Crystal Structure of 1,4,9,10-Tetramethyltriptycene and Barriers to Rotation of Bridgehead-methyl Groups in 1,4,9,10-Tetramethyl- and 1,4-Dichloro-9,10-dimethyl-triptycene

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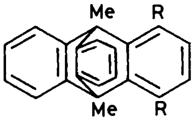
Barriers to rotation of the bridgehead-methyl groups in 1,4,9,10-tetramethyl- (**1**) and 1,4-dichloro-9,10-dimethyl-triptycene (**2**) are investigated both in solution and in the solid. The barrier is larger for (**2**) than for (**1**) not only in the solid state but also in solution, the barriers in solution being somewhat higher than those in the solids for both (**1**) and (**2**). *X*-Ray crystallography for (**1**) [monoclinic, space group $P2_1/n$, $Z = 4$, $a = 20.525(5)$, $b = 9.776(2)$, $c = 8.499(2)$ Å, and $\beta = 99.31(2)°$, $R = 0.0417$ and $R_w = 0.0467$ ($w = 1.0$) for 2 181 reflections] reveals planar benzene rings in the triptycene skeleton of (**1**). Remarkable upfield ^{13}C n.m.r. chemical shifts of the methyl carbon atoms for (**1**) in solution compared with those in the solid suggest deformation of the benzene rings and an increase of the methyl barrier in solution. Molecular mechanics calculations of features of the molecular structure of (**1**) are critically evaluated.

Recent developments in solid-state n.m.r. spectroscopy[1] have provided abundant and significant information not only about molecular structure but also about molecular motions and/or rearrangements in the solid state.[2] One of the interesting problems concerned is whether and/or how the mechanism of molecular motion and its associated activation energy and rate constant in solution vary in the solid. Intermolecular interactions in solids, such as crystal packing forces, usually repress molecular motions involving large changes in molecular structure. Thus, molecular motions in solids can be easily elucidated.

As one of the simplest molecular motions in solids, we have studied the internal rotation of methyl groups in methyltriptycenes to demonstrate intramolecular steric effects on rotation.[3–5] In this paper, we describe the internal rotation of bridgehead-methyl groups in 1,4,9,10-tetramethyl- (**1**)[4] and 1,4-dichloro-9,10-dimethyl-triptycene (**2**) both in the solid and in solution, as elucidated by n.m.r. methods. Measurements of proton spin–lattice relaxation times (T_1) furnish reliable information on the rotation of a methyl group in solids, whereas the dynamic n.m.r. method[6] is appropriate for solution.[7,8] The large steric repulsion between the bridgehead-methyl groups and the *peri*-substituents in (**1**) and (**2**) threw doubt on the planarity of the benzene rings and aroused interest in the manner of strain relief in the triptycene skeleton. Therefore, we have also determined the crystal structure of (**1**) by *X*-ray crystallography to evaluate intra- and inter-molecular effects on the structure of (**1**) in the solid state. The molecular structures of (**1**) and (**2**) in solid and solution have been examined by ^{13}C n.m.r. chemical shifts. Molecular mechanics calculations have also been performed to investigate the molecular structure and the barrier to rotation of the bridgehead-methyl groups in (**1**).



(**1**) R = Me
(**2**) R = Cl

Experimental

Preparation of 1,4-*Dichloro*-9,10-*dimethyltriptycene* (**2**).—To a refluxing solution of 9,10-dimethylanthracene (1.0 g) and isoamyl nitrite (2.2 ml) in dichloromethane (20 ml), a solution of 3,6-dichloroanthranilic acid[9] (1.5 g) in acetone (30 ml) was added dropwise for 1 h with stirring. After further refluxing for 1.5 h, the mixture was condensed and extracted with dichloromethane. The solvent was evaporated and the residual solids were chromatographed over alumina. The fraction eluted with n-hexane was concentrated, and the residual crystals were recrystallized from benzene–light petroleum to give *product* (**2**) as prisms (470 mg, 28%), m.p. >300 °C (Found: C, 75.1; H, 4.7. $C_{22}H_{16}Cl_2$ requires C, 75.2; H, 4.6%).

X-*Ray Structure Determination*.—Crystals of (**1**) were obtained from benzene–light petroleum. Intensity data were obtained on a Rigaku four-circle diffractometer (Mo-K_α radiation, 2θ–ω scanning mode, scan speed 2° min^{-1}). A total of 2 181 reflections [$F > 3\sigma(F)$] were measured for $2\theta < 60°$. The structure was solved by Patterson–Fourier techniques and refined by the block-diagonal least-squares techniques with the X-STANP program.† The 22 hydrogen atoms were found on a *D* map. In the final refinement, positional and anisotropic thermal parameters were varied for non-hydrogen atoms, while the hydrogen atoms were included at their determined positions with isotropic thermal parameters, but hydrogen parameters were not varied. The final agreement factors were $R = 0.0417$ and $R_w = 0.0467$ ($w = 1.0$).

The final atomic parameters are listed in Table 1. Bond lengths and angles involving the carbon atoms are collected in Tables 2 and 3, respectively. Numbering of the atoms in (**1**) and two types of interactions (I and II) are illustrated in Figures 1 and 2, respectively.

Crystal data for (**1**). $C_{24}H_{22}$, $M = 310.44$, monoclinic, $a = 20.525(5)$, $b = 9.776(2)$, $c = 8.499(2)$ Å, $\beta = 99.31(2)°$, $V = 1\,682.9(6)$ Å^3, $D_c = 1.225$ g cm^{-3}, space group $P2_1/n$, $Z = 4$.

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† Written by one of us (Z. T.).

