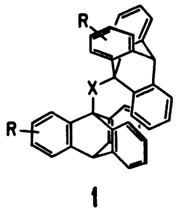
Bull. Chem. Soc. Jpn., 59, 3597—3603 (1986)

Restricted Rotation Involving the Tetrahedral Carbon. LIX. Stereodynamics of Singly *peri*-Substituted 9-(3,5-Dimethylphenoxy)triptycene Derivatives1)

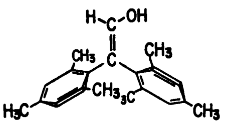
Gaku Yamamoto* and Michinori Ōki
Department of Chemistry, Faculty of Science, The University of Tokyo,
Bunkyo-ku, Tokyo 113
(Received May 26, 1986)

Five singly *peri*-substituted derivatives of 9-(3,5-dimethylphenoxy)triptycene with F, OCH_3, CH_3, Br, and $C(CH_3)_3$ as the *peri*-substituent were synthesized and their dynamic NMR behavior was studied. In any of the compounds, two *m*-methyl groups in the phenoxyl moiety were anisochronous at low temperatures and the signals coalesced into a single peak on raising the temperature. Lineshape analysis afforded the energy barriers to the rate process ranging from 10.1 kcal mol^{-1} (1 cal$_{th}$=4.184 J) for the F compound to 17.6 kcal mol^{-1} for the $C(CH_3)_3$ one. Molecular mechanics calculations (MM2) were performed on closely related model compounds to obtain the relative steric energies of the ground states and the possible transition states. The results from the dynamic NMR and the molecular mechanics studies suggest the following: When the *peri*-substituent is small (F and OCH_3), the complete gear rotational circuit with the passing of the aryl group over the *peri*-substituent as the rate-determining step is the lowest-barrier process, while when the *peri*-substituent is bulky (CH_3, Br, and $C(CH_3)_3$), the "isolated" rotation of the aryl group at the *ap* site has a lower barrier and is responsible for the observed dynamic NMR behavior. In the 1,3-di-*t*-butyl derivative, restricted rotation of the 1-*t*-butyl group was observed below −75 °C, the free energy of activation being 9.5 kcal mol^{-1}.

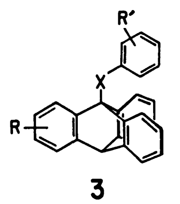
Gear rotation or correlated disrotation of two groups (chemical rotors) attached to a common central atom is a topic of recent interest. Bis(9-triptycyl)-X compounds **1** are chemical bevel gears consisting of a pair of three-toothed wheels.2) In these compounds, two wheels are tightly meshed and energy barriers to gear rotation are extremely low, being below the detection limit by dynamic NMR spectroscopy, while those to slippage of the gear are very high when X is oxygen or methylene, giving rise to isolable "phase" isomers.2a) Diaryl-X compounds may be regarded as a bevel gear system composed of a pair of two-toothed wheels. Static and dynamic stereochemical behavior of these compounds, however, seems diverse depending on the substituents on the aryl and the X moieties.3) Recently, correlated disrotation was clearly proved in 2,2-bis(2,4,6-trimethylphenyl)ethenol (**2**).3b)



1



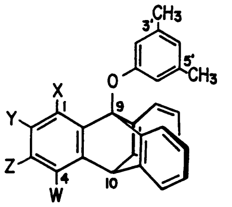
2



3

During the course of our studies on rotational isomerism in 9-substituted triptycene derivatives, we have been interested in the stereodynamics of 9-(arylmethyl)triptycenes (**3**: X=CH_2). These compounds adopt a conformation reminiscent of a bevel gear consisting of a two-toothed wheel and a three-toothed one, an edge of the aryl group being inserted into the notch of the triptycene skeleton.4a–d) A rate process which corresponds to either meshed gear rotation or gear slippage can be of low barrier depending on the substitution pattern on both the aryl and the triptycene moieties. We have extended the studies to 9-aryloxytriptycenes (**3**: X=O) by replacing the methylene group by a divalent oxygen and found that 9-(2-alkylphenoxy)-1,4-dimethyltriptycenes behave as dynamic gears, the meshed gear rotation being the lowest-barrier process.4e,f) The presence of a substituent at the ortho position of the aryloxyl moiety is an important factor for raising the gear slippage barrier and thus rendering the gear rotation solely detectable.

We describe in this paper the dynamic ^{1}H NMR and molecular mechanics studies on the stereodynamics of singly *peri*-substituted 9-(3,5-dimethylphenoxy)triptycenes (**4a**—**e**) which lack an *o*-substituent in the aryloxyl moiety and discuss the results in comparison with those on the carbon counterparts. We also report an almost unprecedented observation of restricted rotation of a *t*-butyl group bonded to a benzene ring found during this investigation.



