myers, R. J. *J. Chem. Phys.* **1959**, *30*, 1096L. (b) Blukis, U.; Kasai, P. H.; Meyers, R. J. *Ibid.* **1963**, *38*, 2753.

(33) Lide, D. R. *J. Chem. Phys.* **1960**, *33*, 1514.

(34) Hayashi, M. *Nippon Kaguka Zasshi* **1957**, *78*, 222.

(35) Presence of the phase isomers of the silane was indicated by ^{13}C NMR and activation energy barrier for isomerization was determined by the conventional DNMR technique to be ca. 19 kcal mol^{-1}. The value was not high enough to warrant separation of the isomers at ambient temperatures. Presented in a preliminary form at the 14th Symposium on Structural Organic Chemistry in Okayama, Japan, October 13, 1981.

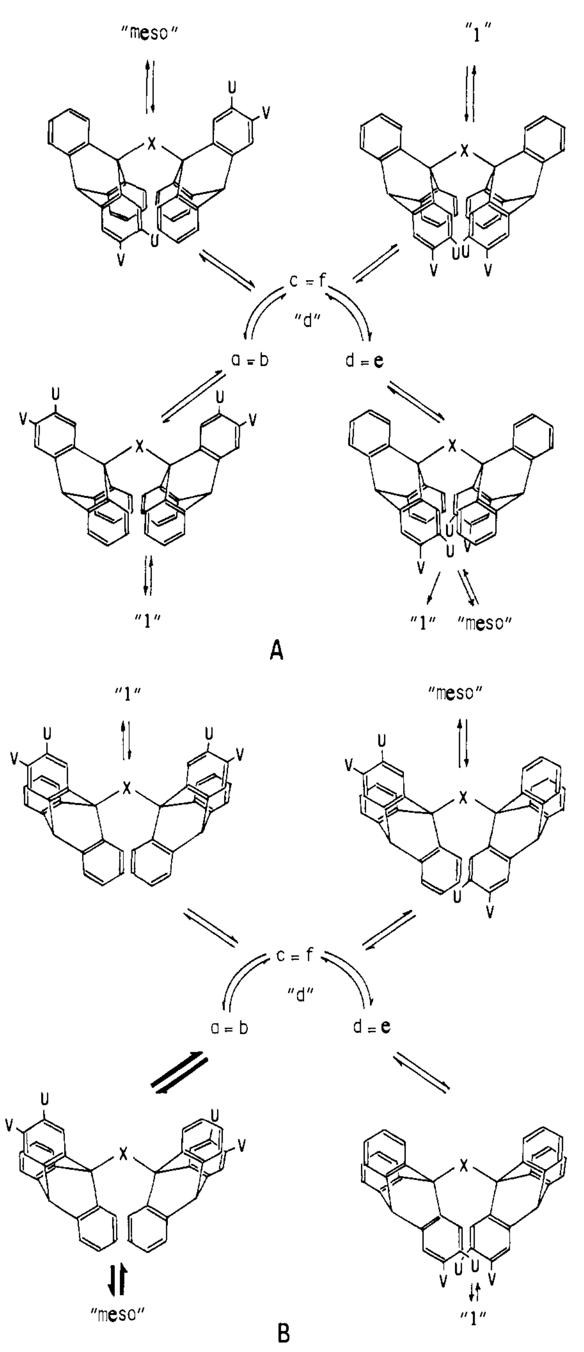

Figure 6. Transition-state structures A and B for the interconversion of the *dl* and meso isomers of the labeled bis(9-triptycyl)-X compounds. The bold arrows indicate the isomerization path in which the substituted benzene rings are not involved in the nonbonded interaction. Conformations a = b, c = f, and d = e (see Figure 1) are assumed to represent the *d* isomer.

Secondly, surprisingly small differences in activation energy between 2- and 3-chloro compounds are noted. According to molecular models, any transition-state structure conceivable for the isomerization of these compounds is extremely congested at the 1- and possibly 2-positions. We need therefore to invoke a transition state in which the substituted benzene rings do not interact very much. Mislow and co-workers proposed two possible transition-state structures A and B as shown in Figure 6.[12] Preliminary molecular mechanical calculations favored A where the two benzene rings of each triptycene unit interact significantly. In B, only one benzene ring in each triptycyl group opposes each other. The stereochemical pathways of the gear slippage starting from one of the optical anipodes of the *dl* isomer through each transition state are given in Figure 6. It is clear that isomerization to the meso isomer through transition state A requires significant interaction of the substituted benzene ring with the other triptycene unit. It would be difficult to rationalize the small difference in activation energy between the 2- and 3-chloro compounds in terms of this transition state. Such an interaction of the substituted benzene ring appears not to be required for transition state B, since there is a channel through which the meso isomer can be formed. According to state-of-the-art empirical force field calculations,[36,37] however, the above discussion based on molecular models seems to be oversimplification; the transition state for gear slippage has two benzene rings within one triptycene unit squeezed together and tucked into the notch between two rings in the other triptycene moiety.

