Restricted Rotation Involving the Tetrahedral Carbon. LII. Rotational Barriers in 1,2,3,4-Tetrafluoro- and 1,4-Dimethoxy-9-(1-cyano-1-methylethyl)triptycenes[1)]

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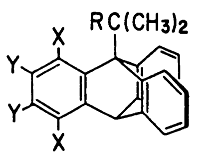
Synopsis. Kinetic measurements of rotamer isomerization of the title compounds show that the rotational barriers in these compounds are considerably higher than those in the *peri*-unsubstituted and the *peri*-chloro or *peri*-methyl compounds, affording a support to our earlier finding that the rotational barrier increases and then decreases as the *peri*-substituent becomes bulkier in 9-*t*-alkyltriptycenes.

We have shown that introduction of a chloro or a methyl group into a *peri*-position of 9-(1-cyano or methoxycarbonyl-1-methylethyl)triptycene (**1** and **2**) causes a decrease of the energy barrier to rotation about the bridgehead-to-substituent bond relative to the *peri*-unsubstituted compound.[2)] A more extensive study on the effect of the *peri*-substituent on the rotational barrier in 9-(1,1-dimethyl-2-phenylethyl)triptycenes (**3**) revealed that a relatively small *peri*-substituent such as fluoro and methoxyl raises the barrier relative to the *peri*-unsubstituted compound **3a**, while a *peri*-group bulkier than chloro decreases the barrier.[3)] Molecular deformation in this highly congested system might partly explain these phenomena.[3)] These findings urged us to examine whether a fluoro or a methoxyl group at a *peri*-position raises the rotational barrier in compounds **1** and **2** as well. The results are presented in this note.



	R
1	CN
2	CO_2CH_3
3	$CH_2C_6H_5$

	X	Y
a	H	Cl
b	F	F
c	OCH_3	H
d	Cl	Cl
e	CH_3	H

Results and Discussion

Reactions of 9-(1-cyano-1-methylethyl)anthracene with tetrafluoro- and 3,6-dimethoxybenzynes gave stereoselectively the ±*sc* atropisomers of **1b** and **1c**, respectively. Kinetic measurements of isomerization were carried out in 1-chloronaphthalene at three to four points of temperature. The equilibrium and rate constants obtained are compiled in Table 1 and the kinetic parameters therefrom are given in Table 2. The rotational barriers in these compounds are actually higher not only than that in the *peri*-unsubstituted derivative **1a** but also than those in the *peri*-chloro (**1d**) and the *peri*-methyl (**1e**) compounds. As shown in Fig. 1, the dependence of the energy barrier upon the *peri*-substituent in compounds **1** is very similar to that found in compounds **3**. This clearly shows that the appearance of the maximal barrier at a relatively small

TABLE 1. EQUILIBRIUM AND RATE CONSTANTS

$ap \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \pm sc : K=k_1/k_{-1}$

Compd	Temp / °C	K	k_1 / s^{-1}
1b	240	1.66	1.44×10^{-4}
	211	1.83	1.52×10^{-5}
	196	1.93	4.53×10^{-6}
1c	220	4.11	1.09×10^{-4}
	211	4.39	4.24×10^{-5}
	197	4.73	1.60×10^{-5}
	189	4.36	7.90×10^{-6}

TABLE 2. EYRING PARAMETERS FOR ISOMERIZATION[a)]

Compd	Process	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{473}$ / kcal mol^{-1}
1b	*ap*→±*sc*	36.7±3.6	−5.7±7.3	39.4
	±*sc*→*ap*	38.4±2.8	−3.5±5.6	40.0
1c	*ap*→±*sc*	36.2±9.9	−4.4±20.8	38.3
	±*sc*→*ap*	37.4±11.9	−4.9±24.9	39.7

a) 1 cal=4.184 J.

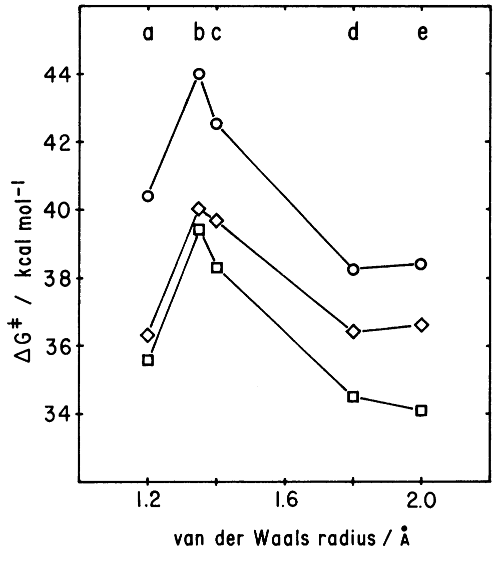


Fig. 1. Dependence of rotational barriers on the bulkiness of the *peri*-substituents.
□: $\Delta G^{\ddagger}_{473}$ for *ap*→±*sc* in **1**. ◇: $\Delta G^{\ddagger}_{473}$ for ±*sc*→*ap* in **1**. ○: $\Delta G^{\ddagger}_{500}$ for *ap*→±*sc* in **3**.

peri-substituent is a general phenomenon in 9-*t*-alkyltriptycenes.