Table 1. Final least-squares fractional co-ordinates for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(1)	0.617 6(1)	0.616 1(2)	0.960 5(2)	H(2)	0.553(1)	0.754(2)	0.821(2)
C(2)	0.562 2(1)	0.648 9(2)	0.850 1(3)	H(3)	0.484(1)	0.581(2)	0.701(2)
C(3)	0.521 4(1)	0.551 4(2)	0.775 2(2)	H(5)	0.554(1)	0.063(2)	1.183(2)
C(4)	0.532 1(1)	0.411 4(2)	0.804 2(2)	H(6)	0.565(1)	0.086(2)	1.461(3)
C(4a)	0.587 9(1)	0.375 2(2)	0.915 1(2)	H(7)	0.635(1)	0.270(2)	1.593(3)
C(5)	0.583 1(1)	0.138 9(2)	1.237 5(2)	H(8)	0.692(1)	0.420(2)	1.441(2)
C(6)	0.591 1(1)	0.153 8(2)	1.401 8(3)	H(13)	0.819(1)	0.396(2)	1.052(2)
C(7)	0.629 5(1)	0.257 1(3)	1.475 9(2)	H(14)	0.862(1)	0.224(2)	0.894(3)
C(8)	0.662 6(1)	0.346 2(2)	1.387 8(2)	H(15)	0.791(1)	0.052(2)	0.762(3)
C(8a)	0.655 3(1)	0.330 3(2)	1.224 3(2)	H(16)	0.676(1)	0.044(2)	0.797(3)
C(9)	0.688 5(1)	0.419 0(2)	1.111 4(2)	H(17A)	0.704(1)	0.738(2)	1.003(3)
C(9a)	0.630 0(1)	0.477 7(2)	0.992 2(2)	H(17B)	0.662(1)	0.744(3)	1.158(3)
C(10)	0.609 9(1)	0.227 8(2)	0.967 9(2)	H(17C)	0.640(1)	0.817(3)	0.978(3)
C(10a)	0.614 9(1)	0.228 4(2)	1.148 9(2)	H(18A)	0.496(1)	0.246(3)	0.636(3)
C(11)	0.681 4(1)	0.217 3(2)	0.938 0(2)	H(18B)	0.458(1)	0.251(2)	0.779(3)
C(12)	0.722 6(1)	0.318 9(2)	1.013 3(2)	H(18C)	0.446(1)	0.364(3)	0.644(3)
C(13)	0.788 6(1)	0.322 7(2)	0.995 3(3)	H(19A)	0.759(1)	0.577(2)	1.131(2)
C(14)	0.813 0(1)	0.223 8(3)	0.903 1(3)	H(19B)	0.715(1)	0.587(2)	1.273(3)
C(15)	0.772 5(1)	0.123 1(3)	0.830 1(3)	H(19C)	0.772(1)	0.465(2)	1.280(3)
C(16)	0.706 2(1)	0.118 3(2)	0.847 3(2)	H(20A)	0.564(1)	0.102(2)	0.774(2)
C(17)	0.658 6(1)	0.735 8(2)	1.032 3(3)	H(20B)	0.523(1)	0.114(2)	0.920(2)
C(18)	0.481 7(1)	0.317 0(3)	0.711 6(3)	H(20C)	0.589(1)	0.019(2)	0.940(2)
C(19)	0.737 8(1)	0.517 7(2)	1.204 6(3)				
C(20)	0.568 2(1)	0.109 0(2)	0.893 7(3)				

Table 2. Bond lengths involving the carbon atoms in (1) with estimated standard deviations in parentheses

Atoms	Bond length (Å)	Atoms	Bond length (Å)
C(1)–C(2)	1.389(3)	C(8a)–C(9)	1.533(3)
C(1)–C(9a)	1.395(3)	C(8a)–C(10a)	1.386(2)
C(1)–C(17)	1.512(3)	C(9)–C(9a)	1.551(2)
C(2)–C(3)	1.357(3)	C(9)–C(12)	1.526(3)
C(3)–C(4)	1.401(3)	C(9)–C(19)	1.525(3)
C(4)–C(4a)	1.405(2)	C(10)–C(10a)	1.525(3)
C(4)–C(18)	1.510(3)	C(10)–C(11)	1.533(3)
C(4a)–C(9a)	1.413(2)	C(10)–C(20)	1.518(3)
C(4a)–C(10)	1.554(3)	C(11)–C(12)	1.391(3)
C(5)–C(6)	1.387(3)	C(11)–C(16)	1.385(3)
C(5)–C(10a)	1.384(3)	C(12)–C(13)	1.389(3)
C(6)–C(7)	1.369(3)	C(13)–C(14)	1.388(3)
C(7)–C(8)	1.395(3)	C(14)–C(15)	1.370(3)
C(8)–C(8a)	1.382(3)	C(15)–C(16)	1.392(3)

Table 3. Bond angles involving the carbon atoms in (1) with estimated standard deviations in parentheses