Coming back to the comparison of our results with simple two-stop molecules, we recall that one of the simplest forms for the potential function can be given as

$$V(\alpha_1, \alpha_2) = \frac{1}{2}V_3(1 - \cos 3\alpha_1) + \frac{1}{2}V_3(1 - \cos 3\alpha_2) + \frac{1}{2}V_{33}(\cos 3\alpha_1)(\cos 3\alpha_2) + \frac{1}{2}V_{33}'(\sin 3\alpha_1)(\sin 3\alpha_2) \qquad (1)$$

where α_1 and α_2 are the torsional angle of the neighboring two C–X bonds. The first two terms are for independent rotation around the 3-fold axis and the last two cross terms represent coupled rotation. Analyses of multiplet splitting patterns of microwave transitions in the ground and first two torsional excited states have given the following potential coefficient values:

$V_3 = 3325$ and $V_{33}' = -170$ cal mol^{-1} for propane[9]

$V_3 = 2599$ and $V_{33}' = -14.5$ cal mol^{-1} for dimethyl ether[10]

V_{33}' values are not greater than ca. 5% of V_3 in both cases. Our present results correspond to the case $|V_{33}'| \simeq |V_{33}| >> V_3$, which leads to the potential function as

$$V(\alpha_1, \alpha_2) = -\frac{V_{33}' - V_{33}}{2}\cos 3(\alpha_1 + \alpha_2) + \frac{V_{33} + V_{33}'}{2}\cos 3(\alpha_1 - \alpha_2) \qquad (2)$$

The Ramachandran diagram showing the two-dimensional potential energy contour map will then have a series of steep valleys of the depth of $(|V_{33}| + |V_{33}'|)/2$ along $\alpha_1 = -\alpha_2 \pm (2n\pi/3)$. There will be shallow basins in the valley at every 60° disrotation.[36]

For a third, the values of the equilibrium constants *K* are very close to 2 as expected statistically. A closer examination of the data in Table II reveals, however, a significant deviation of population toward the meso isomers. In the temperature ranges studied, no dependence of the *K* values on temperature was observed. Therefore some of the conformers in the *dl* isomers must be less populated than the statistically expected $^1/_6$. Assuming the C_s ground-state geometry for the molecular framework of **1** and **2** and the central C–X–C angles of ca. 130°,[36,37] we get from molecular models a fairly long distance (≥9 Å) between the two chlorine atoms and a large angle (≥120°) between the two C–Cl bond dipoles (ca. 1.5 D) for all the conformations of the meso isomers. Thus the meso isomers are considered to be perturbed only slightly and rather stabilized in terms of the electrostatic interaction between the two C–Cl dipoles. In contrast, the electrostatic interactions are expected to be larger in the *dl* isomers because of a close disposition of the two chlorine atoms and to be strongly dependent on the conformations. Conformations a = b and c = f of **1c** and **2c** will be destabilized, while d = e will be favored. Thus the deviation of the *K* values from 2 favoring

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(36) The picture is consistent with preliminary molecular mechanics calculations: Osawa, E., private communications. See also the preceding papers by Mislow et al. in this issue.

(37) By the analogy of the observed central C–C–C bond angles in several bis(9-triptycyl)methanes[12b,21] and the similarly expanded central bond angle in bis(triphenylmethyl) ether (Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 696). See also: Blount, J. F.; Gutierrez, A.; Mislow, K. *J. Org. Chem.* **1982**, *47*, 4359.

the meso isomers is qualitatively in the expected direction when the chlorine atoms are taken into account.

Experimental Section

General Methods. ^{1}H NMR spectra were taken on Varian EM-390 (90 MHz) and JEOL FX-100 (99.6 MHz) spectrometers. Chemical shift values (δ) are reported in ppm downfield from internal tetramethylsilane. ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer (25.0 MHz) with tetramethylsilane as an internal standard. Routine measurements were performed by using 8K data points over 4000-Hz spectral width under a 45° pulse. Higher resolution was achieved by using 8 or 16K data points over 800-Hz spectral width or less. High-resolution solid ^{13}C NMR spectra (75.46 MHz) were taken on a Bruker CXP-300 spectrometer by employing magic angle spinning, cross polarization, and high-power decoupling techniques. A cross polarization time of 2.5 ms and recycle time of 2 s were applied to a sample rotating at 3.1 and 3.5 kHz. Infrared spectra were recorded on a Hitachi 295 infrared spectrophotometer.

Melting points were determined by use of a Laboratory Device Mel-Temp melting point apparatus and are uncorrected. For some compounds that had a high melting point or were prone to decomposition, a Du Pont 990 Thermal Analyzer was used in the differential scanning calorimetry mode, and the extrapolated temperature of onset of an endothermic curve obtained with a scanning rate of 2–5 °C min^{-1} was taken as the melting point. Microanalyses were performed either at the Microanalysis Center of Wako Pure Chemical Co., Ltd., or the Elemental Analysis Center of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparative chromatography was done with quartz columns packed either with Wako C-200 silica gel or Wako activated alumina containing 1% fluorescence indicator, Lobar columns (size B, Merck) equipped with a Duramat pump and an Altex UV detector, and PLC plates of silica gel 60 F^{254} (25 × 25 cm, 2-mm thick, Merck) with a mixture of hexane and methylene chloride as eluent. Gel permeation chromatography (GPLC) was performed on a series of JAIGEL 1H and 2H columns with a flow of 2.5–3 mL min^{-1} of chloroform on an LC-08 Liquid Chromatograph of Japan Analytical Industry Co. Ltd. HPLC was performed on a Waters Model ALC/GPC 244 apparatus with μPorasil columns. Preparative work on a $^3/_8$ in. × 1 ft column was done with a flow of 2.5–5 mL min^{-1} of a mixture either of benzene/hexane or chloroform/hexane. A flow of 1–2 mL min^{-1} was employed in analytical works on two or three $^1/_4$ in. × 1 ft columns connected in series.

