Restricted Rotation Involving the Tetrahedral Carbon. XXXIX. 9-(2-Methoxy-1-methylethyl)triptycene Derivatives[1)]

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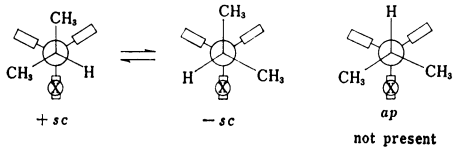
9-(2-Methoxy-1-methylethyl)triptycenes were prepared from 9-(2-methoxy-1-methylethyl)anthracene and corresponding benzynes to examine the feasibility of isolating rotational isomers of 9-isopropyltriptycene derivatives at room temperature. They afforded crystalline *ap* forms which underwent internal rotation with activation energies of *ca.* 23 kcal/mol. 9-(2-Acetoxy-1-methylethyl)-1,2,3,4-tetrachlorotriptycene gave similar results. Based on the results, the barrier to rotation of 9-isopropyl-1,2,3,4-tetrabromotriptycene was reexamined to show that it must be corrected as 23.5 kcal/mol at 175 °C.

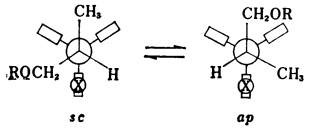
Stable rotamers of triptycene derivatives carrying a *t*-alkyl group in 9-position have been isolated at room temperature.[2)] It is also possible to isolate rotamers of a compound carrying a primary alkyl group in 9-position of triptycene at room temperature, if it carries three substituents in three peri-positions which are close to the alkyl group.[3)] To date, however, no rotamers have been isolated of compounds which carry a *s*-alkyl group in 9-position of triptycene. The possibility of the isolation has long been suggested because 9-isopropyltriptycenes were shown to have barriers to rotation of more than 23 kcal/mol (1 cal=4.18 J):[4)] it is suggested that if the barrier is over 23 kcal/mol, the rotamer is stable at room temperature.[5)]

The problem for isolating the rotamers of 9-isopropyltriptycene is that they exist as a pair of enantiomers and a diastereomeric *ap* form is not found for the steric reasons: it is necessary to resolve the racemate into enantiomers. Although a functionality for the resolution



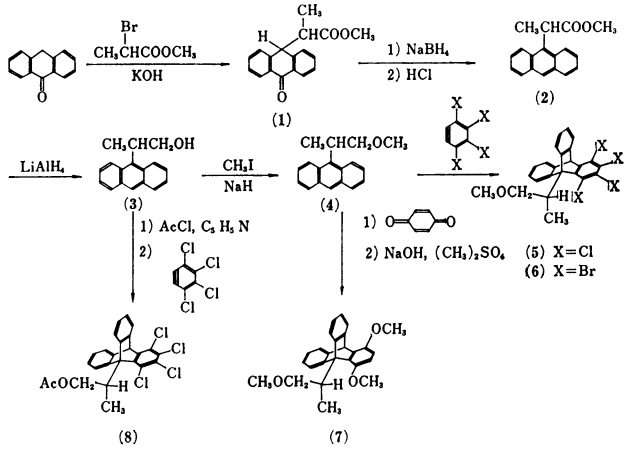
may be introduced into these compounds, the similar results may be obtained by modifying the isopropyl group, because modifying a methyl of the isopropyl group should produce diastereomers, if the rotation in question is slow, which should be separable by ordinary physical methods. Thus we introduced a methoxyl or an acetoxyl group to one of the methyls of the isopropyl group. This paper reports the results of such an investigation.

There is a problem of naming the stereochemistry of these comformations, as discussed elsewhere,[1)] because the conformations involve a chiral center. However, we should like to use *ap* and *sc* as designated for simplicity of the discussion: although, in principle, there is another *sc* form in which a methyl and an $ROCH_2$ group flank the substituted benzeno bridge, in practice that conformation is nonexistent for the steric reasons because



it is a substituted derivative of the *ap* conformation of 9-isopropyltriptycenes.