Atoms	Bond angles (°)	Atoms	Bond angles (°)
C(2)–C(1)–C(9a)	117.3(2)	C(12)–C(9)–C(19)	111.5(2)
C(2)–C(1)–C(17)	115.8(2)	C(1)–C(9a)–C(4a)	121.3(2)
C(9a)–C(1)–C(17)	126.9(2)	C(1)–C(9a)–C(9)	125.7(2)
C(1)–C(2)–C(3)	122.0(2)	C(4a)–C(9a)–C(9)	113.1(2)
C(2)–C(3)–C(4)	122.4(2)	C(4a)–C(10)–C(10a)	104.9(1)
C(3)–C(4)–C(4a)	116.8(2)	C(4a)–C(10)–C(11)	104.8(1)
C(3)–C(4)–C(18)	115.5(2)	C(4a)–C(10)–C(20)	118.2(1)
C(4a)–C(4)–C(18)	127.7(2)	C(10a)–C(10)–C(11)	104.9(1)
C(4)–C(4a)–C(9a)	120.2(2)	C(10a)–C(10)–C(20)	111.3(2)
C(4)–C(4a)–C(10)	126.5(2)	C(11)–C(10)–C(20)	111.7(2)
C(9a)–C(4a)–C(10)	113.3(1)	C(5)–C(10a)–C(8a)	120.2(2)
C(6)–C(5)–C(10a)	119.4(2)	C(5)–C(10a)–C(10)	125.9(2)
C(5)–C(6)–C(7)	120.4(2)	C(8a)–C(10a)–C(10)	114.0(2)
C(6)–C(7)–C(8)	120.5(2)	C(10)–C(11)–C(12)	113.8(2)
C(7)–C(8)–C(8a)	119.1(2)	C(10)–C(11)–C(16)	126.0(2)
C(8)–C(8a)–C(9)	125.4(2)	C(12)–C(11)–C(16)	120.2(2)
C(8)–C(8a)–C(10a)	120.3(2)	C(9)–C(12)–C(11)	114.3(2)
C(9)–C(8a)–C(10a)	114.3(2)	C(9)–C(12)–C(13)	125.7(2)
C(8a)–C(9)–C(9a)	104.0(1)	C(11)–C(12)–C(13)	120.0(2)
C(8a)–C(9)–C(12)	105.6(1)	C(12)–C(13)–C(14)	119.3(2)
C(8a)–C(9)–C(19)	111.0(2)	C(13)–C(14)–C(15)	120.6(2)
C(9a)–C(9)–C(12)	104.8(1)	C(14)–C(15)–C(16)	120.5(2)
C(9a)–C(9)–C(19)	118.9(2)	C(11)–C(16)–C(15)	119.3(2)

N.m.r. Chemical Shifts.—^{1}H and ^{13}C Chemical shifts for (**1**) and (**2**) in $CDCl_3$ solutions at room temperature were recorded on a JEOL GX-400 spectrometer operating at 399.8 and 100.5 MHz for ^{1}H and ^{13}C nuclei, respectively. Isotropic ^{13}C chemical shifts in solids at room temperature were measured on a home-built spectrometer operating at 15.0 and 22.6 MHz for (**1**) and (**2**), respectively, by using the CPMAS technique:[10] mixing times, repetition times, and sample-spinning frequencies were 0.75 ms, 6 s, and 2.3 kHz for (**1**) and 0.5 ms, 40 s, and 2.4 kHz for (**2**), respectively. ^{13}C Chemical shifts in solids were calibrated in units of p.p.m. relative to $(CH_3)_4Si$ as described previously.[11]

^{1}H *Spin–Lattice Relaxation Times* (T_1).—A sample of (**2**) for T_1 measurements was degassed by several freeze–pump–thaw cycles in a glass tube. T_1 Values were determined by using the home-built spectrometer operating at 90.0 MHz as described elsewhere.[3]

Dynamic N.m.r. Spectra.—Temperature-dependent ^{1}H spectra for the bridgehead-methyl protons were recorded with (**1**) and (**2**) (5 mg) in CD_2Cl_2 (0.5 ml) on the JEOL GX-400 spectrometer operating at 399.8 MHz. Temperatures were controlled with a temperature-control unit attached to the spectrometer, which had been calibrated before measurements with a thermocouple immersed in the sample tube. Resonance frequencies were measured from an internal $(CH_3)_4Si$ standard. Digital outputs of the ^{1}H spectra on floppy disks were transferred to the memory of a FACOM M382 computer at Kyoto University. Exchange-broadened bridgehead-methyl signals for (**1**) and (**2**) were simulated by using the DNMR5 program[12] to obtain exchange rates for the bridgehead-methyl protons.

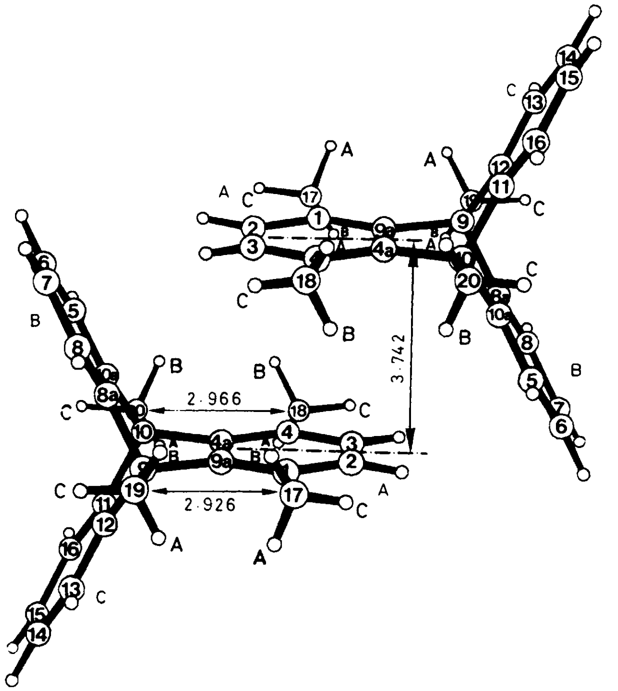

Figure 1. Numbering of the atoms in 1,4,9,10-tetramethyltriptycene (1) and interaction I in the crystalline state of (1). Distance between average planes for the two A rings in the stacked molecules and distances between bridgehead- and *peri*-methyl carbon atoms are given in Å