The equilibrium constant at 200 °C, K_{473}(±*sc*/*ap*), becomes larger as the *peri*-substituent becomes bulkier with an exception of **1b**: **1a**, 2.3; **1b**, 1.9; **1c**, 4.4; **1d**, 6.8; **1e**, 15. This trend is reasonable from the standpoint of steric effects because methyl is bulkier than cyano. Deviation from the trend by **1b**, where K_{473} is smaller than the statistical value of 2.0, may be ascribed to the electrostatic repulsion between the fluoro and cyano groups overweighing the steric effect.

9-(1-Methoxycarbonyl-1-methylethyl)anthracene failed to react with tetrafluorobenzyne to give **2b**, but reacted with 3,6-dimethoxybenzyne to afford stereoselectively the ±*sc* rotamer of **2c**. Heating a sample of ±*sc*-**2c** in 1-chloronaphthalene for *ca.* 5 h at 189 °C caused the complete equilibration of the rotamers but the equilibrium population of *ap*-**2c** was *ca.* 2-3%, which made the kinetic measurement of isomerization impossible. The overwhelming abundance of the ±*sc* rotamer may be due to the attractive interaction[4] between the methoxycarbonyl and the *peri*-methoxyl groups in ±*sc*-**2c** together with the steric effect also favoring the ±*sc* rotamer.

Experimental

Melting points are not corrected. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer at 90 MHz at ambient temperature of *ca.* 35 °C. Experimental procedures of the kinetic measurements were described before.[2,3]

9-(1-Cyano-1-methylethyl)-1,2,3,4-tetrafluorotriptycene (1b). Reaction of 9-(1-cyano-1-methylethyl)anthracene[2] with pentafluorophenyllithium according to the procedure described in the literature[5] followed by column chromatography on silica gel with hexane–benzene as the eluent gave ±*sc*-**1b** in 41% yield, mp 239—240 °C (from tetrahydrofuran–hexane). Found: C, 73.23; H, 3.78; N, 3.66%. Calcd for $C_{24}H_{15}F_4N$: C, 73.28; H, 3.78; N, 3.56%. ^{1}H NMR ($CDCl_3$, δ): 2.39 (3H, d, J=7.0 Hz), 2.43 (3H, s), 5.73 (1H, br d, J=1.8 Hz), 7.0—7.2 (4H, m), 7.3—7.7 (3H, m), 8.0—8.2 (1H, m). The *ap* rotamer of **1b** was purely isolated from the equilibrated mixture of rotamers by column chromatography on silica gel, mp 231—232 °C (from tetrahydrofuran–hexane). Found: C, 73.11; H, 3.77; N, 3.56%. ^{1}H NMR ($CDCl_3$, δ): 2.41 (6H, d, J=6.3 Hz), 5.77 (1H, br d, J=1.8 Hz), 7.0—7.2 (4H, m), 7.3—7.6 (2H, m), 7.8—8.1 (2H, m).

9-(1-Cyano-1-methylethyl)-1,4-dimethoxytriptycene (1c). Reaction of 9-(1-cyano-1-methylethyl)anthracene[2] with 3,6-dimethoxyanthranilic acid[6] according to the general procedure described before[3] gave ±*sc*-**1c** in 50% yield, mp 293—296 °C (from tetrahydrofuran–ethanol). Found: C, 81.81; H, 5.83; N, 3.63%. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67%. ^{1}H NMR ($CDCl_3$, δ): 2.40 (3H, s), 2.42 (3H, s), 3.81 (3H, s), 3.82 (3H, s), 5.85 (1H, s), 6.58 (2H, s), 6.9—7.1 (4H, m), 7.3—7.7 (3H, m) 8.1—8.3 (1H, m). Column chromatography of the equilibrated rotamer mixture on alumina gave *ap*-**1c**, mp 297—298.5 °C (from ethanol). Found: C, 81.64; H,5.92; N, 3.64%. ^{1}NMR ($CDCl_3$, δ): 2.43 (6H, s), 3.72 (3H, s), 3.82 (3H, s), 5.90 (1H, s), 6.58 and 6.67 (2H, AB-q, J=9 Hz), 6.9—7.1 (4H, m), 7.3—7.5 (2H, m), 7.9—8.1 (2H, m).

±sc-*1,4-Dimethoxy-9-(1-methoxycarbonyl-1-methylethyl)triptycene (*±sc-***2c****),* mp 222—224 °C, was synthesized similarly as ±*sc*-**1c** from 9-(1-methoxycarbonyl-1-methylethyl)anthracene[2] and 3,6-dimethoxyanthranilic acid[6] in 6% yield. Found: C, 78.28; H, 6.38%. Calcd for $C_{27}H_{26}O_4$: C, 78.24; H, 6.32%. ^{1}H NMR ($CDCl_3$, δ): 2.18 (6H, s),[7] 3.59 (3H, s), 3.65 (3H, br s), 3.80 (3H, s), 5.84 (1H, s), 6.48 and 6.59 (2H, AB-q, J=9 Hz), 6.7—7.1 (4H, m), 7.2—7.9 (4H, m).

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7) The *gem*-dimethyl protons are accidentally isochronous. In benzene two singlets are observed for them.