	X	Y	Z	W
4a	F	F	F	F
4b	OCH_3	H	H	OCH_3
4c	CH_3	H	H	CH_3
4d	Br	Br	Br	Br
4e	$C(CH_3)_3$	H	$C(CH_3)_3$	H

Figure 1 shows six conformers corresponding to energy minima and possible interconversion processes among them. Three rotameric sites, *ap*, +*sc*, and −*sc*, are conceivable about the C_9–O bond, and in each site CH_3^A may look outwards (subscript 1) or inwards (subscript 2). Interconversion between ap_1 and $\pm sc_2$ and between ap_2 and $\pm sc_1$ occurs by gear rotation in which the aryl group passes over a *peri*-hydrogen

(GR(H)), while that between $\pm sc_1$ and $\mp sc_2$ occurs by gear rotation of the aryl group over the *peri*-substituent (GR(X)). Another possible process is "isolated" rotation (IR) in which the aryl group rotates by 180° without changing the rotameric site with respect to the C_9–O bond. This process corresponds to slippage of the gear and can occur either at the *ap* site (IR(*ap*)) or at the $\pm sc$ sites (IR(*sc*)).

Results and Discussion

Syntheses. 9-(3,5-Dimethylphenoxy)anthracene (**5**) was prepared in 36% yield by Ullmann reaction of 9-bromoanthracene with 3,5-dimethylphenol.[5] **5** was also obtained by acid-catalyzed condensation of anthrone[6] with 3,5-dimethylphenol but the yield was low (21%). Reactions of **5** with appropriate benzynes gave the triptycenes **4a**—**e**. 3,5-Di-*t*-butylbenzyne added to **5** to give **4e** and the corresponding 2,4-di-*t*-butyl derivative in ca. 3:1 ratio. Preferential formation of the more crowded regioisomer in the Diels–Alder reaction of benzynes is not unprecedented and has been discussed.[7]

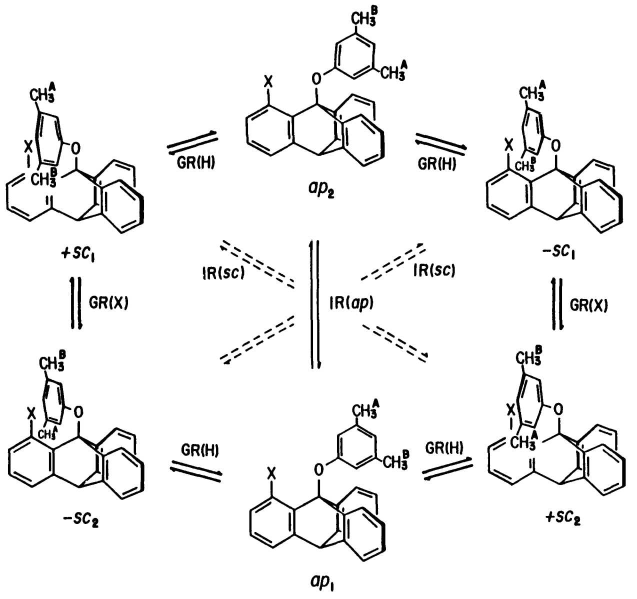
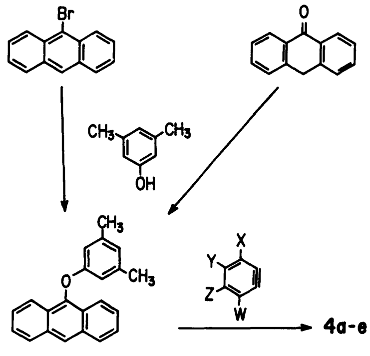


Fig. 1. Conformers of 1-substituted 9-(3,5-dimethylphenoxy)triptycenes and possible interconversion processes among them.



5

Dynamic NMR Studies. Variable temperature ^1H NMR study of the triptycenes **4a**—**e** revealed a common feature of the temperature dependence of the spectra. In any of the compounds, the signals derived from the *m*-methyl groups in the aryloxyl moiety appear as two equally intense singlets at low temperatures (Table 1) and they broaden and coalesce into a single peak upon raising the temperature. The lineshape change was analyzed as a coalescing AB spin system without mutual coupling using the DNMR3 program.[8] The kinetic parameters obtained are given in Table 2. By the same token, the *o*-protons in the aryloxyl moiety are anisochronous at low temperatures and isochronous at high temperatures. The substituents at 1 and 4 positions in **4b** and **4c** as well as the 3-*t*-butyl group in **4e** give rise to a sharp singlet for each throughout the temperature range

Table 1. Low Temperature ^1H chemical Shifts at 400 MHz[a)]

Compd	Temp / °C	Solvent	3′,5′-CH_3	10-H	1-X	3-Z or 4-W	2′,6′-H	4′-H
4a	−80	CD_2Cl_2	2.148 2.395	5.940			6.395 7.022	6.778
4b	−56	$CDCl_3$	2.087 2.414	5.952	3.205	3.876	6.340 7.074	6.663
4c	−56	$CDCl_3$	2.032 2.430	5.694	2.854	2.463	6.087 7.119	6.673
4d	−40	$CDCl_3$	2.055 2.386	6.142			6.041 7.108	6.680
4e	−96	CD_2Cl_2	1.923 2.437	5.507	1.489[b)] 1.815[b)]	1.264	5.673 ~7.19[c)]	6.669

a) Aromatic protons in the triptycene moiety are omitted. Chemical shifts are given in δ. All the signals shown in the table are singlets although 2′-, 4′-, and 6′-H are slightly broad. b) See text. c) Overlapped with other aromatic signals.