All the reactions employing lithium reagents were carried out under dry nitrogen atmosphere on a standard Schlenk line. All the chemicals were used as accepted except for drying when necessary.

2-Chloroanthracene. 2-Chloroanthraquinone was reduced with aluminum tris(cyclohexyl oxide) in cyclohexanol according to the procedure described in the literature[38] to give 2-chloroanthracene in 65% yield: mp 223–224 °C (lit.[39] mp 215 °C).

2-Chloro- (3c) and 3-Chloro-9-bromoanthracenes (3d). 2-Chloroanthracene was brominated with copper(II) bromide in a procedure similar to the bromination of anthracene[40] to give a ca. 3:1 mixture of **3c** and **3d**[18] in quantitative yield. To the contrary, the mixture obtained by bromination to 2-chloro-9,10-dibromoanthracene with 2 equiv of copper(II) bromine (in quantitative yield) followed by debromination with successive treatment with 1.05 equiv of butyllithium and water in diethyl ether (85% yield) was slightly dominated by **3d** (**3c**:**3d** = 49:51). Separation of **3c** and **3d** was performed by GPLC. About 300 mg of the mixture were separated after 1 day of recycling, **3c** being eluted first: light yellow needles, mp 139–140 °C (from CH_2Cl_2/hexane) (lit.[41] mp 129–131 °C); ^{1}H NMR ($CDCl_3$) [18]δ 7.27–7.73 (m, 3 H), 7.87–8.03 (d_o + d_od_m, 2 H), 8.38 (s, 1 H), 8.37–8.60 (d_m + d_od_m, 2 H).

3d: light yellow needles, mp 134–135 °C (from CH_2Cl_2/hexane); ^{1}H NMR ($CDCl_3$) δ 7.27–7.70 (m, 3 H), 7.77–8.00 (d_m + d_od_m, 2 H), 8.23 (s, 1 H), 8.33–8.56 (d_o + d_od_m, 2 H). Anal. Calcd for $C_{14}H_8BrCl$: C, 57.76; H, 2.76; Br, 27.41; Cl, 12.16. Found: C, 57.75; H, 2.48; Br, 27.39; Cl, 12.15.

2-Chloro-9,10-dibromoanthracene: bright yellow needles, mp 182–183 °C(from benzene); ^{1}H NMR ($CDCl_3$) δ 7.40–7.80 (m, 3 H), 8.40–8.70 (m, 4 H). Anal. Calcd for $C_{14}H_7Br_2Cl$: C, 45.39; H, 1.90; Br, 43.14; Cl, 9.56. Found: C, 45.30; H, 1.67; Br, 43.41; Cl, 9.63.

2-Chloro-9-anthracenecarboxyaldehyde (5c). To a suspension of **3c** (2 g, 6.8 mmol) in diethyl ether (70 mL) was added butyllithium (5.1 mL of 1.6 M in hexane (Merck), 1.2 equiv) at -20 °C. After 30 min, DMF (1 mL, excess) was added, and the resultant mixture was stirred overnight at room temperature. Usual workup gave 1.63 g of the crude product. Recrystallization from benzene/hexane gave 1.14 g (70%) of **5c**: bright yellow needles, mp 151–152 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 7.27–7.73 (m, 3 H), 7.24–8.00 (d_o + d_od_m, 2 H), 8.34 (s, 1 H), 8.75 (d_od_m, 1 H), 8.95 (d_m, 1 H), 11.28 (s, 1 H). Anal. Calcd for $C_{15}H_9ClO$: C, 74.85; H, 3.77. Found: C, 75.05; H, 3.56.

3-Chloro-9-anthracenecarboxyaldehyde (5d). 5d was similarly obtained in 75% yield: mp 122.5–123.5 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 7.37–7.74 (m, 3 H), 7.80–8.07 (d_m + d_od_m, 2 H), 8.38 (s, 1 H), 8.67–8.93 (d_o + d_od_m, 2 H), 11.37 (s, 1 H). Anal. Calcd for $C_{15}H_9ClO$: C, 74.85; H, 3.77. Found: C, 74.71; H, 3.62.

9-Bromotriptycene (4a). To a refluxing solution of 9-bromoanthracene (5.2 g, 20 mmol) in dichloromethane (100 mL) were added a solution of isoamyl nitrite (7 mL, 60 mmol) in dichloromethane (70 mL) and a solution of anthranilic acid (5.4 g, 40 mmol) in dimethoxyethane (70 mL) at the same rate by mechanically driven syringes over 4–6 h. After the addition was complete, the mixture was refluxed for 0.5–1 h. The solvent was removed under reduced pressure, and the solid insoluble to methanol was collected by filtration to give slightly brown but pure solid of **4a** (4 g, 60%): mp 256–257 °C (from cyclohexane) (lit.[42] mp 250–254 °C).

4-Methyl- (4b) and 1-Methyl-9-bromotriptycenes (4b′). Addition of a benzyne generated from 2-amino-3-methylbenzoic acid (6 g, 40 mmol) to 9-bromoanthracene (5.2 g, 20 mmol) was carried out as described above. After evaporation of the solvent, the residue was chromatographed on alumina (1000 g, hexane to CH_2Cl_2/hexane (3:7)) to give a mixture of **4b** and **4b′**. Washing with warm hexane left a ca. 2:1 mixture of **4b** and **4b′** (3.0 g, 43%). Fractional crystallization from benzene/methanol gave pure **4b**. The residue (300 mg) was subjected to GPLC to effect complete separation after 1 day of recycling, **4b** being eluted first: mp 228–229 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3 H), 5.66 (s, 1 H), 6.86–7.20 (m, 6 H), 7.37 (d_od_m, 2 H), 7.67 (d_od_m, 1 H), 7.79 (d_od_m, 2 H). Anal. Calcd for $C_{21}H_{15}Br$: C, 72.63; H, 4.35. Found: C, 72.44; H, 4.20.