The compounds examined in this study were prepared in the following way. Anthrone was alkylated with methyl 2-bromopropionate in the presence of a base and the resulted ester (**1**) was reduced with sodium tetrahydridoborate to corresponding alcohols which were dehydrated with hydrochloric acid to produce an anthracene-ester (**2**). The ester was reduced with lithium tetrahydridoaluminate to afford the corresponding alcohol (**3**). The alcohol was methylated with sodium hydride and methyl iodide. Treatment of the methyl ether (**4**) with tetrahalobenzynes afforded desired triptycenes (**5** and **6**). Treatment of the methyl ether (**4**) with *p*-benzoquinone followed by enolization of the adduct and then methylation gave a 1,4-dimethoxytriptycene (**7**). Acetylation of the alcohol (**3**) followed by treatment with tetrachlorobenzyne afforded 1,2,3,4-tetrachloro-9-(2-acetoxy-1-methylethyl)triptycene (**8**).



Experimental

10-(1-Methoxycarbonylethyl)anthrone (1). To a mixture of 35 g (0.18 mol) of anthrone and 29 g (0.174 mol) of methyl 2-bromopropionate in 200 mL of methanol was added with stirring a solution of 10 g (0.179 mol) of potassium hydroxide in 150 mL of methanol during a 3 h period at room temperature under a nitrogen atmosphere. Insoluble anthrone was filtered off and the filtrate was concentrated. The residue was taken up in dichloromethane and the solution was washed with water, aqueous ammonium chloride, and then water. The solution was dried over magnesium sulfate

and evaporated to give 42 g (86%) of an oil which was directly used for the next preparation. ^{1}H NMR ($CDCl_3$, δ): 0.63 (3H, d, J=7.5 Hz), 2.91 (1H, dq, J=7.5, 4.5 Hz), 3.70 (3H, s), 4.83 (1H, d, J=4.5 Hz), 7.2—7.7 (6H, m), 8.1$_5$—8.4 (2H, m).

9-(1-Methoxycarbonylethyl)anthracene (2). To a solution of 35 g (0.125 mol) of 10-(1-methoxycarbonylethyl)anthrone in 500 mL of methanol was added 35 g (0.925 mol) of sodium tetrahydridoborate with ice-cooling and the mixture was allowed to stand for 15 min. The mixture was treated with ice and dilute hydrochloric acid and extracted with dichloromethane. The extract was washed and evaporated. The residue was taken up in 300 mL of benzene and the solution was shaken with 300 mL of concentrated hydrochloric acid for 10 min. The benzene layer was separated, washed, and dried. Evaporation of the solvent afforded 31 g (94%) of the desired compound. Recrystallization from acetone–pentane gave a pure sample, mp 117—119 °C. Found: C, 81.69; H, 5.83%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%. ^{1}H NMR ($CDCl_3$, δ): 1.80 (3H, d, J=7 Hz), 3.54 (3H, s), 5.10 (1H, q, J=7 Hz), 7.3—7.6 (4H, m), 7.8—8.3 (4H, m), 8.38 (1H, s).

9-(2-Hydroxy-1-methylethyl)anthracene (3). A solution of 227 mg (0.86 mmol) of 9-(1-methoxycarbonylethyl)anthracene in 20 mL of dry ether was added to a slurry of 65.3 mg (1.72 mmol) of lithium tetrahydridoaluminate in 30 mL of dry ether and the mixture was stirred for 30 min at room temperature. The excess of the hydride was decomposed with ethyl acetate. The whole was treated with dilute hydrochloric acid and the ether layer was washed with aqueous sodium hydrogencarbonate and then with water, and dried over magnesium sulfate. Evaporation of ether afforded an oil in 192 mg (96.5%) yield. The crude product was directly used for the next reaction. ^{1}H NMR ($CDCl_3$, δ): 1.69 (3H, d, J=7 Hz), 4.24 (2H, br d, J=7 Hz), 4.3—4.7 (1H, m), 7.0—7.6 (4H, m), 7.8—8.1 (2H, m), 8.1—8.5 (3H, m).