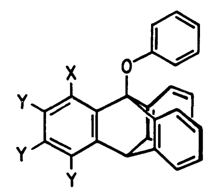
examined. The 1-*t*-butyl signal in **4e** behaves differently, which will be discussed later in detail. The two *o*-benzeno bridges carrying no substituent are magnetically equivalent in the whole temperature range in any compound.

The spectral feature observed at low temperatures suggests that the molecules exist either solely in *ap* conformation or as a rapidly interconverting mixture of *ap* and ±*sc*, preserving the diastereotopicity of the *m*-methyl groups in the aryloxyl moiety.

The two *m*-methyl groups should remain diastereotopic so far as the *ap* and ±*sc* rotamers rapidly interconvert by to-and-fro gear rotation via GR(H), $+sc_1 \rightleftarrows ap_2 \rightleftarrows -sc_1$ or $+sc_2 \rightleftarrows ap_1 \rightleftarrows -sc_2$. As discussed in the later section, compounds **4a—d** are thought to exist as a mixture of rotamers with respect to the C_9–O bond, while **4e** exists solely as the *ap* rotamer. Observation of only a single pair of methyl signals in **4a—d** in spite of the presence of both *ap* and ±*sc* rotamers should mean that GR(H) processes are too fast for the rotamers to be separately observed even at the lowest temperature examined.

Coalescence of the *m*-methyl signals occurs when either the GR(X) or the IR process becomes fast on the NMR time scale. However, which of these processes is the lowest-barrier one responsible for the observed dynamic NMR behavior is neither a priori evident nor is concluded by the NMR analysis.

Molecular Mechanics Calculations. In order to solve the above problem, we planned to resort to molecular mechanics calculations employing the MM2 program.[9] For simplifying the calculations, we adopted compounds **6a—e** as the respective models of **4a—e**; *m*-methyl groups in the aryloxyl moiety and 3- and 4-substituents in **4b**, **4c**, and **4e** were omitted by assuming that the buttressing effects of these groups against the neighboring hydrogen atoms are negligibly small, but halogen atoms at 2, 3, and 4 positions in **4a** and **4d** were included because the possible buttressing effect should be adequately considered.



6

	X	Y
6a	F	F
6b	OCH_3	H
6c	CH_3	H
6d	Br	Br
6e	$C(CH_3)_3$	H

Calculated steric energies of the ground states, *ap* and ±*sc*, and of the transition states for the possible dynamic processes, GR(H), GR(X), IR(*ap*), and IR(*sc*), are given in Table 3. We did not make efforts to construct the whole energy surface. In calculating the GR(X) and IR(*ap*) transition states, we assumed geometries of C_s symmetry; the substituted *o*-benzeno bridge coincides with the mirror plane and the phenoxyl benzene ring is perpendicular to it.

The *ap* ground state in any compound is shown to have C_s symmetry; the C_9–O–$C_{1'}$–$C_{6'}$ dihedral angle is 0°, giving rise to a static meshed gear. The ±*sc* isomer also resides in a meshed gear conformation, the C_9–O–$C_{1'}$–$C_{6'}$ angle being ca. −5° for the +*sc* forms of **6a—d** and −19° for +*sc*-**6e**. The ±*sc* form is calculated to be less stable than *ap* in any compound, and the detailed discussion on this point is given in the later section.

Table 2. Dynamic NMR Data

Compd	Solvent	Freq / MHz	Temp Range[a)] / °C	T_c[b)] / °C	ΔH^* / kcal mol^{-1}	ΔS^* / cal mol^{-1} K^{-1}	ΔG^*_{300K} / kcal mol^{-1}
4a	CD_2Cl_2	400	−80.7—−34.6	−58	$10.0_6 \pm 0.02$	−0.9±0.1	10.3
4b	$CDCl_3$	400	−34.7—5.0	−18	11.8±0.2	−0.9±0.7	12.1
4c	$CDCl_3$	60	−4.0—36.0	24	15.4±0.6	0.6±2.0	15.2
4d	$CDCl_3$	400	25.0—50.4	48	14.3±0.3	−3.4±1.0	15.3
4e	C_2Cl_4	60	51.4—100.6	75	17.6±0.2	−0.2±0.5	17.6

a) The range in which rate constants were obtained. b) Coalescence temperature.

Table 3. Relative Steric Energies by MM2 Calculations[a)]

Compd	X	Y	Ground States		Transition States			
			ap	±*sc*	GR(H)	GR(X)[b)]	IR(*ap*)[b)]	IR(*sc*)
6a	F	F	0	0.61	8.9	11.9	16.4	18.6
6b	OCH_3	H	0	0.52	9.0	14.0	16.5	c)
6c	CH_3	H	0	2.48	10.6	21.4	16.3	c)
6d	Br	Br	0	2.70	11.6	25.4	15.5	23.7
6e	$C(CH_3)_3$	H	0	7.78	14.3	33.1	15.3	c)

a) Values relative to that of *ap* for each compound are shown in kcal mol^{-1}. b) Geometry of C_s symmetry is assumed. c) Not calculated.