4b′: mp 241–242 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ 2.84 (s, 3 H), 5.32 (s, 1 H), 6.67–6.93 (m, 2 H), 6.97–7.13 (m, 4 H), 7.13–7.26 (m, 1 H), 7.26–7.44 (m, 2 H), 7.79–8.02 (m, 2 H). Anal Calcd for $C_{21}H_{15}Br$: C, 72.63; H, 4.35. Found: C, 72.82; H, 4.26.

2-Chloro- (4c) and 3-Chloro-9-bromotriptycenes (4d). A mixture of **4c** and **4d** slightly dominated by the latter was obtained in 42% yield from a reaction of anthranilic acid with the mixture of **3c** and **3d** described before in a manner similar to the preparation of **4a**. The reaction of 9-bromoanthracene and 2-amino-4-chlorobenzoic acid gave a mixture of **4c** and **4d** in a ratio of 2:1. Separation of these isomers was achieved by GPLC. After 1 day of recycling, **4c** was eluted first: mp 237–238 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ 5.40 (s, 1 H), 6.97–7.20 (m, 5 H), 7.20–7.45 (d_o + d_od_m, 3 H), 7.67–7.90 (m, 3 H). Anal. Calcd for $C_{20}H_{12}BrCl$: C, 65.23; H, 3.29. Found: C, 65.34; H, 3.29.

4d: mp 211–212 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 1 H), 6.90–7.22 (m, 5 H), 7.30–7.44 (m, 3 H), 7.63–7.90 (d_o + d_od_m, 3 H). Anal. Calcd for $C_{20}H_{12}BrCl$: C, 65.33; H, 3.29. Found: C, 65.39; H, 3.22.

4-Methyl-9-tritycenecarboxylic Acid (10b). To **4b** (1.04 g, 3 mmol) dissolved in benzene/diethyl ether (60/120 mL) was added butyllithium (2.3 mL of 1.6 M in hexane, 3.6 mmol, 1.2 equiv) at -50 °C. After 30 min at this temperature and another 30 min at room temperature, the suspension of the 9-triptycyllithium was treated with a rapid stream of dry carbon dioxide gas at -50 °C. Usual workup gave **10b** (0.83 g, 89%) as well as 1-methyltriptycene (0.06 g, 8%).

10b: mp 306–308 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3 H), 5.67 (s, 1 H), 6.86–7.20 (m, 6 H), 7.37–7.53 (m, 2 H), 7.76 (d_od_m, 1 H), 7.92–8.08 (m, 2 H), 8.50–9.50 (br s, 1 H). Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.64; H, 5.05.

1-Methyltritycene: mp 189–190 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3 H), 5.38 (s, 1 H), 5.64 (s, 1 H), 6.78–7.10 (m, 6 H), 7.37 (d_od_m, 5 H). Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 94.00; H, 6.00.

2-Chloro- (10c) and 3-Chloro-9-triptycenecarboxylic Acids (10d). They were similarly obtained from **4c** and **4d**.

10c: 91%; mp 273–275 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 1 H), 6.93–7.20 (m, 5 H), 7.27–7.50 (d_o + d_od_m, 3 H), 7.80–7.97 (d_od_m, 2 H), 8.02 (d_m, 1 H), 8.77 (br s, 1 H). Anal. Calcd for $C_{21}H_{13}ClO_2$: C, 75.79; H, 3.94. Found: C, 75.74; H, 3.83.

10d: 95%; mp 274.5–276.5 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 1 H), 6.74–7.20 (m, 5 H), 7.33–7.54 (m, 3 H), 7.74–8.03 (m, 3 H). Anal. Calcd for $C_{21}H_{13}ClO_2$: C, 75.79; H, 3.94. found: C, 75.41; H, 3.84.

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A byproduct for both the reactions was 2-chlorotriptycene: mp 166.5–167.5 °C (from benzene/hexane): ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 1 H), 5.39 (s, 1 H), 6.88–7.08 (m, 5 H), 7.26–7.48 (m, 6 H). Anal. Calcd for $C_{20}H_{13}Cl$: C, 83.18; H, 4.53. Found: C, 83.02; H, 4.69.

Conversion of 9-Triptycenecarboxylic Acids to the Corresponding Acid Chlorides (12a–12d). To a large excess of refluxing thionyl choride was added slowly a solution of **10** (3 mmol) in chloroform (100 mL or a minimum amount to dissolve the acid). The mixture was refluxed for 3–4 h after the addition was complete. After evaporation of the solvent and unreacted thionyl chloride under reduced pressure, **12** was obtained as slightly brown solid. A benzene solution of **12** was used without further purification for the synthesis of peroxyesters **11**.