9-(2-Methoxy-1-methylethyl)anthracene (4). A mixture of 0.32 g (13 mmol) of sodium hydride, 621 mg (2.64 mmol) of 9-(2-hydroxy-1-methylethyl)anthracene and 10 mL of tetrahydrofuran was stirred for 30 min at room temperature. To the mixture was added 1.6 mL (26 mmol) of methyl iodide and the whole was stirred overnight. The excess of the hydride was decomposed with ethanol and then with water and the mixture was extracted with ether. The ethereal extract was washed with dilute hydrochloric acid and then with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel, dichloromethane–hexane (1 : 3) being used as an eluent. The desired product was obtained in 429 mg (65%) yield. The product was directly used for the next reaction. ^{1}H NMR ($CDCl_3$, δ): 1.70 (3H, d, J=7.2 Hz), 3.27 (3H, s), 3.77 (1H, dd, J=5.1, 9.0 Hz), 4.11 (1H, dd, J=8.6, 9.0 Hz), 4.35—4.80 (1H, m), 7.0—7.5 (4H, m), 7.7—8.0 (2H, m), 8.1—8.5 (3H, m).

1,2,3,4-Tetrachloro-9-(2-methoxy-1-methylethyl)triptycene (5). To a boiling solution of 429 mg (1.72 mmol) of **4** and 0.9 mL of isopentyl nitrite in 10 mL of dichloromethane was added 1.18 g (4.29 mmol) of tetrachloroanthranilic acid[6] in 10 mL of acetone in 1 h under a nitrogen atmosphere. The mixture was heated for another hour. Insoluble materials were filtered off and the filtrate was evaporated. The residue was submitted to silica gel chromatography and eluted with hexane–dichloromethane (1 : 1). A mixture of the desired material and the starting material (6 : 4) was obtained. Treatment of the mixture with the benzyne was repeated. An eluted fraction from silica gel was recrystallized from tetrahydrofuran–hexane to give 198 mg (25%) of the desired compound, mp 190—192 °C. Found: C, 62.03; H, 3.72; Cl, 30.28%. Calcd for $C_{24}H_{18}OCl_4$: C, 62.09; H, 3.91; Cl, 30.55%. When the crystals of the compound were dissolved in chloroform-*d* at low temperatures, the ^{1}H NMR signals could be attributed to the *ap* conformation (δ): 1.97 (3H, d, J=7.2 Hz), 3.45 (3H, s), 3.8—4.6 (3H, m), 5.94 (1H, s), 6.7—7.9 (8H, m). On standing at room temperature, the solution exhibited a set of NMR signals which could be attributed to the *sc* conformation of which signals were obtained by subtracting those due to the *ap* conformation from those of the mixture. *sc* ($CDCl_3$, δ): 1.78 (3H, d, J=7.2 Hz), 3.48 (3H, s), 3.8—4.6 (3H, m), 5.94 (1H, s), 6.7—7.9 (8H, m).

1,2,3,4-Tetrabromo-9-(2-methoxy-1-methylethyl)triptycene (6). To a boiling solution of 1.10 g (4.40 mmol) of **4** and 2.1 mL of isopentyl nitrite in 20 mL of dichloromethane was added 5.5 g (12.1 mmol) of tetrabromoanthranilic acid[7] in 20 mL of acetone in 30 min. The mixture was heated for another hour and filtered. The filtrate was concentrated and the residue was chromatographed as above. The obtained crystals were recrystallized from acetone–pentane to give the desired product, mp 220—222 °C, in 818 mg (29%) yield. Found: C, 44.98; H, 2.83; Br, 50.29%. Calcd for $C_{24}H_{18}OBr_4$: C, 44.89, H, 2.83; Br, 49.79%. The following ^{1}H NMR data ($CDCl_3$, δ) were obtained as were described for **5**. *ap*: 1.93 (3H, d, J=7.2 Hz), 3.41 (3H. s), 3.8—4.7 (3H, m), 5.97 (1H, s), 6.8—7.9 (8H, m). *sc*: 1.74 (3H, d, J=6.3 Hz), 3.48 (3H, s), 3.8—4.7 (3H, m), 5.97 (1H, s), 6.8—7.9 (8H, m).