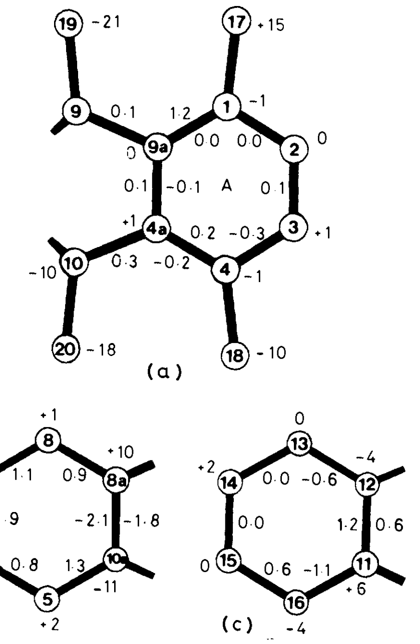

Figure 3. Distances (× 1 000 Å) of the carbon atoms from the respective best planes and dihedral angles (°) in the molecular structure for 1,4,9,10-tetramethyltriptycene (1): (a) for ring A; (b) for ring B; (c) for ring C

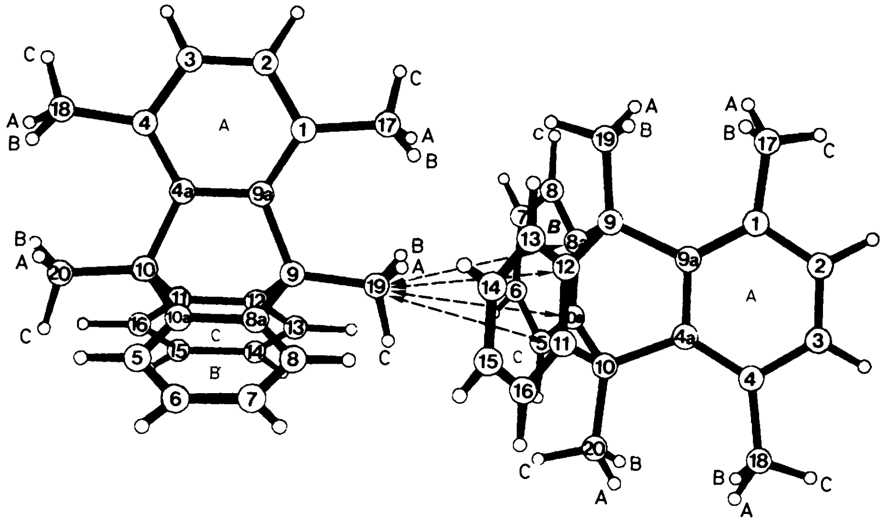

Figure 2. Intraction II in the crystalline state of 1,4,9,10-tetramethyltriptycene (1)

Results and Discussion

Crystal Structure of (**1**).—As shown in Figures 1 and 2, two types of interactions (I and II) exist in the crystalline state of (**1**). In interaction I, which is centrosymmetric, two molecules of (**1**) have structure stacked parallel to rings A with a distance of 3.742 Å: the C(1), C(2), C(3), C(4), C(4a), and C(18) atoms nearly overlap with the C(18), C(4), C(4a), C(2), C(3), and C(1) atoms of the other ring A. In interaction II, one of the bridgehead-methyl groups is surrounded by rings B and C of the other molecule. C(19) is located at the top of a square-based pyramid, of which the base atoms are C(8a), C(10a), C(11), and C(12): the distances of the base atoms from C(19) are 3.753, 3.703, 3.762, and 3.801 Å for C(8a), C(10a), C(11), and C(12), respectively.*

To prove the planarity of the three benzene rings in (**1**), the best planes through the six carbon atoms constituting each of the three benzene rings were determined with respect to the orthogonal crystal axes [equations (1)—(3) for rings A—C,

$$0.6776\,X - 0.0394\,Y - 0.7344\,Z = 1.541\text{ Å} \quad (1)$$

$$0.7813\,X - 0.6151\,Y + 0.1059\,Z = 8.284\text{ Å} \quad (2)$$

$$0.1009\,X - 0.5796\,Y + 0.8086\,Z = 6.417\text{ Å} \quad (3)$$

respectively, where X and Y coincide with the unit cell x and y

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* The distance between C(20) and the closest carbon atom of the neighbouring molecule is as much as 3.955 Å.

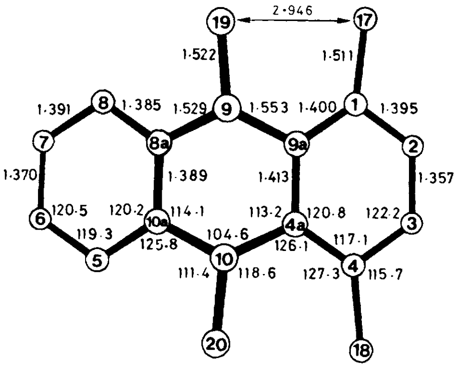


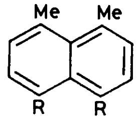
Figure 4. Averages over non-crystallographic symmetry-related values for bond lengths (Å) and bond angles (°) of the carbon atoms and nonbonding distances (Å) between the bridgehead- and *peri*-methyl carbon atoms in 1,4,9,10-tetramethyltriptycene (**1**)

axes and Z is normal to x and y]. Deviations of the carbon atoms from the best planes are shown in Figure 3, where the torsional angles determined by X-ray analysis are also displayed. The three benzene rings in (**1**) are considered to be essentially planar in view of the root-mean-square distances of the aromatic carbon atoms from the best planes: 0.001, 0.009, and 0.003 Å for rings A—C, respectively. Although they are very small, slight trends to take a 'boat' conformation are seen for rings B and C, which do not contain methyl substituents. Similar trends are also observed in crystal structures of 1,2,3,4-tetrachloro-9-(2-oxopropyl)triptycene rotamers.[13]

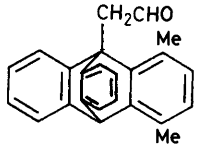
The planarity of ring A is of particular interest.* The departure of the four methyl carbon atoms from the best plane for ring A is at most 0.021 Å, in directions which are the same for three of the four methyl groups, implying no particular deformation for ring A. As shown in Figure 1, two molecules of (**1**) assume a position with rings A stacked. The distance between the two A rings (3.742 Å) and the van der Waals radius for carbon atoms in benzene (1.77 Å)[14] differs by 1.97 Å, which is more than Charton's minimum value (1.72 Å),[15] but shorter than Charton's maximum value (2.23 Å)[15] for the van der Waals radius of a methyl group. The usual van der Waals radius for a methyl group (2.0 Å)[16] is quite similar to this difference. The stacking of the two A rings is related to the planarity of ring A in the crystalline state.