9-Triptycyl 9-Triptyceneperoxycarboxylate (11a). A suspension of 9-triptycyllithium (3 mmol) prepared as described above was slowly (2–4 h) added through a cannula to diethyl ether (100 mL) cooled at −70 °C or below and through which dry oxygen was bubbled. To the resultant almost clear solution was added a solution of **12a** (3 mmol) in benzene (30 mL) with the aid of a syringe (5–10 min). After completion of the addition, the cold bath was removed and stirring was continued overnight to effect precipitation of LiCl. After usual workup, the residue was chromatographed on silica gel (200 g, CH_2Cl_2/hexane (3:7 to 1:0)) to give **11a** as colorless flakes (2nd band, 0.83 g, 49%) as well as triptycene (1st band, 0.23 g, 30%) and 9-hydroxytriptycene (3rd band, 0.14 g, 17%).

11a: mp 105–155 °C dec on DSC; ^{1}H NMR ($CDCl_3$) δ 5.38 (s, 1 H), 5.40 (s, 1 H), 6.80–7.10 (m, 12 H), 7.30–7.50 (m, 6 H), 7.70–7.90 (m, 6 H); IR (KBr disk) 1780 cm^{-1} (C=O). Anal. Calcd for $C_{41}H_{26}O_3$: C, 86.90; H, 4.63. Found: C, 86.61; H, 4.67.

4-Methyl-9-triptycyl 4-Methyl-9-triptyceneperoxycarboxylate (11b). This was obtained as above in 30% yield. 1-Methyltriptycene (30%) and 4-methyl-9-hydroxytriptycene (14%) were also produced.

11b: mp 105–155 °C dec on DSC; ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 6 H), 5.64 (s, 2 H), 6.76–7.10 (m, 12 H), 7.30–7.50 (m, 4 H), 7.53–7.91 (m, 6 H).

4-Methyl-9-hydroxytriptycene: mp 181.5–182.5 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3 H), 3.37 (br s, 1 H), 5.64 (s, 1 H), 6.80–7.20 (m, 6 H), 7.34–7.67 (m, 5 H). Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.71; H, 5.66.

2-Chloro-9-triptycyl 2-Chloro-9-triptyceneperoxycarboxylate (11c). **11c** was similarly obtained as above in 43% yield: mp 100–150 °C dec on DSC; ^{1}H NMR ($CDCl_3$) δ 5.38 (s, 1 H), 5.41 (s, 1 H), 6.92–7.13 (m, 10 H), 7.32–7.52 (m, 6 H), 7.72–7.88 (m, 6 H). The byproduct was 2-chlorotriptycene (43%) and 2-chloro-9-hydroxytritycene (30%): mp 176–177 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ 3.38 (br s, 1 H), 5.37 (s, 1 H), 6.89–7.16 (m, 5 H), 7.30–7.42 (m, 3 H), 7.42–7.58 (m, 3 H). Anal. Calcd for $C_{20}H_{13}ClO$: C, 78.82; H, 4.30. Found: C, 79.05; H, 4.25.

3-Chloro-9-triptycyl 3-Chloro-9-triptyceneperoxycarboxylate (11d). **11d** was obtained as above in 34% yield: mp 105–155 °C dec on DSC; ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 1 H), 5.38 (s, 1 H), 6.77–7.20 (m, 10 H), 7.34–7.53 (m, 6 H), 7.57–7.90 (m, 6 H).

The byproducts were 2-chlorotriptycene (25%) and 3-chloro-9-hydroxytriptycene (46%): mp 195–196 °C (from benzene/hexane); ^{1}H NMR ($CDCl_3$) δ 3.28 (br s, 1 H), 5.35 (s, 1 H), 6.96–7.22 (m, 5 H), 7.28–7.57 (m, 6 H). Anal. Calcd for $C_{20}H_{13}ClO$: C, 78.82; H, 4.30. Found: C, 78.64; H, 4.13.

Bis(9-triptycyl) Ether (2a). Peroxyester **11a** (560 mg, 1 mmol) was suspended in perfluorodecalin (10 mL), gradually heated to 150 °C over a 1-h period, and maintained at that temperature for 30 min. After evaporation of the solvent, the brown residue was chromatographed on a Lobar column to give colorless solid (520 mg, nearly quantitative): mp 470 °C (DSC) (from benzene); ^{1}H NMR ($CDCl_3$) δ 5.50 (s, 2 H), 6.70–7.10 (m, 12 H), 7.50 (d_od_m, 6 H), 7.74 (d_od_m, 6 H); IR (KBr disk) 1235 cm^{-1} (C–O–C). Anal. Calcd for $C_{40}H_{26}O$: C, 91.92; H, 5.02. Found: C, 91.94; H, 4.95.

Bis(4-methyl-9-triptycyl) Ether (2b). The ether was similarly obtained from **11b** in 85% yield. Separation of the meso and *dl* isomers was not achieved even under the conditions where the isomers of **2c** and **2d** were separated. The isomeric mixture of **2b** (*dl*/meso = ca. 2 on the basis of ^{13}C NMR integration, see Table I) was characterized: ^{1}H NMR ($CDCl_3$, 200 MHz[43]) δ 2.59 (s, 6 H), 5.74 (s, 2 H), 6.71–6.96 (m, 8 H), 6.98–7.09 (t_od_m + t_od_m, 2.7 H + 1.3 H), 7.49 (d_od_m, 4 H), 7.62 (br d_o, 2 H), 7.71 (br d_o, 4 H). Anal. Calcd for $C_{42}H_{30}O$: C, 91.60; H, 5.49. Found: C, 91.49; H, 5.38.