Steric energies of the transition states as given relative to that of the most stable ground state are nothing but the energy barriers to the respective processes. Dependence of the calculated barriers on the bulkiness of the *peri*-substituents is compatible with what comes from the intuitive considerations on the molecular models of the compounds: The GR barriers as well as the IR(*sc*) one are highly dependent on the *peri*-substituent but the IR(*ap*) one is rather insensitive to the size of the *peri*-substituent. We must note that, although a bromo group is usually thought to be smaller than a methyl group,[10] the 1-bromo group in **4d** is effectively bulkier than the 1-methyl group in **4c** because of the buttressing effect in **4d**.

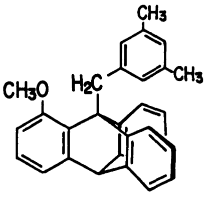
The GR(H) barriers calculated for **6a—d** are small enough to be consistent with the fact that slowing down of this process is not observed in the ^{1}H NMR spectra of **4a—d**.

The IR(*sc*) barrier is inferred to be much higher than the IR(*ap*) one in any compound, although the calculations were made only for **6a** and **6d**, bacause the increased degrees of rotational freedom of the 1-substituent prevented the ready calculation of the IR(*sc*) transition states for **6b**, **6c**, and **6e**. Therefore the IR(*sc*) process may be disregarded as an actually occurring process.

The GR(X) barrier is calculated to be lower than the IR(*ap*) one in **6a** and **6b**, but the situation is reversed in **6c—e**. Although the inaccuracy of the absolute values of the barrier heights should be allowed for, the following deduction would be reasonable. In **4a** and **4b**, the rate process observed by dynamic NMR corresponds to GR(X), while the IR(*ap*) process is responsible for the dynamic NMR behavior in **4c—e**. Therefore, the full gear rotational circuit involving GR(X) as the rate-determining step is the lowest-barrier process when the *peri*-substituent is small (F and OCH_3), but the gear slippage occurs more easily than the full gear rotation when the *peri*-substituent is bulkier (CH_3, Br, and $C(CH_3)_3$). The calculation underestimates the IR(*ap*) barrier in **6e** but the origin is uncertain.

Previously we reported that, in 1-methoxy-9-(3,5-dimethylbenzyl)triptycene (**7**), the free energy barrier to the *ap*→±*sc* conversion at −28 °C is 12.4 kcal mol^{-1} while the one to the exchange of the *m*-methyl groups is roughly estimated to be 12.6 kcal mol^{-1}.[4b] The former process corresponds to GR(H) and the latter to either GR(X) or IR(*ap*). Assuming that the GR(X) barrier should be considerably higher than the GR(H) one, we can assign IR(*ap*) to the process responsible for the *m*-methyl exchange.

A comparison of the data for **4b** with those for **7** reveals the effects of the central group (CH_2 or O) on the barriers to gear rotation and gear slippage. Here the effect of the 4-methoxyl group in **4b** is assumed to be negligible. The GR(H) barrier in **4b** is undetectably low, being calculated as 9.0 kcal mol^{-1} for **6b**, and thus is considerably lower than that in **7**. This may be explained in terms of the large valency effect (tetravalent in C and divalent in O) and the bond length effect partially cancelling the former, as discussed in detail in the previous paper.[4f] The IR(*ap*) barrier is far lower in **7** than in **4b** as calculated for **6b**, suggesting the importance of the bond length effect which causes tighter meshing of the gear in the oxygen compound **4b**. A similar trend in the gear slippage barriers has been observed in bis(9-triptycyl)-X compounds (**1**: X=CH_2 vs. O).[2a]



7

Rotamer Equilibria. No direct information on the rotamer distributions in **4a—e** is experimentally obtained because the rotamers interconvert rapidly even at the lowest temperature examined. However some information is indirectly obtained by careful examination of the NMR data. The chemical shift difference between the two *m*-methyl signals observed at low temperatures varies from 0.25 ppm for **4a** to 0.51 ppm for **4e** (Table 1), which may reflect the rotamer distribution between *ap* and ±*sc*. As the observed value is the difference between the chemical shift of $CH_3{}^A$ averaged over the rotamers and that of $CH_3{}^B$ also averaged over the rotamers and it should be very small if the two rotamers populate comparably and the larger it will be the more the equilibrium shifts to one side. In 9-(3,5-dimethylbenzyl)triptycene derivatives, where the rotamers were separately observed in the NMR spectra, the chemical shift differences between the *m*-methyl groups were 0.45—0.57 ppm.[11b] If the similar values of chemical shift differences are assumed for 9-(3,5-dimethylphenoxy)-triptycene rotamers, it is inferred that the rotamer equilibrium is moderately shifted to one side in **4a—d** and is almost exclusively one-sided in **4e**.

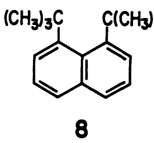
Similar inference can be made from the temperature dependence of the chemical shift difference: It decreases almost linearly with the temperature in **4a—d**, the increment being −0.40, −0.20, −0.33, and −0.27 Hz/deg, respectively, reflecting the increasing population of the minor rotamer at higher temperatures. The chemical shift differences in **4e** is almost independent of the temperature (+0.05 Hz/deg), and thus it is reasonable to conclude that **4e** exists solely as a single rotamer.