1,4-Dimethoxy-9-(2-methoxy-1-methylethyl)triptycene (7). A solution of 1.47 g of **4** and 0.95 g of *p*-benzoquinone in 8 mL of acetonitrile was heated overnight under reflux. The acetonitrile and the benzoquinone were washed off with hot water. The residue was treated with a small portion of aqueous sodium hydroxide and then with a small portion of dimethyl sulfate. The process was repeated several times to use a total of 0.75 g of sodium hydroxide in 5 mL of water and 1 mL of dimethyl sulfate. After one night, the mixture was poured into water and the mixture was extracted with benzene. The benzene solution was dried and evaporated. The residue was chromatographed on silica gel, using eluents from hexane–dichloromethane (1 : 1) to dichloromethane. Some fractions were taken up in pentane–dichloromethane to remove anthraquinone as an insoluble material. The desired product, mp 218—220 °C, crystallized out on addition of pentane. Yield was 741 mg (32.6%). Found: C, 80.66; H, 6.61%. Calcd for $C_{26}H_{24}O_3$: C, 80.80; H, 6.78%. The crystals of this compound, on dissolution in chloroform-*d* at −40 °C, gave ^{1}H NMR signals of the almost pure *ap*-form but the isomerization was much faster than other compounds. From these results, the crystals may be assumed to be composed of the pure *ap*-forms. The following ^{1}H NMR data ($CDCl_3$, δ) were obtained as described for other compounds. *ap*: 1.88 (3H, d, J=6.3 Hz), 3.41 (3H, s), 3.63 (3H, s), 3.72 (3H, s), 3.9—4.2 (3H, m), 5.77 (1H, s), 6.42 (2H, s), 6.8—7.8 (8H, m). *sc*: 1.79 (3H, d, J=6.3 Hz), 3.46 (3H, s), 3.67 (3H, s), 3.72 (3H, s), 3.9—4.2 (3H, m), 5.77 (1H, s), 6.42 (2H, s), 6.8—7.8 (8H, m).

9-(2-Acetoxy-1-methylethyl)-1,2,3,4-tetrachlorotriptycene (8). A solution of 1.154 g (4.89 mmol) of **3** in 50 mL of benzene was mixed with 0.8 mL of pyridine and 0.5 mL of acetyl chloride. The mixture was treated, after 10 min, with ethanol and then with water. The aqueous layer was removed and the organic layer was washed with dilute hydrochloric acid and then with aqueous sodium hydrogencarbonate. Evaporation of the solvent and chromatography of the residue on silica gel, using dichloromethane–hexane (1 : 1), afforded a yellow oil of 9-(2-acetoxy-1-methylethyl)anthracene in

1.349 g (99.3%) yield. ^{1}H NMR ($CDCl_3$, δ): 1.72 (3H, d, J=7.2 Hz), 1.97 (3H, s), 4.4—5.1 (3H, m), 7.1—7.6 (4H, m), 7.8—8.1 (2H, m), 8.2—8.5 (3H, m).

A solution of the acetate (1.349 g or 4.85 mmol) and 2.6 mL of isopentyl nitrite in 20 mL of dichloromethane was treated with 4.00 g (14.6 mmol) of tetrachloroanthranilic acid in 30 mL of acetone as described in the preparation of **5**. The single treatment with the benzyne afforded 404.8 mg (17%) of the desired compound, mp 218—220 °C, on recrystallization from acetone–hexane after chromatography. Found: C, 61.14; H, 3.45; Cl, 28.86%. Calcd for $C_{25}H_{18}O_2Cl_4$: C, 61.00; H, 3.69; Cl, 28.81%. The following ^{1}H NMR data ($CDCl_3$, δ) were obtained as described above. *ap*: 1.96 (3H, d, J=6.3 Hz), 2.24 (3H, s), 4.3—5.2 (3H, m), 5.94 (1H, s), 6.9—7.8 (8H, m). *sc*: 1.76 (3H, d, J=6.3 Hz), 2.11 (3H, s), 4.3—5.2 (3H, m), 5.94 (1H, s), 6.9—7.8 (8H, m).