Bis(2-chloro-9-triptycyl) Ether (2c). **2c** was obtained in 62% yield together with 2-chlorotriptycene (8%). Separation of the meso and *dl* isomers of **2c** was carried out by HPLC.

***dl* isomer**: mp 397 °C (DSC) (from benzene); ^{1}H NMR($CDCL_3$) δ 5.48 (s, 2 H), 6.66 (t_od_m, 2 H), 6.84–7.20 (m, 8 H), 7.28–7.56 (m, 8 H), 7.71 (d_od_m, 2 H), 7.89 (d_m, 2 H). Anal. Calcd for $C_{40}H_{24}Cl_2O$: C, 81.22; H, 4.26. Found: C, 81.17; H, 4.00.

Meso isomer: mp 383 °C (DSC) (from benzene); ^{1}H NMR ($CDCl_3$) δ 5.48 (s, 2 H), 6.82–7.16 (m, 10 H), 7.33–7.75 (d_o + d_m + $2d_od_m$, 12 H).[44]

Bis(3-chloro-9-triptycyl) Ether (2d). **2d** was obtained in 60% yield from **11d** and separated into the meso and *dl* isomers as above.

***dl* isomer**: mp 389–390 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 5.46 (s, 2 H), 6.73–7.17 (m, 10 H), 7.40–7.57 (m, 6 H), 7.57–7.83 (m, 6 H). Anal. Calcd for $C_{40}H_{24}Cl_2O$: C, 81.22; H, 4.26. Found: C, 81.52; H, 4.21.

Meso isomer: mp 378–379 °C (from benzene); ^{1}H NMR ($CDCl_3$) δ 5.46 (s, 2 H), 6.76–7.20 (m, 10 H), 7.42–7.77 (m, 12 H).

Bis(9-anthryl)methane (8a). **8a** was prepared according to a procedure of Applequist[15] with a slight modification as described below for **6c**. **8a**: mp 309–310 °C (from benzene) (lit.[13] mp 313–315 °C). NMR and IR data were identical with those reported in the literature.

Bis(2-chloro-9-anthryl)carbinol (6c). To a suspension of **3c** (900 mg, 3.6 mmol) in diethyl ether (70 mL) was added butyllithium (2.7 mL of 1.6 M in hexane, 1.2 equiv) by a syringe over a 15-min period at −30 °C. After 30 min, **5c** (860 mg, 3.6 mmol) in benzene (20 mL) was added dropwise over 30 min to the resultant clear solution of the lithium reagent. A cold bath was removed, and the mixture was stirred overnight at room temperature. Usual workup followed by recrystallization from benzene/hexane gave **6c** (980 mg, 60%) as yellow solid. The mother liquor was chromatographed on silica gel (70 g, deactivated with 5 wt % water, eluted with CH_2Cl_2/hexane (1:1 to 1:0) to give additional **6c** (240 mg, 15%): total yield 75%; mp 154–156 °C dec (from benzene); ^{1}H NMR ($CDCl_3$) δ 3.20 (d, 1 H, (OH), 7.25–7.50 (m, 7 H), 7.80–8.00 (d_o + d_od_m, 4 H), 8.15–8.35 (d_od_m, 2 H), 8.35 (s, 1 H), 8.57 (d_m, 2 H). Anal. Calcd for $C_{29}H_{18}Cl_2O$: C, 76.83; H, 4.00. Found: C, 76.51; H, 4.08.

Bis(2-chloro-9-anthryl)methane (8c). Reduction of **6c** (850 mg, 1.9 mmol) with lithium aluminum hydride/aluminum chloride (0.6/4.2 g, 15.6/7.8 mmol) in diethyl ether (200 mL) as described by Applequist[15] gave 9-((2-chloro-9-anthryl)methylidene)-2-chloro-9,10-dihydroanthracene (**7c**) containing a small amount of **8c** in ≥95% yield. The crude product was dissolved in THF (50 mL) and DBU (1 mL), and the mixture was refluxed overnight to give light yellow precipitates. Filtration after cooling gave **8c** (580 mg, 78%): no melting below 400 °C with darkening started at ca. 300 °C; ^{1}H NMR ($CDCl_3$) δ 5.48 (s, 2 H), 7.10–7.40 (m, 6 H), 7.80–8.00 (d_o + d_od_m, 4 H), 8.07–8.27 (d_m + d_od_m, 4 H), 8.38 (s, 2 H). Anal. Calcd for $C_{29}H_{18}Cl_2$: C, 79.64; H, 4.15. Found: C, 79.44; H, 3.89.

7c: ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 2 H), 6.30–6.50 (m, 2 H), 6.77–7.04 (m, 1 H), 7.27–7.67 (m, 7 H), 7.80–8.30 (m, 5 H), 8.37 (s, 1 H).

Bis(3-chloro-9-anthryl)methane (8d). From **3d** was similarly obtained **6d** (82%): mp 136–138 °C (from CH_2Cl_2/benzene); ^{1}H NMR ($CDCl_3$) δ 3.30 (br s, 1 H), 7.22–7.72 (m, 6 H), 7.56 (s, 1 H), 7.76–8.33 (m, 8 H), 8.36 (s, 2 H). Anal. Calcd for $C_{29}H_{18}Cl_2O$: C, 76.83; H, 4.00. Found: C, 76.61; H, 4.06.

7d: ^{1}H NMR ($CDCl_3$) δ 4.08 (s, 2 H), 6.32–6.46 (m, 2 H), 6.80–7.07 (m, 0.6 H), 7.10–7.63 (m, 7.4 H), 7.87–8.30 (m, 5 H), 8.30 (s, 1 H).