The next question to answer is to which side the equilibrium is shifted. The above reasoning together with the results of molecular mechanics calculation concludes that **4e** exists solely as the *ap* rotamer. As for **4b** and **4c**, the chemical shifts of the 1-substituent give some information. The 1-methoxyl proton signal in **4b** appears at a considerably high field of δ 3.21 at −56 °C and shifts slightly downfield upon raising the temperature (δ 3.24 at 24 °C). The facts are consistent with the reasoning that the ±*sc* rotamer, in which the 1-methoxyl group is located in the shielding region of the aryl group, is predominant and the population of the less stable *ap* rotamer increases with temperature. In various 1-methoxy-9-(arylmethyl)triptycene derivatives ever examined,[11] the 1-methoxyl group gives its signal at δ 2.89—2.95 in the ±*sc* rotamers and at δ 3.78—3.85 in *ap*. The Winstein–Holnes relation using these values suggests that about two thirds of **4b** exists as ±*sc*. Predominance of the ±*sc* rotamer in **4b** is in line with the behavior observed in the 1-methoxy-9-(arylmethyl)-triptycene derivatives.[11] The population of the *ap* rotamer in 1,4-dimethyl-9-phenoxytriptycene was previously suggested to be about 80% at room temperature from the 1-methyl chemical shift[4f] and the similar value may also be applicable to **4c**.

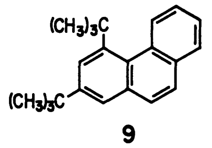
The population of *ap* of 33 and 80% at room temperature corresponds to the energy difference ($E_{\pm sc}-E_{ap}$) of 0.0 and 1.24 kcal mol^{-1}, respectively, if the statistical factor of 2 for ±*sc* is assumed to be the sole contributor to the entropy term. As the MM2 calculation (Table 3) gives the energy differences of 0.52 and 2.48 kcal mol^{-1} for **6b** and **6c**, respectively, it somewhat overestimates the relative instability of the ±*sc* rotamers. The discrepancies between the NMR and MM2 results may be at least partly ascribed to the insufficiency of the force field used in the calculation as discussed before.[4f]

Restricted Rotation of the 1-*t*-Butyl Group in 4e.[12] In the 400 MHz ^{1}H NMR spectrum of **4e** at ambient temperature, the singlet at δ 1.715 due to the 1-*t*-butyl group appears considerably broader than the one at δ 1.247 assigned to the 3-*t*-butyl group. On lowering the temperature, the low-field signal further broadens and below −75 °C it splits into two peaks. At −96.2 °C, they appear as a three-proton singlet at δ 1.489 and a six-proton singlet at δ 1.815, while the high-field signal remains a sharp nine-proton singlet at δ 1.264. The phenomenon should be ascribed to the restricted internal rotation of the 1-*t*-butyl group. Lineshape analysis of the spectra at −83 to −56 °C using the DNMR3 program[8] gave the following activation parameters: $\Delta H^{\neq}=9.2\pm0.6$ kcal mol^{-1}, $\Delta S^{\neq}=-1.7\pm2.9$ cal mol^{-1} K^{-1}, $\Delta G^{\neq}_{200\mathrm{K}}=9.5$ kcal mol^{-1}.

This high energy barrier to rotation of a *t*-butyl group bonded to an *sp*^{2}-hydridized carbon atom is unprecedented.[13] Several attempts at observing the restricted rotation of C_{sp^2}–Bu^t bonds by NMR spectroscopy were unsuccessful.[14] The failure might result from the fact that the presence of a supposedly rotation-hindering group raised not only the transition state energy but also the ground state one. An apparent exception may be 1,8-di-*t*-butylnaphthalene (**8**) derivatives, where an energy barrier of 6.5 kcal mol^{-1} was reported for the internal rotation of the *t*-butyl groups,[15a] although the geometry around the 1- and 8-carbons is far from what is expected for the normal *sp*^{2}-hybridization.[15b]



8



9

The ORTEP drawing[17] of the lowest-energy conformation of **6e** obtained by the MM2 calculation is shown in Fig. 2. Compound **4e** should reasonably adopt a similar conformation as **6e**. The molecule has a plane of symmetry and two enantiotopic methyl groups (CH$_3^{\mathrm{A}}$) in the 1-*t*-butyl group face the oxygen atom and the other methyl (CH$_3^{\mathrm{B}}$) eclipses C-2. The geometrical features that the benzene ring carrying the *t*-butyl group is completely planar, that the C$_1$–Bu^t bond shows no out-of-plane deformation in spite of the large in-plane distortion, and that the C$_9$–O bond is also in plane of the benzene ring, are in sharp contrast with those observed in the 1,8-di-*t*-butylnaphthalenes[15b] and 2,4-di-*t*-butylphenanthrene (**9**),[16] where significant distortion from planarity has been noticed. This rigidity of the triptycene skeleton together with the rather small oxygen atom as the obstacle to rotation should cause the high energy barrier to rotation of the 1-*t*-butyl group: The transition state for rotation is effectively raised while the ground state is not raised too much. It will be