The adjacent bridgehead- and *peri*-methyl groups in (**1**) take a clashed-gear conformation.[17,18] This conformation has been predicted by force field calculations for 1,9-dimethyltriptycene[4,17] and (**1**),[4] and is observed for the *peri*-methyl groups in 1,8-dimethylnaphthalene (**3**)[19] and 1,4,5,8-tetramethylnaphthalene (**4**).[20,21] The stability of the staggered conformation for the bridgehead-methyl groups relative to the bridgehead carbon atoms [C(9) and C(10)] is enhanced owing to steric repulsion between the bridgehead-methyl protons and the *peri*-hydrogen atoms in rings B and C [H(5), H(8), H(13), and H(16)]. Therefore, the simultaneous clashed-gear conformation for the two pairs of the four methyl groups in (**1**) also leads to ring A remaining planar.

To discuss details of the geometry of (**1**), we use the average bond lengths and angles indicated in Figure 4. The geometry



(3) R = H
(4) R = Me



(5)

of ring A shows characteristic features of a symmetrically congested planar aromatic ring as observed for (**4**):[21] elongation of all the bonds connected to the condensed carbon atoms [C(4a) and C(9a)], shortening of the C(2)–C(3) bond, and a small change in the bond angles about the condensed carbon atoms. The C(9a)–C(9)–C(19) bond angle is expanded by 5.3° compared with the corresponding bond angle (113.3°) in triptycene,[22] and the C(9a)–C(1)–C(17) bond angle is expanded by 1.4° in comparison with the C(9a)–C(1)–C(11) bond angle (125.9°) in (**4**).[21] These two bond angles are similar to the corresponding bond angles in 1,4-dimethyl-9-(formylmethyl)-triptycene (**5**),[23] whereas the C(1)–C(9a)–C(9) bond angle in (**5**) is 2.3° wider than the bond angle in (**1**). Accordingly, the non-bonding distance (2.946 Å) between the bridgehead- and *peri*-methyl carbon atoms becomes substantially shorter than the corresponding distance (3.011 Å) in (**5**). This distance is, however, longer than the distance (2.890 Å) between the *peri*-methyl carbon atoms in (**4**),[21] and is comparable with the distance (2.932 Å) in (**3**).[19]

Molecular mechanics calculations by the MMI[4,24] and MM2 methods[25] for (**1**) predict planar structures for all three benzene rings in (**1**). The calculated geometry slightly improved by the MM2 method is as follows: standard deviations from the experimental values of the bond lengths and angles involving the carbon atoms are 0.013 Å and 1.0°. The non-bonding distance between the bridgehead- and *peri*-methyl carbon atoms by the MM2 method (2.969 Å) is nearly equal to the experimental value. The bond lengths calculated for the C(2)–C(3) and C(6)–C(7) [C(14)–C(15)] bonds are 1.388 and 1.394 Å, respectively, somewhat longer than the corresponding experimental lengths,† and a large value of 120.9° is obtained for the C(9a)–C(9)–C(19) [C(4a)–C(10)–C(20)] bond angle.‡

^{1}H *and* ^{13}C *N.m.r. Chemical Shifts.*—Table 4 collects ^{1}H and ^{13}C chemical shifts in $CDCl_3$ solutions and ^{13}C chemical shifts in solids at room temperature for (**1**) and (**2**). Selective decoupling techniques[28] were used to assign ^{13}C resonance lines of protonated carbon atoms in solution. Delayed decoupling techniques[29] and ^{13}C chemical shifts in solution were employed to assign ^{13}C resonance signals in solids. Thus, the lower-field peak of the two ^{13}C methyl signals in solid (**1**) was assigned to the *peri*-methyl carbon atoms. Signals from the C(1), C(4), and methyl carbon atoms in solid (**2**) were not observed over a wide range of mixing times.

The ^{13}C chemical shifts of the triptycene skeletons do not differ much in the two states: at most by 2.3 or 0.8 p.p.m. in (**1**) or (**2**), respectively. Although ring A in (**1**) is stacked up on the other ring A in the crystalline state, particular changes in ^{13}C chemical shifts beyond the linewidth (*ca.* 1.8 p.p.m.) are not detected for the triptycene skeletons. The equivalence of the two *peri*-methyl groups in (**1**) as has been proved by a ^{1}H spin–lattice relaxation study in the solid state[4] also supports weak intermolecular magnetic interactions. However, remarkable downfield shifts are found for the bridgehead- and *peri*-methyl carbon atoms (6.1 and 3.1 p.p.m., respectively) of (**1**) in the solid compared with the values in solution. Such large changes in ^{13}C chemical shifts have so far not been seen for aromatic compounds substituted with congested methyl groups.[30] The bridgehead- and *peri*-methyl carbon atoms are separated by

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* The equivalent isotropic temperature factors, B_{eq}, for the aromatic carbon atoms in ring A are at most 4 Å^2, suggesting no significant displacement of the atoms due to static disorder of molecules with twisted structures or a molecular motion such as an overall rotation.

† The observed short length is partly attributed to the relatively large thermal vibration of the atoms concerned (Table 1).

‡ These trends for the structure of (**1**) were not reproduced even by MMPI[26,27] molecular mechanics calculations.

