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Restricted Rotation Involving the Tetrahedral Carbon. LVI. NMR and Molecular Mechanics Studies on the Stereodynamics of 8,13-Dichloro-9-methoxy-1,4-dimethyltriptycene[1)]

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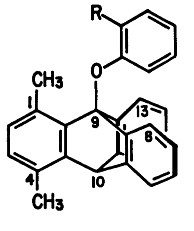
The 400 MHz ^{1}H NMR spectrum of the title compound at −100 °C in dichloromethane revealed the presence of two isomers in a ratio of 88:12, which results from restricted rotation about the triptycyl-oxygen single bond. The major isomer was assigned to the *ap* rotamer on the basis of the low temperature ^{13}C NMR spectrum. Dynamic NMR studies gave the activation parameters for the $ap \rightarrow \pm sc$ conversion: $\Delta H^{\ddagger}=11.9\pm0.5$ kcal/mol ($1\ \text{cal}_{\text{th}}=4.184$ J), $\Delta S^{\ddagger}=2.6\pm2.5$ eu, $\Delta G^{\ddagger}_{200\text{K}}=11.4$ kcal/mol. Results of molecular mechanics calculations on the compound are discussed.

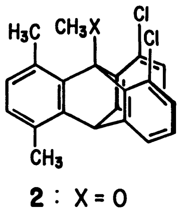
Abundant reports have appeared on dynamic NMR studies of restricted rotation about carbon–carbon single bonds including sp^3-sp^3, sp^3-sp^2, and sp^2-sp^2 combinations.[2)] On the other hand, only a few examples have been reported on restricted rotation of carbon–oxygen bonds studied by NMR spectroscopy. In most cases, the bond in question is the one between an oxygen and an sp^2-hybridized carbon atoms, as in aryl esters,[3)] diaryl ethers,[4)] and most recently in chromium complexes of substituted anisoles.[5)] While our interest is focused on rotational barriers which mainly originate from the differential steric effects in the ground and the transition states, several examples are known for another type of C(sp^2)–O rotational barriers which are mainly caused by destruction of conjugative stabilization.[6)]

As for NMR studies on restricted rotation about sp^3-carbon-to-oxygen bonds, few reports have appeared. As far as we know, temperature dependence of ^{1}H NMR spectra of a quinone acetal, 4-ethoxy-2,3,5,6-tetramethylphenoxy dimer,[7)] and more recently that of bis(9-anthrylmethyl) ether derivatives[8)] have been reported. In both reports, mechanistic details of the dynamic process are not discussed, only the possible structure of the stable conformation being speculated.

We recently reported the preliminary results of dynamic NMR studies on the stereodynamics of 9-(2-alkylphenoxy)triptycenes (**1**).[9)] Molecules of compounds **1** constitute a bevel gear system with a two-toothed and a three-toothed wheels in both static and dynamic sense: Correlated disrotation of the triptycyl–oxygen and aryl–oxygen bonds is observed by dynamic NMR spectroscopy. In this system, ground state conformations and the dynamic processes occurring are well defined.



Ia : R = CH_3
Ib : R = $CH(CH_3)_2$



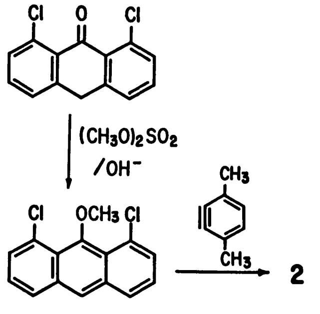
2 : X = O
3 : X = CH_2

We felt it essential to study a simpler and more fundamental system, 9-methoxytriptycenes, in order to get deeper insight into the general nature of rotational barriers of C–O bonds in comparison with those of C–C bonds. As a methyl group is considerably smaller than the aryl group in **1**, it seemed necessary to introduce substituents at three *peri*-positions (1, 8, and 13 positions) to obtain a sufficient steric congestion in the transition state for rotation so that the restricted rotation is observed by NMR spectroscopy. We therefore chose 8,13-dichloro-9-methoxy-1,4-dimethyltriptycene (**2**) as the target, taking also the synthetic ease into account.

In this article, we report on the dynamic NMR and molecular mechanics studies of **2** and discuss the results in comparison with those of the corresponding 9-ethyl derivative (**3**)[1)] and of related compounds.

Results and Discussion

Synthesis. 1,8-Dichloroanthrone was methylated with dimethyl sulfate and alkali to give 1,8-dichloro-9-methoxyanthracene (**4**). Reaction of **4** with 3,6-dimethylbenzyne afforded **2** as colorless crystals with low solubility in common solvents.