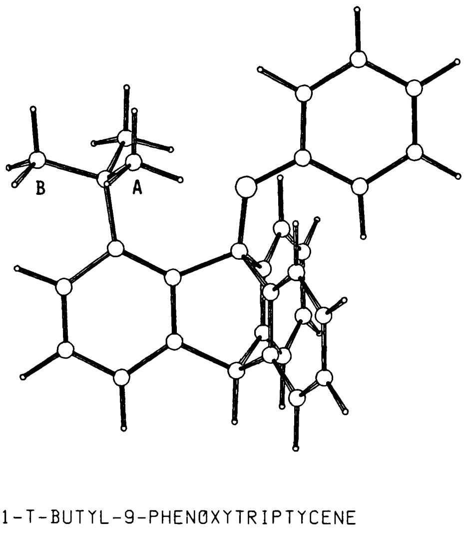


Fig. 2. ORTEP drawing of the most stable conformation of 1-*t*-butyl-9-phenoxytriptycene (**6e**) obtained by the MM2 calculation.

interesting to examine whether 9-substituted 1-*t*-butyltriptycenes generally have high energy barrier to rotation of the 1-*t*-butyl group, and further studies on this point is in progress.

Judging from the relative signal intensities, the CH$_3^A$ protons resonate at a lower field than the CH$_3^B$ protons. The anisotropy and/or the field effect of the oxygen atom as well as the ring current effect of the phenoxyl benzene ring might cause the deshielding of the CH$_3^A$ protons, which should exceed the deshielding effect of the *o*-benzeno ring carrying the *t*-butyl group on the protons of the in-plane CH$_3^B$ group.

Below −90 °C, the CH$_3^B$ signal showed further broadening probably because of the slow-down of the internal rotation of this methyl group, although no discrete splitting of the signal was observed down to −111 °C. The staggered conformation of the methyl group and the presence of the 2-hydrogen atom as the effective obstacle might be responsible for the high rotational barrier of the methyl group.

Experimental

General Methods. ^{1}H NMR spectra at ambient temperature were obtained on a Varian EM-390 spectrometer at 90 MHz in the CW mode and on a JEOL GX-400 spectrometer at 399.65 MHz in the pulse FT mode. Variable temperature ^{1}H NMR spectra were recorded either on a Hitachi R-20B spectrometer at 60 MHz in the CW mode or on GX-400. With R-20B, temperatures were calibrated with a methanol or ethylene glycol sample[18] while they were read as digital outputs and are not corrected with GX-400. ^{19}F NMR spectra were obtained on EM-390 at 84.67 MHz. ^{1}H NMR data given in the Experimental section are those obtained on GX-400 at 21—24 °C, unless otherwise stated.

Preparative gel permeation chromatography was performed on an LC-08 Liquid Chromatograph of Japan Analytical Industry Co., Ltd. using a series of JAIGEL 1H and 2H columns and chloroform as the eluent.

Theoretical spectra for the dynamic NMR simulations were obtained on a HITAC M-280H computer system at the Computer Center of the University of Tokyo (CCUT) using the DNMR3 program.[8]

Molecular mechanics calculations were performed on the M-280H system using the MM2 program in the CCUT Program Library with some modifications of the parameters as described before.[4f,19] In obtaining the transition state energies, the C$_{9a}$–C$_9$–O–C$_{1'}$ and C$_9$–O–C$_{1'}$–C$_{6'}$ bonds were driven near the supposed transition state geometries and the saddle points of energy were sought. In cases of GR(X) and IR(*ap*) transition states, the geometries of C_s symmetry were assumed, although such geometries are not necessarily a prerequisite for the transition states.[20]

9-(3,5-Dimethylphenoxy)anthracene (5). (A) A mixture of 5.14 g (20 mmol) of 9-bromoanthracene, 12.2 g (100 mmol) of 3,5-dimethylphenol, 2.8 g of potassium hydroxide, and 1.0 g of copper powder was heated at 230 °C for 2 h. The cooled mixture was extracted with benzene–water. The benzene layer was washed successively with aqueous sodium hydroxide and water, and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on alumina with hexane–dichloromethane as the eluent. A fraction containing 1.11 g (6.2 mmol) of anthracene eluted first, followed by a fraction containing **5**. Recrystallization of the eluate from tetrahydrofuran–hexane gave 2.12 g (36%) of **5**, mp 174—175 °C. Found: C, 88.79; H, 6.02%. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%. ^{1}H NMR (CDCl$_3$, 90 MHz, 35 °C) δ=2.15 (6H, s), 6.45 (2H, s), 6.61 (1H, s), 7.2—7.5 (4H, m), 7.8—8.2 (4H, m), 8.31 (1H, s).

(B) A solution of 5.82 g (30 mmol) of anthrone and 7.33 g (60 mmol) of 3,5-dimethylphenol in 100 mL of toluene containing 1.0 mL of concentrated sulfuric acid was heated with a Dean–Stark water collector for 140 h. The solution was washed successively with aqueous sodium hydroxide and water, dried over magnesium sulfate, and concentrated. Column chromatography of the residue on alumina gave 1.86 g (21%) of **5**.