Table 4. ^{1}H and ^{13}C chemical shifts for (**1**) and (**2**)[a]

	^{13}C				^{1}H	
	(**1**)		(**2**)		(**1**)	(**2**)
Position	Solution[b]	Solid[c]	Solution[b]	Solid[c]	Solution[b]	Solution[b]
1,4	130.6	131.4	128.3	*d*		
2,3	130.0	131.4	129.9	130.7	6.57	6.83
5,8,13,16	120.7	122.7	121.4	121.7	7.40[e]	7.46[f]
6,7,14,15	124.6	124.2	125.2	125.3	7.05[e]	7.12[f]
4a,9a	146.1	145.7	146.4	146.9		
8a,10a,11,12	148.8	151.1	147.4	146.9		
9,10	50.5	52.0	50.5	51.1		
17,18	23.4	26.5			2.58	
19,20	18.8	24.9	18.6	*d*	2.63	2.78

[a] Chemical shifts are given in p.p.m. from $(CH_3)_4Si$. Coupling patterns appearing in ^{1}H spectra are analysed by use of the LAOCN3 program (A. A. Bothner-By and S. Castellano, *QCPE*, 1967, **11**, 111). [b] In $CDCl_3$. [c] In solid. [d] Not observed. [e] $J_{5,6} = J_{7,8} = 7.5, J_{5,7} = J_{6,8} = 1.2, J_{5,8}$ 0.0, and $J_{6,7}$ 7.0 Hz. [f] $J_{5,6} = J_{7,8} = 7.6, J_{5,7} = J_{6,8} = 1.2, J_{5,8}$ 0.0, and $J_{6,7}$ 7.0 Hz.

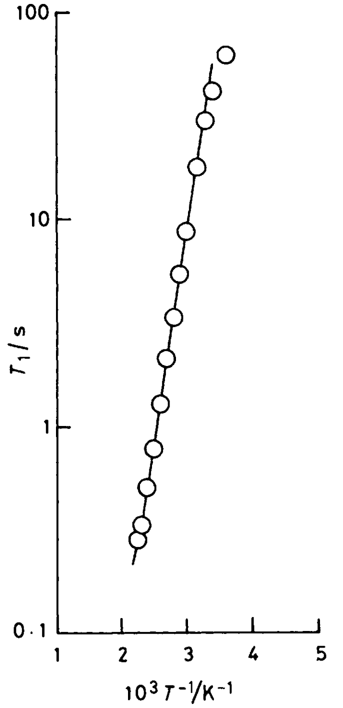

Figure 5. The temperature dependence of the ^{1}H spin–lattice relaxation times (T_1) at 90.0 MHz for 1,4-dichloro-9,10-dimethyltriptycene (**2**) in solids. The solid curve through the data points is the 'best fit' described by the parameters in Table 5

Table 5. Best-fit parameters to the T_1 data in solids and the rate constants at 298 K for the rotation of bridgehead-methyl groups in (**1**) and (**2**)[a]

	(**1**)[5]	(**2**)
10^{-9} K/s^{-2}	6.9 ± 1.1	5.43 ± 0.80
E_a/kcal mol^{-1}	9.06 ± 0.30	9.58 ± 0.10
10^{14} τ_0/s	7.2 ± 3.9	5.9 ± 1.5
k_{298K}/s^{-1}	2.1 × 10^6	1.1 × 10^6

[a] Error is 2.5σ (variance).

four bonds and the C–methyl bonds are nearly parallel to each other. When we recall that the δ effect on ^{13}C chemical shifts causes downfield shifts for the carbon atoms in such a '*syn*-parallel' orientation,[31] the distance between the two congested methyl groups in (**1**) is considered to be lengthened by deformation of ring A in solution. To confirm this consideration we carried out MMPI molecular mechanics calculations,[26,27] capable of treating non-planar aromatic rings. The most stable geometry for (**1**) thus calculated is a nonplanar C_2 structure, which is 1.78 kcal mol^{-1} more stable than the planar C_{2v} structure, in contrast to the results by MMI and MM2 calculations. The non-bonding distance between the bridgehead- and *peri*-methyl carbon atoms is 0.068 Å longer in the nonplanar structure than that in the planar one, although dihedral angles in the nonplanar structure are distinctly larger: 21.5, 13.1, and −32.1° for the C(1)–C(9a)–C(9)–C(19), C(9)–C(9a)–C(1)–C(17), and C(1)–C(9a)–C(4a)–C(4) angles, respectively.

Rotation of Bridgehead-methyl Groups.—In solids. Experimental values of proton T_1 values for (**2**) in the solid state are plotted against the reciprocal temperature in Figure 5. Taking into account only the intramethyl contribution to the relaxation process, one can write the initial relaxation rate as (4)[32] where ω

$$\frac{1}{T_1} = \frac{N_{Me}}{N_{all}} K\left(\frac{\tau}{1 + \omega^2\tau^2} + \frac{4\tau}{1 + 4\omega^2\tau^2}\right) \qquad (4)$$

is the Larmor frequency, N_{all} is the total number of protons in the molecule, N_{Me} is the number of protons in the methyl group, and $K = 9\gamma^4\hbar^2/20r^6$, r being the intramethyl proton–proton distance. The correlation time, τ, is assumed to have an Arrhenius dependence on temperature according to equation (5) where E_a is the activation energy and τ_0 is the correlation

$$\tau = \tau_0 \exp\left(E_a/RT\right) \qquad (5)$$

time at infinite temperature. The T_1 values for (**2**) are fitted to equation (4), taking K in equation (4) and E_a and τ_0 in equation (5) as adjustable parameters. The best-fit parameters together with those for (**1**) obtained previously[4] are listed in Table 5.