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NMR Spectra and Rotamer Equilibria. In the ^{1}H NMR spectrum of **2** at ambient temperature, three singlets are observed for the methyl groups reflecting fast internal rotation about the C_9–OCH_3 bond (Table 1). Of the two singlets ascribed to the aromatic methyl groups, the high-field one at δ 2.31 is unambiguously assigned to 4-methyl on the basis of nuclear Overhauser

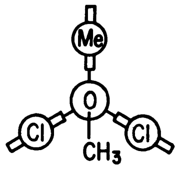
Table 1. ^{1}H NMR data of **2** in CD_2Cl_2 at 400 MHz[a)]

Temp °C	Pop %	1-CH_3	4-CH_3	OCH_3	10-H	Rotamer assigned
25		2.71_0	2.31_4	3.98_4	5.44_0	
−100	88	2.69_2	2.30_2	3.95_0	5.54_2	*ap*
	12	2.73_5	2.53_8	3.85_4	5.51_3	±*sc*
		(-0.04_3)	(-0.23_6)	(0.09_6)	(0.02_9)	

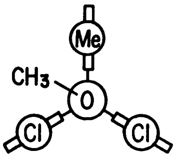
a) Data for aromatic protons are omitted; see Experimental. Chemical shifts are given in δ. In parentheses are chemical shift differences in ppm between the rotamers at −100 °C.

effect (NOE) experiments: Irradiation of this signal causes the intensity enhancement by *ca.* 20% of the signal at δ 5.44 ascribed to the bridgehead proton (10-H), while irradiation of the low-field methyl signal at δ 2.71 leaves the 10-H signal intact.

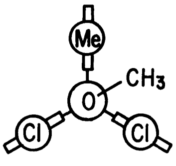
On lowering the temperature, each of the singlets broadens and splits into two unequally intense peaks. At −100 °C in dichloromethane-d_2, two sets of signals are observed indicating the presence of two isomers in a ratio of 88:12. It may be quite reasonable to assume that these isomers are rotamers about the C_9–OCH_3 bond, *ap* and ±*sc* (an equimolar mixture of +*sc* and −*sc*), but the rotamer assignment is not so straightforward from the ^{1}H NMR spectra, because the compound does not contain a prochiral group (*e.g.* -CX_2Y), which would definitely identify the chiral nature of the ±*sc* rotamer. The aromatic proton signals of the major rotamer appear rather simple, however, implying that it is *ap*.



ap



+*sc*



−*sc*

We expected that the unambiguous assignment of the rotamers could be made from the ^{13}C NMR spectrum at low temperature: The ±*sc* rotamer should give rise to eighteen different signals in the aromatic carbon region while the *ap* rotamer twelve peaks according to the molecular symmetry. Therefore we measured a 100 MHz ^{13}C NMR spectrum of **2** at −82 °C. Actually twelve large peaks assignable to the major isomer were observed in the region of δ 120—150 together with more than twelve small peaks derived from the minor isomer. This strongly suggests that the major isomer is *ap*, although all of the eighteen peaks are not detected for the minor isomer because of the overlap with the major peaks and the interference by noise peaks. The ^{13}C NMR data are given in Table 2 together with tentative assignments of the major peaks.

Table 2. ^{13}C NMR data of **2**[a)]

at 25 °C	at −82 °C major	 minor	Tentative assignment
18.39 q	18.20	17.93	4-CH_3
20.24 q	20.05	19.15	1-CH_3
51.20 d	49.72	≈49.9[b)]	10
57.18 q	56.69	55.86	OCH_3
92.17 s	91.00	c)	9
122.35 d	121.92		5,16
126.80 d	125.70		2
127.43 d	126.89		7,14
129.27 d	128.38		6,15
129.47 s	129.15		1
129.52 d	128.47		3
130.20 s	129.25		8,13
131.73 s	130.17		4
141.34 s	140.06		4a
141.56 s	140.18		10a,11
145.03 s	145.35		9a
146.49 s	144.69		8a,12

a) Obtained at 100.5 MHz in CD_2Cl_2. Chemical shifts of the aromatic carbons of the minor rotamer are not read. b) Shoulder. c) Not identified.

Predominance of the *ap* rotamer is reasonable on the basis of the generally accepted order of bulkiness of the *peri*-substituents, CH_3>Cl:[10)] The methoxyl methyl group should be more comfortable when it is flanked by two Cl's than by CH_3 and Cl. Similar rotamer distribution was observed in the corresponding 9-ethyl compound (**3**), where the population of *ap* is 57% in chloroform-*d* at 35 °C.[1)]

Inspection of Table 1 reveals an intriguing feature. The signals at −100 °C due to the 4-methyl group, which is remoter from the site of restricted rotation than 1-methyl, show a larger chemical shift difference (0.24 ppm) between the rotamers than those due to the latter (0.04 ppm). This seems quite unusual but the reason is not certain.