1,2,3,4-Tetrafluoro-9-(3,5-dimethylphenoxy)triptycene (4a). To a chilled (−78 °C) solution of 0.5 mL (ca. 4.3 mmol) of chloropentafluorobenzene in 30 mL of diethyl ether was added 2.0 mL (ca. 3.1 mmol) of a 10% (w/v) solution of butyllithium in hexane and the solution was stirred for 2 h at −78 °C. To this solution was added 448 mg (1.5 mmol) of **5** and the mixture was allowed to warm up to room temperature with stirring, stirred at room temperature for 2 h and heated under reflux for 2 h. The reaction mixture was washed with water, dried over magnesium sulfate and concentrated. The residue was heated under reflux overnight with 0.5 g (ca. 5 mmol) of maleic anhydride in 10 mL of acetonitrile. After evaporation of the solvent, the residue was chromatographed on alumina with hexane–dichloromethane as the eluent, affording 33 mg (5%) of **4a**, mp 250—252 °C. Found: C, 75.09; H, 4.15%. Calcd for $C_{28}H_{18}F_4O$: C, 75.33; H, 4.06%. ^{1}H NMR (CDCl$_3$) δ=2.241 (6H, s), 5.783 (1H, d, *J*=1.5 Hz), 6.657 (2H, s), 6.691 (1H, s), 7.00—7.10 (4H, m), 7.40—7.50 (4H, m). ^{19}F NMR (CDCl$_3$, ppm downfield from internal hexafluorobenzene) 3.13 (dd, *J*=19 and 21 Hz, 2-F), 3.81 (ddd, *J*=3, 19, and 21 Hz, 3-F), 13.10 (dd, *J*=15 and 21 Hz, 4-F), 20.39 (br m, 1-F).

1,4-Dimethoxy-9-(3,5-dimethylphenoxy)triptycene (4b). To a boiling solution of 298 mg (1.0 mmol) of **5** in 20 mL of 1,2-dimethoxyethane(DME) was added a solution of 986 mg (5.0 mmol) of 3,6-dimethoxyanthranilic acid[21] in 20 mL of DME and a solution of 1.0 mL (ca. 7.4 mmol) of isopentyl nitrite in 10 mL of DME during the course of 2 h so that excess of isopentyl nitrite always existed in the reaction mixture. The mixture was heated under reflux for 0.5 h and concentrated. The residue was chromatographed on alumina with hexane–dichloromethane as the eluent, affording 70 mg (16%) of **4b**, mp 264—265 °C after recrystallization from tetrahydrofuran-hexane. Found: C, 82.79; H, 5.95%. Calcd for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03%. ^{1}H NMR (CDCl$_3$) δ=2.221 (6H, br s), 3.236 (3H, s), 3.859 (3H, s), 5.898 (1H, s), 6.509 and 6.611 (2H, AB-q, *J*=8.9 Hz), 6.608 (1H, s), 6.668 (2H, br s), 6.90—7.05 (4H, m), 7.35—7.60 (4H, m).

1,4-Dimethyl-9-(3,5-dimethylphenoxy)triptycene (4c). Similar reaction as above of **5** with 3,6-dimethylanthranilic acid[22] gave **4c**, mp 261—262 °C, in 58% yield. Found: C, 89.33; H, 6.56%. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51%. ^{1}H NMR (CDCl$_3$) δ=2.031 (3H, br s), 2.372 (3H, br s), 2.440 (3H, s), 2.792 (3H, s), 5.622 (1H, s), 6.154 (1H, br s), 6.628

(1H, s), 6.640 and 6.667 (2H, AB-q, J=7.2 Hz), 6.85—7.05 (5H, m), 7.25—7.45 (4H, m).

1,2,3,4-Tetrabromo-9-(3,5-dimethylphenoxy)triptycene (4d). Similar reaction as above of **5** with tetrabromoanthranilic acid[23] gave **4d**, mp 330—332 °C (decomp), in 11% yield. Found: C, 48.62; H, 2.67; Br, 46.80%. Calcd for $C_{28}H_{18}Br_4O$: C, 48.73; H, 2.63; Br 46.32%. ^{1}H NMR ($CDCl_3$) δ=2.054 (3H, br s), 2.344 (3H, br s), ca. 6.1 (1H, br), 6.100 (1H, s), 6.654 (1H, s), 6.95—7.15 (5H, m), 7.30—7.55 (4H, m).

1,3-Di-*t*-butyl-9-(3,5-dimethylphenoxy)triptycene (4e). Similar reaction as above of **5** with 3,5-di-*t*-butylanthranilic acid[7b] gave a ca. 3:1 mixture of **4e** and the isomeric 2,4-di-*t*-butyl-9-(3,5-dimethylphenoxy)triptycene. Separation of the regioisomers was performed by gel permeation chromatography. Even after 20 recycles, complete baseline separation of the isomers was not attained. **4e** was isolated in ca. 18% yield, mp 203—205 °C. Found: C, 88.62; H, 7.58%. Calcd for $C_{36}H_{38}O$: C, 88.84; H, 7.87%. ^{1}H NMR ($CDCl_3$) δ=1.227 (9H, s), 1.722 (9H, s), 1.905 (3H, s), 2.429 (3H, s), 5.322 (1H, s), 5.720 (1H, s), 6.601 (1H, s), 6.8—7.5 (11H, m). The 2,4-di-*t*-butyl compound was isolated in ca. 6% yield, mp 238—239 °C. Found: C, 88.90; H, 7.59%. ^{1}H NMR ($CDCl_3$, 90 MHz, 35 °C): δ=1.14 (9H, s), 1.58 (9H, s), 2.23 (6H, s), 6.14 (1H, s), 6.65 (1H, s), 6.73 (2H, s), 6.8—7.1 (5H, m), 7.3—7.5 (5H, m).