In the solid state the barrier to rotation of the bridgehead-methyl group in (**2**) is 0.52 kcal mol^{-1} higher than that in (**1**). The stacked structure of (**1**) in the crystalline state keeps ring A planar during rotation of the methyl group. A nearly symmetric four-fold potential for the C(19) -methyl group generated by the base atoms of the square-based pyramid (Figure 2) has little effect on the rotation of the methyl group. Little intermolecular steric effect is also presumed for the rotation of the C(20)-methyl

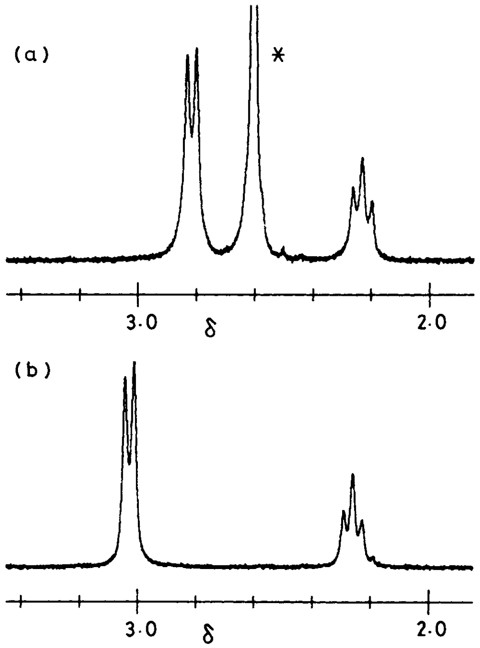

Figure 6. Low-temperature ^{1}H n.m.r. spectra for methyl protons in 1,4,9,10-tetramethyl- (**1**) and 1,4-dichloro-9,10-dimethyl-triptycene (**2**) in CD_2Cl_2 solutions at 399.8 MHz: (a) for (**1**) at 171.7 K (peak marked * is for the *peri*-methyl protons); (b) for (**2**) at 184.3 K

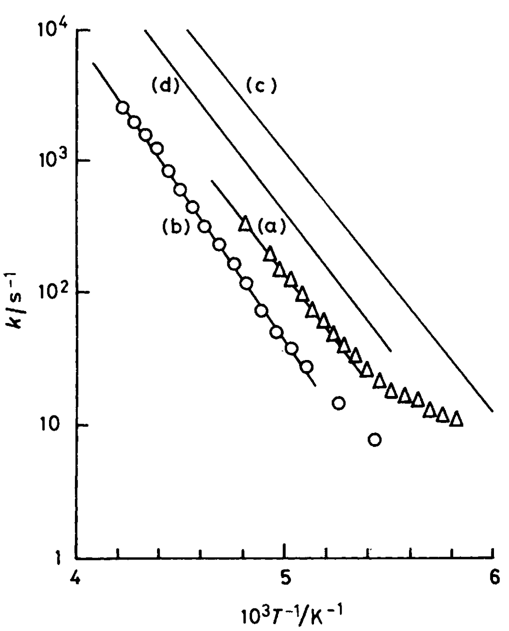

Figure 7. Temperature dependence of the exchange rates for the bridgehead-methyl protons in 1,4,9,10-tetramethyl- (**1**) and 1,4-di-chloro-9,10-dimethyltriptycene (**2**). (a) Observed rates (△) for (**1**). The solid line through the data points is the 'best fit' for the Arrhenius plot, described by the parameters in Table 6. (b) Observed rates (○) for (**2**). The solid line through the data points is the 'best fit' for the Arrhenius plot described by the parameters in Table 6. (c) Exchange rates for (**1**) in the solid extrapolated by the parameters in Table 5. (d) Exchange rates for (**2**) in the solid extrapolated by the parameters in Table 5

group. The main origin of the barrier is, therefore, ascribed to an increase in steric repulsion between the bridgehead- and *peri*-methyl groups in the transition state accompanied by enhancement of steric interactions between the bridgehead-methyl group and the *peri*-hydrogen atoms of rings B and C. The steric bulk of a methyl group in the clashed-gear conformation is well represented by Charton's minimum value for the van der Waals radius of a methyl group, which is slightly smaller than the van der Waals radius of a chlorine atom (1.75 Å),[14] in line with the smaller barrier for (**1**), suggesting the similarity between the structures for (**1**) and (**2**) in the solids.

In solution. Rates in solution for rotation of the bridgehead-methyl groups in (**1**) and (**2**) were determined by bandshape analyses of exchange-broadened ^{1}H spectra for the methyl protons. As shown in Figure 6, low-temperature spectra for the bridgehead-methyl groups display well-resolved AB_2 patterns with shifts and J values of 233.85 and -13.56 Hz for (**1**) and 306.69 and -12.81 Hz for (**2**), respectively. The shift (0.585 p.p.m.) for (**1**) is larger than that (0.42 p.p.m.) estimated for 1,4,9-trimethyltriptycene,[8] indicating an increase in steric compression in (**1**). Variations of the spectra for the bridgehead-methyl protons with temperature were simulated by use of the DNMR5 program, where the chemical shifts and J values were assumed to be independent of temperature. Effective spin–spin relaxation times for the bridgehead-methyl protons were estimated[33] from a sum of the linewidth* for H(2) and H(3) and the difference between the linewidths of these protons at room temperature. The logarithms of the rate constants thus obtained are plotted against the reciprocal temperature in Figure 7, where the rate constants for temperatures higher than 207.5 K for (**1**) cannot be determined due to overlap by a signal of the *peri*-methyl protons.

In solution the barrier to rotation of the bridgehead-methyl group in (**2**) is also larger than that in (**1**). The difference (1.12 kcal mol^{-1} on the basis of activation energies) between the barriers is about twice as large in solution as in the solids.