8d (89% yield), yellow needles: mp 299–301 °C dec (from benzene); ^{1}H NMR ($CDCl_3$) δ 5.90 (s, 2 H), 7.10 (d_od_m, 2 H), 7.28–7.56 (m, 4 H), 7.88–8.36 (m, 8 H), 8.30 (s, 2 H). Anal. Calcd for $C_{29}H_{18}Cl_2$: C, 79.64; H, 4.15. Found: C, 79.56; H, 3.89.

Bis(9-triptycyl)methane (1a). To a solution of **8a** (800 mg, 2.2 mmol) in *p*-dioxane (100 mL)[45] were added a solution of anthranilic acid (17.8 g, 130 mmol) in *p*-dioxane (100 mL) and a solution of isoamyl nitrite (22.8 mL, 195 mmol) in *p*-dioxane (100 mL) at the same rate by mechanically driven syringes over a 15-h period. The temperature was maintained at 100 °C throughout the reaction. After completion of the addition, heating was continued for an additional few hours. The residue obtained after removal of the solvent under reduced pressure was dissolved in chloroform and chromatographed on an alumina column (400 g) with hexane and CH_2Cl_2/hexane (3:7) to give 460 mg (61%) of **1a** as colorless solid: mp 416 °C (DSC) (from benzene); ^{1}H NMR ($CDCl_3$) δ 4.87 (s, 2 H), 5.49 (s, 2 H), 6.79 (t_od_m, 6 H), 7.03 (t_od_m, 6 H), 7.49

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(43) We are grateful to Analytica Corp., Osaka, for the access to a Varian XL-200 spectrometer. We thank Prof. T. Miyazawa of the University of Tokyo for the ^{13}C NMR spectrum of **2b** recorded at 67.9 MHz.

(44) Routine analyses were not performed on the meso isomers as the amount of the samples was limited and the isomeric relationship with the corresponding *dl* isomers was self-evident.

(45) Because of the low solubility of bis(anthryl)methanes, dichloromethane and dimethoxyethane, typical solvents for the benzyne reaction, were not employed here.

(d_od_m, 6 H), 7.59 (d_od_m, 6 H). Anal. Calcd for $C_{41}H_{28}$: C, 94.58; H, 5.42. Found: C, 94.60; H, 5.27.

Bis(2-chloro-9-triptycyl)methane (1c). 1c was similarly obtained in 68% yield and separated into the meso and *dl* isomers by HPLC on a μPorasil column.

***dl* isomer**: mp 395 °C (DSC)[46] (from benzene/hexane); ^1H NMR ($CDCl_3$) δ 4.75 (s, 2 H), 5.46 (s, 2 H), 6.68 (t_od_m, 2 H), 6.82–7.13 (m, 8 H), 7.32–7.61 (m, 8 H), 7.63–7.80 ($d_od_m + d_m$, 4 H). Anal. Calcd for $C_{41}H_{26}Cl_2$: C, 83.53; H, 4.45. Found: C, 83.82; H, 4.34.

Meso isomer: mp 395 °C (DSC)[46] (from benzene/hexane); ^1H NMR ($CDCl_3$) δ 4.77 (s, 2 H), 5.47 (s, 2 H), 6.78–7.18 ($t_od_m + d_od_m + t_od_m$, 10 H), 7.27–7.70 ($d_o + d_m + d_od_m + d_od_m$, 12 H).

Bis(3-chloro-9-triptycyl)methane (1d), 1d was similarly obtained from **8d** in 40% yield.

***dl* isomer**: mp 374 °C (DSC)[46] (from benzene/hexane); ^1H NMR ($CDCl_3$) δ 4.80 (s, 2 H), 5.45 (s, 2 H), 6.58–7.20 ($d_od_m + t_od_m + t_od_m + t_od_m$, 10 H), 7.30 ($d_o$, 2 H), 7.38–7.80 (m, 10 H). Anal. Calcd for $C_{41}H_{26}Cl_2$: C, 83.53; H, 4.45. Found: C, 83.82; H, 4.19.

Meso isomer: mp 374 °C (DSC)[46] (from benzene/hexane); ^1H NMR ($CDCl_3$) δ 4.78 (s, 2 H), 5.43 (s, 2 H), 6.64–7.16 ($d_od_m + t_od_m + t_od_m$, 10 H), 7.27–7.70 (m, 12 H).

Kinetic Measurements. The rates of isomerization were measured in the temperature ranges 200–330 °C for a solution of ethers **2** in diphenylmethane (ca. 2 mg mL^{-1}, ca. 3 mM) and 110–210 °C for a solution of methanes **1** in *o*-dichlorobenzene. At each temperature, small glass ampules (ca. 2-mm i.d. and 4-cm long) containing the solution were immersed in a refluxing solvent (>100 mL). After a given period of time (a few minutes to several days), they were taken out of the bath and cooled in ice–water to stop the isomerization reaction. In order to obtain the *dl*/meso ratios at infinite time, they were subjected to continued heating for at least several half-lives in the temperature range of fairly rapid isomerization. When isomerization was very slow, the sample solution was first equilibrated at higher temperatures and then maintained at the given temperature for a few half-lives.