^{1}H NMR Spectra and Kinetic Data. ^{1}H NMR spectra were obtained on a Hitachi R-20B spectrometer equipped with a temperature variation accessory and operating at 60 MHz.

Rates of isomerization at room temperature were obtained by observing the change of ^{1}H NMR spectra as chloroform-*d* solutions in a probe of the NMR spectrometer. Temperatures were read directly by a thermocouple. The data were treated as the first order reversible reaction. Dynamic NMR spectra were obtained as hexachlorobutadiene solutions and the line shapes were simulated with the use of the modified Binsch program.[8] The temperature was calibrated with the use of the chemical shift differences of the protons of ethylene glycol. Some selected rate constants ($ap \rightarrow sc$, s^{-1}) are given below (numericals in parentheses are temperatures in °C). **5**: 0.82 (116.7), 1.23 (122.7), 1.67 (125.8), **6**: 0.80 (116.6), 1.32 (123.7), 1.76 (127.3), **7**: 0.76 (114.5), 1.22 (120.3), 1.61 (124.0), **8**: 0.52 (126.0), 0.61 (129.2), 0.93 (133.9), 1.33 (138.0).

These data were put into the Eyring equation and the kinetic parameters were obtained.

Results and Discussion

Assignment of Conformations. Assignment of conformations poses a difficult problem. We have succeeded in assigning conformations of ethenoanthracene derivatives by looking at aromatic proton signals of NMR spectra[2] but this method is apparently not applicable to the present case. The only differences are found in chemical shifts of protons due to methyl groups in the 9-substituents. One of the possibilities which give a solution to the problem is to utilize the chemical shifts of the methyl protons. In triptycene derivatives which carry a *t*-butyl group in the 9-position, the two methyl groups which are close to a peri-subsituent (usually a halogen) give a ^{1}H NMR signal at a lower magnetic field than that which is *ap* to the substituent.[9] This is reasonable if we assume van der Waals shift because the two groups are in a congested state. It is also true for other tertiary alkyl groups: methyls in an *ap* conformation which possesses the methyls $\pm sc$ to the peri-substituent give ^{1}H NMR signals at a lower field which corresponds to one of the methyls, that gives its signal at a lower magnetic field, in $\pm sc$ conformations.[10] If these generalities are applicable to the present case, then a conformation which gives the methyl signal at a lower field than another must be *ap*. However, since the steric requirements of a *t*-alkyl and a *s*-alkyl group are so different that the deformation of the molecules in question may differ to some extent. Indeed, 1,2,3,4,5,6,7,8-octachloro-9-isopropyltriptycene in which both methyl groups in the isopropyl are flanked by a tetrachlorobenzo and a benzo groups give a methyl signal at a higher magnetic field: it corresponds to a higher one of the two methyls in 1,2,3,4-tetrachloro-9-isopropyltriptycene.[4] We may have to wait to draw a definite conclusion until direct unambiguous evidence such as X-ray crystallography is obtained. We tentatively assign here, therefore, that, by taking advantage of the analogy from the *t*-alkyl compounds, it is the *ap* conformation that gives methyl proton signals at a relatively low magnetic field. Then the crystalline forms which we obtain by recrystallization are *ap* and those which appear on dissolution are *sc*.