Comparison of Rotation.—While only a slight increase (0.38 kcal mol^{-1}) is found for the bridgehead-methyl barrier of (**1**) in solution compared to that in the solid, a notable increase (0.98 kcal mol^{-1}) is observed for (**2**). The rate constant, k, in the solid is related to the correlation time, τ,[34,35] by equation (6). Figure

$$k = 2/3\tau \qquad (6)$$

7 contains the plots of the rate constants in the solid state against the reciprocal temperature. For both (**1**) and (**2**), the rotation rates of the bridgehead-methyl groups are faster in the solids than in solution in the region of temperature shown. These differences in the rates are, however, insignificant, when one considers that the data are derived from different kinds of measurements. Thus, the similarity of bridgehead-methyl group rotation in the two phases may be inferred.

Generally, barriers to molecular motions in solids are considered to be larger than those in solution, as observed, for example, in the Cope rearrangement of semibullvalene.[36] Intermolecular interactions among molecules in the transition state of molecular motion in solids are usually larger than those in the ground state, increasing the barrier to molecular motion in solids. On the other hand, if there occurs little change in intermolecular interactions during molecular motion in solids, barriers similar to those in solution are found as in the Cope rearrangement of bullvalene.[37] As has been discussed in the previous sections, direct intermolecular interactions are not significant for rotation of the bridgehead-methyl groups in (**1**) and (**2**). The intermolecular effects on the barriers for the bridgehead-methyl groups should be also less important in solution, since activation entropies from the Eyring plots are very small: -2.8 ± 2.3 and 0.39 ± 0.94 kcal mol^{-1} K^{-1} for

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* The linewidths were estimated by fitting the digital data for the singlets to Lorentzian bandshape functions.

Table 6. Best-fit parameters to the dynatic n.m.r. data in CD_2Cl_2 and the rate constants at 298 K for the rotation of bridghead-methyl groups in (**1**) and (**2**)[a]

	(**1**)	(**2**)
$10^{-12}\,A/s^{-1}$	2.8 ± 3.2	14.6 ± 6.7
E_a/kcal mol^{-1}	9.44 ± 0.44	10.56 ± 0.20
k_{298K}/s^{-1}	3.3 × 10^5	2.6 × 10^5
$\Delta H^{\ddagger}$/kcal mol^{-1}	9.05 ± 0.45	10.14 ± 0.21
$\Delta S^{\ddagger}$/kcal mol^{-1} K^{-1}	−2.8 ± 2.3	0.39 ± 0.94
$\Delta G^{\ddagger}_{298}$/kcal mol^{-1}	9.88	10.02

[a] Error is 2.5σ (variance).

(**1**) and (**2**), respectively (Table 6). Non-planar structures for benzene rings of (**1**) in solution suggested by the ^{13}C chemical shifts may lead to lowering of the ground-state energies in solution compared with those in the solids, and thus to increasing the barriers in solution.

Molecular Mechanics Calculations.—The previous MMI calculations[4] for rotation of the bridgehad-methyl groups in (**1**), where the benzene rings kept their planarity during the rotation, gave an extremely large value (17.00 kcal mol^{-1}) for the barrier, which should be compared with the barrier in the solid (9.06 ± 0.30 kcal mol^{-1}). We pointed out the existence of nonbonded attractive interactions in the rotational transition state.[3,4] Here, we have now recalculated the barriers by another molecular mechanics method. Since the overestimation of the barriers is mainly due to excessively repulsive nonbonded interactions between hydrogen atoms in close proximity,[38,39] we have tried to alleviate it by using the MM2′ method,[40] which reproduces barriers for internal rotation in hydrocarbons reasonably well. MM2′ Calculations using the same parameter set[41] for aromatic carbon atoms as in the MM2 method still give a large barrier height of 14.48 kcal mol^{-1} for the rotation of the bridgehead-methyl group in (**1**).

We then investigated the rotation of the methyl group in but-1-ene, which is a model system for rotation of the bridgehead-methyl groups in 9-methyltriptycenes. Experimental V_3 potentials for *sp*- and ±*ac*-forms of but-1-ene are 3.99 ± 0.01 and 3.16 ± 0.04 kcal mol^{-1}, respectively.[42] MM2′ Calculations, however, yield substantially large values of 5.43 and 4.24 kcal mol^{-1} for the methyl barriers of the *sp*- and ±*ac*-forms, respectively. From examination of individual terms in the steric energy, we conclude that these overestimations originate from the large value (0.500 kcal mol^{-1}) of the V_3 torsional parameter for the C_{sp^2}–C_{sp^3}–C_{sp^3}–H bond. The V_3 parameters for the C_{sp^2}–C_{sp^3}–O–H and C_{sp^2}–C_{sp^3}–N–H bonds employed in the MM2 parametrizations[25] are 0.090 and 0.0 kcal mol^{-1}, respectively. If the V_3 parameter for the C_{sp^2}–C_{sp^3}–C_{sp^3}–H bond is changed to 0.0 kcal mol^{-1}, the methyl barriers reduce to 3.93 and 2.74 kcal mol^{-1}, respectively, in good agreement with the corresponding experimental potentials.

Thus, by the MM2′ method with a revised V_3 torsional parameter, we have finally obtained 10.01 kcal mol^{-1} for the bridgehead-methyl barrier of (**1**), which is only 0.95 kcal mol^{-1} higher than the experimental value in the solid.* Similar calculations for the barriers to rotation of the bridgehead-methyl groups in 9-methyl-, 9,10-dimethyl-, and 1,9-dimethyltriptycene yield 5.77, 6.39, and 8.40 kcal mol^{-1}, respectively, which are very close to the corresponding experimental values in the solid:[4] 5.20 ± 0.13, 6.36 ± 0.07, and 8.47 ± 0.41 kcal mol^{-1}, respectively.

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