References

1) Part LVIII: Ref. 12.

2) a) H. Iwamura, *J. Mol. Struct.*, **126**, 401 (1985); Y. Kawada and H. Iwamura, *J. Am. Chem. Soc.*, **105**, 1449 (1983); H. Iwamura, T. Ito, H. Ito, K. Toriumi, Y. Kawada, E. Ōsawa, T. Fujiyoshi, and C. Jaime, *ibid.*, **106**, 4712 (1984); b) H.-B. Bürgi, W. D. Hounshell, R. B. Nachbar, Jr., and K. Mislow, *ibid.*, **105**, 1427 (1983); A. Guenzi, C. A. Johnson, F. Cozzi, and K. Mislow, *ibid.*, **105**, 1438 (1983).

3) a) D. Gust and K. Mislow, *J. Am. Chem. Soc.*, **95**, 1535 (1973) and references cited therein; b) D. A. Nugiel, S. E. Biali, and Z. Rappoport, *ibid.*, **106**, 3357 (1984); c) cf. B. F. Bononi, L. Grossi, L. Lunazzi, and D. Macchiantelli, *J. Org. Chem.*, **51**, 517 (1986).

4) a) G. Yamamoto, *J. Mol. Struct.*, **126**, 413 (1985); b) G. Yamamoto and M. Ōki, *Chem. Lett.*, **1979**, 1251; G. Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 473 (1981); c) G. Yamamoto and M. Ōki, *Chem. Lett.*, **1979**, 1255; G, Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 491 (1981); d) G. Yamamoto and M. Ōki, *J. Org. Chem.*, **48**, 1233 (1983); e) G. Yamamoto and M. Ōki, *Chem. Lett.*, **1984**, 92; f) G. Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 1953 (1985).

5) cf. W. Theilacker, U. Berger-Brose, and K.-H. Beyer, *Chem. Ber.*, **93**, 1658 (1960).

6) cf. W. H. Pirkle and J. M. Finn, *J. Org. Chem.*, **48**, 2779 (1983).

7) a) G. Yamamoto, M. Suzuki, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 306 (1983); b) R. W. Franck and E. G. Leser, *J. Org. Chem.*, **35**, 3932 (1970); c) J. E. Anderson, R. W. Franck, and W. L. Mandella, *J. Am. Chem. Soc.*, **94**, 4608 (1972).

8) D. A. Kleier and G. Binsch, *QCPE*, No. 165.

9) N. L. Allinger and Y. H. Yuh, *QCPE*, No. 395.

10) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, New York (1960), p. 260; G. Bott, L. D. Field, and S. Sternhell, *J. Am. Chem. Soc.*, **102**, 5618 (1980). See also: W. D. Hounshell, L. D. Iroff, D. J. Iverson, R. J. Wrozynski, and K. Mislow, *Isr. J. Chem.*, **20**, 65 (1980).

11) a) F. Suzuki and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 596 (1975); b) G. Yamamoto and M. Ōki, *ibid.*, **54**, 473 (1981); c) G. Yamamoto and M. Ōki, *ibid.*, **54**, 481 (1981).

12) Preliminary results have been reported: G. Yamamoto and M. Ōki, *Tetrahedron Lett.*, **27**, 49 (1986).

13) Restricted rotation of a trimethylsilyl group attached to an *sp*^{2}-hybridized carbon atom has been reported: J.-C. Clinet, E. Dunach, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **105**, 6710 (1983); H. Butenschön, M. Winkler, and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, **1986**, 388.

14) M. Ōki and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **44**, 1880 (1971); B. Miller and K.-H. Lai, *Tetrahedron Lett.*, **1971**, 2957.

15) a) J. E. Anderson, R. W. Franck, and W. L. Mandella, *J. Am. Chem. Soc.*, **94**, 4608 (1972); b) J. Handal, J. G. White, R. W. Franck, Y. H. Yuh, and N. L. Allinger, *ibid.*, **99**, 3345 (1977); **101**, 5456 (1979).

16) The 4-*t*-butyl proton signal of 2,4-di-*t*-butylphenanthrene (**9**) does not split down to −90 °C and the X-ray crystal structure of this compound shows considerable distortion of the 4-*t*-butyl group as well as the phenanthrene ring itself: H. J. Lindner, H. Scherübl, and A. Mannschreck, unpublished results. We are grateful to Professor Mannschreck for informing us the results.

17) C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1965).

18) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

19) G. Yamamoto and M. Ōki, *Bull. Chem. Soc.*, **56**, 1690 (1985).

20) L. Salem, J. Durup, G. Bergeron, D. Cazes, X. Chapuisat, and H. Kagan, *J. Am. Chem. Soc.*, **92**, 4472 (1970).

21) M. Ōki, Y. Tanaka, G. Yamamoto, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **56**, 302 (1983).

22) S. Gronowitz and G. Hansen, *Arkiv Kemi*, **27**, 145 (1967).

23) H. Heaney, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc., C*, **1971**, 567.