Analysis of the rate data was carried out according to eq 3 and 4,

$$\text{meso} \overset{kK}{\underset{k}{\rightleftharpoons}} dl \tag{3}$$

$$k(K + 1)t = \ln (x_\infty(1 + x/\epsilon)/(s_\infty - x)) \tag{4}$$

where k, K, $\epsilon = \epsilon_{dl}/\epsilon_{\text{meso}}$, and $x = A_{dl}/A_{\text{meso}}$ are the rate constants for isomerization from the *dl* to meso isomers, the equilibrium constant defined as $C_{\text{dl}}/C_{\text{meso}}$, the ratio of molar absorptivitiy at 254 nm, and the observed ratio of absorbance of the two isomers at the same wavelength, respectively. The experimentally determined ϵ's were in the range 1.00–1.03. Since the right-hand side of eq 4 is rather insensitive to ϵ near $\epsilon \simeq 1.00$, the ϵ values were assumed to be unity. Equation 4 now reduces to eq

$$k(K + 1)t = \ln (x_\infty(1 + x)/(x_\infty - x)) \tag{4'}$$

The solvents and chemicals used for the constant-temperature bath were as follows: anthracene (344 °C), nonadecane (333 °C), octadecane (319 °C), heptadecane (305 °C), bibenzyl (286 °C), biphenyl (258 °C), tridecane (238 °C), 1,2,4-trichlorobenzene (217 °C), undecane (197.1 °C), *o*-dichlorobenzene (181.0 °C), mesitylene (167.2 °C), 1,1,2,2-tetrachloroethane (150.0 °C), chlorobenzene (132.9 °C), and toluene (112.7 °C). The temperatures given above are slightly but not greater than a few degrees higher than the reported boiling points of these chemicals, since both the samples for the kinetic measurements and a thermocouple (chromel–alumel for ≥200 °C and copper–constantan for <200 °C) were directly immersed in the liquid. The temperature reading is considered to be accurate to ±1 and ±0.3 °C above and below 200 °C, respectively.

Analyses of the isomer ratios were carried out by an HPLC instrument equipped with a Shimadzu CR 1-A data processor.

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Registry No. 1a, 73611-46-8; *dl*-**1c**, 84065-14-5; *meso*-**1c**, 84065-15-6; *dl*-**1d**, 84065-16-7; *meso*-**1d**, 84065-17-8; **2a**, 73611-45-7; **2b**, 84065-18-9; *dl*-**2c**, 84065-19-0; *meso*-**2c**, 84065-20-3; *dl*-**2d**, 78150-15-9; *meso*-**2d**, 78129-63-2; **3c**, 84065-21-4; **3d**, 84065-22-5; **4a**, 15364-55-3; **4b**, 84065-23-6; **4b**, 84065-24-7; **4c**, 78129-64-3; **4d**, 78129-59-6; **5c**, 23716-41-8; **5d**, 84065-25-8; **6c**, 84065-26-9; **6d**, 84065-27-0; **7c**, 84065-28-1; **7d**, 84065-29-2; **8a**, 15080-14-5; **8c**, 84065-30-5; **8d**, 84065-31-6; **10b**, 84065-32-7; **10c**, 84065-33-8; **10d**, 78129-60-9; **11a**, 73597-15-6; **11b**, 84065-34-9; **11c**, 84065-35-0; **11d**, 78129-62-1; **12a**, 73597-17-8; 2-chloroanthracene, 17135-78-3; 9-bromoanthracene, 1564-64-3; anthranilic acid, 118-92-3; 2-amino-3-methylbenzoic acid, 4389-45-1; 1-methyltriptycene, 20711-97-1; 4-methyl-9-hydroxytriptycene, 84065-36-1; 2-chloro-9-hydroxytriptycene, 84065-37-2; 2-chlorotriptycene, 20711-99-3; 2-chloro-9,10-dibromoanthracene, 84065-38-3.

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[46] The apparently identical melting point was obtained either for the meso or *dl* isomers of the methanes, showing the isomerization in the solid state during DSC (see text).

MCSCF/CI Investigation of the Low-Lying Potential Energy Surfaces of the Formyloxyl Radical, $HCO_2\cdot$

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Abstract: Configuration interaction calculations have been performed on the low-lying potential energy surfaces of the formyloxyl radical. Minima and transition-state geometries were determined by an MCSCF procedure. The energies were then refined by large CI calculations. These calculations show the radical to have a σ ground state and a low-energy π excited state. On the ground-state surface, the lowest C_{2v} $^2B_2$ and $^2A_1$ energies are connected by a low-energy path passing through $^2A'$ points with unequal C–O bond lengths. This surface contacts the second $^2A'$ surface at the $^2B_2$–$^2A_1$ crossing point to form a Jahn–Teller double cone. On the lowest surface for a π radical, a C_{2v} $^2A_2$ energy is found to be a minimum, but there is very little energy change for large-amplitude asymmetric stretching. The transition states for fragmentation of $HCO_2\cdot$ to $H\cdot + CO_2$ and for rearrangement to $\cdot CO_2H$ have also been determined.

Introduction

As a prototype acyloxyl radical, $HCO_2\cdot$ has been the subject of several recent theoretical investigations that have dealt with the three lowest energy states. These states are obtained by singly occupying one of the energetically similar $6a_1$, $4b_2$, and $1a_2$ oxygen lone-pair orbitals, which are respectively the in-phase and out-of-phase combinations of oxygen nonbonding σ orbitals and the out-of-phase combination of oxygen π orbitals. We find that the corresponding orbital energies in the HCO_2^- anion, in which all

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