Rotational Barriers. Rates of rotation at room temperature, as examined by the classical method, and free energies of activation are given in Table 1. Every compound examined was, at least, almost pure *ap* form

Table 1. Rates of rotation ($ap \rightarrow sc$) and equilibrium constants of 9-[2-methoxy(or acetoxy)-1-methylethyl]triptycenes

Compound	Substituents		Temp	$\Delta G^{\ddagger}$	$k \times 10^4$	K
	Bridgehead	Peri	K	kcal/mol	s^{-1}	(*sp*/*ap*)
5	$CH_3OCH_2CH(CH_3)$	Cl	306	23.5	1.03	0.40
6	$CH_3OCH_2CH(CH_3)$	Br	307	23.4	1.52	0.28
7	$CH_3OCH_2CH(CH_3)$	OCH_3	306			0.65
8	$AcOCH_2CH(CH_3)$	Cl	305	23.2	1.49	0.64

Table 2. Kinetic parameters for rotation ($ap \rightarrow sc$) obtained by total line shape analysis

Compound	$\frac{K}{(sc/ap)}$(Temp/°C)	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ e.u.	$\Delta G^{\ddagger}_{298}$ kcal/mol
5	0.56 (126)	22.9±2.4	−0.7±6.2	23.1
6	0.41 (132)	24.1±1.7	2.2±4.4	23.4
7	0.96 (124)	22.2±0.4	−2.3±1.1	22.9
8	0.56 (138)	25.7±1.9	3.9±4.5	24.5

soon after the dissolution in chloroform-*d*. The dimethoxy compound (**7**) was no exception but it isomerized fast at room temperature. Thus, although it was possible to isolate *ap* isomers, we had to abandon isolation of *sc* isomers at room temperature.

As expected from a minute difference in structures, compounds **5** and **8** exhibit similar barriers to rotation. The barriers observed are in good agreement with those obtained by dynamic NMR study of 9-isopropyltriptycenes except the bromo compound (**6**): the barriers to rotation of 9-isopropyl compounds have been reported to be 23.6 ± 1.9, 25.5 ± 2.3, and >26 kcal/mol for compounds carrying a methoxyl, chloro, and bromo group in the peri-position, respectively.[4] Disagreement of the data obtained prompted us to reexamine the barrier to rotation of 1,2,3,4-tetrabromo-9-isopropyltriptycene. We found that the coalescence temperature of the methyl signals of the isopropyl group in the ^{1}H NMR spectrum was 175 °C instead of >200 °C as reported. From the coalescence temperature and the chemical shift difference, the free energy of activation for rotation was calculated to be 23.5 kcal/mol, which is in accordance with the data investigated here. Probably some accidental mishaps caused errors in reading the temperature in the literature.

The results obtained by the dynamic NMR study are given in Table 2. They are generally in good agreement with the data obtained by the classical method. Although the barriers to rotation of these compounds might be considered similar from the free energies of activation at 298 K, yet we can point out that the methoxy compound (**7**) has a lower barrier. The tendency is usually more revealing in the rate constants than the free energies but the difference is obscure in the rate constants obtained by the line shape analysis (see Experimental section). Rather the difference is definite in the rates of rotation at ambient temperatures (Table 1). If we can take the difference between the bromo (**6**) and the chloro compound (**5**) significant, the chloro compound does exhibit a higher barrier to rotation.

We have recently reported that the barriers to rotation in triptycene systems having a *t*-alkyl group show an interesting trend. Namely, in [1-cyano(or methoxycarbonyl)-1-methylethyl]triptycene series, barriers to rotation are higher if that compound carries no substituent in the peri-position[11] than those carrying a substituent in the peri-position.[10] Investigation of a series of 1-substituted 9-(2-phenyl-1,1-dimethylethyl)-triptycenes has revealed that there is a maximum barrier to rotation when the 1-substituent is medium-sized.[12] Thus the results reported here supplement that there is a same trend in the triptycene series which carries a *s*-alkyl group. The only difference is that, whereas the maximum barrier to rotation in the *t*-alkyl series has been observed at the substituent of a methoxyl or a fluoro, it is a chloro (and a bromo) in the case presented here. This shift must be caused by the fact that congestedness in molecules is much more severe in the *t*-alkyl compounds than in the *s*-alkyl compounds in the ground state.

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