Dynamic NMR Studies and Rotational Barriers. Pairs of signals at low temperatures which are ascribed to the 1-methyl, 4-methyl, and methoxyl groups coalesce to single peaks at about −71, −62, and −50 °C, respectively, upon raising the temperature. While rigorous determination of the coalescence temperatures was not made, rate constants for the *ap*$\rightleftharpoons$±*sc* interconversion were obtained by simulating the three sets of signals at six temperatures between −81 and −56 °C. The data are given in Table 3 together with the activation parameters therefrom.

Comparison of the data with those of the carbon analog **3** reveals some interesting points. Generally, rotational barriers about C–O bonds are lower than those about the corresponding C–C bonds as typically illustrated by methanol *vs.* ethane (1.07 *vs.* 2.88 kcal/mol), and dimethyl ether *vs.* propane (2.7 *vs.* 3.4

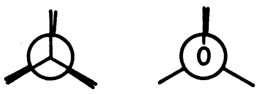
TABLE 3. DYNAMIC NMR DATA OF 2 IN CD_2Cl_2 AT 400 MHz[a)]

$$ap \underset{k_{-1}}{\overset{2k_1}{\rightleftharpoons}} \pm sc \qquad K = 2k_1/k_{-1}$$

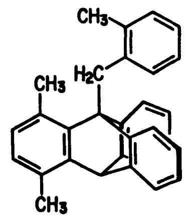
Temp	K	k_1	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$
°C		s^{-1}	kcal/mol	kcal/mol	eu
−81.0	0.143	0.45	11.39	11.9±0.5	2.6±2.5
−76.0	0.156	1.0	11.38		
−70.9	0.156	2.0	11.40		
−65.9	0.163	4.6	11.35		
−60.8	0.176	9.7	11.33		
−55.7	0.176	18.5	11.33		

a) The parameters refer to the $ap \rightarrow \pm sc$ process.

kcal/mol).[11] This seems to be principally resulted from the fact that there are three eclipsing interactions in the transition state for C–C rotation, while only one for C–O rotation. As the lone pair electrons on oxygen are much smaller in their effective size than hydrogen or alkyl groups and highly polarizable, steric interaction involving the lone pair electrons are considered to be negligible.



In this sense, the lower barrier in **2** than in **3** ($\Delta G^{\neq}$=20.2 kcal/mol at 94 °C)[1] may be quite reasonable. However the larger barrier difference of about 9 kcal/mol is in striking contrast to the rather small difference found between **1a** and its carbon analog (**5**):[9,12] The gearing process in which the aryl group passes over the *peri*-methyl group has $\Delta G^{\neq}$ of 18.1 kcal/mol in **1a** and 20.0 kcal/mol in **5**.



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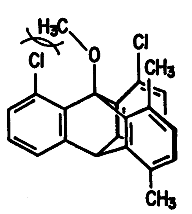
In order to understand this apparent discrepancy, secondary factors affecting the barrier difference should be considered. Among them, the difference in bond length between C–C and C–O would be the most important. In the following discussion, the effects of bond lengths in the transition states are considered, the other secondary factors being neglected. Effects of these factors as well as the bond lengths in the ground states are assumed to be smaller than in the transition states.

The probable transition states for the $ap \rightleftharpoons \pm sc$ interconversion in **2** and **3** are shown by **6** and **7**, respectively. Local steric interaction due to eclipsing of the β-methyl group in the 9-substituent and the *peri*-chloro group will not differ largely between **6** and **7**, because not only the C_9–O bond but also the O–CH_3 bond in **6** are shorter than the corresponding C–C bonds in **7**. Therefore the presence or absence of the eclipsing interaction between the α-hydrogen in the 9-substituent and the *peri*-chloro or *peri*-methyl group most effectively affects the transition state energy, resulting in the large barrier difference between **2** and **3**.



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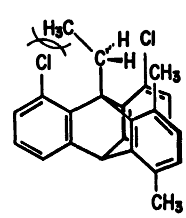

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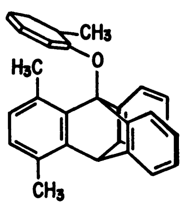

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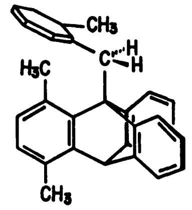

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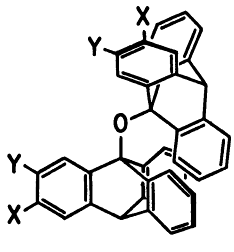
On the other hand, in the probable transition states (**8** and **9**) for the $ap \rightleftharpoons \pm sc$ gearing process in **1a** and **5**, respectively, the repulsive interaction between the *peri*-methyl and the aryl groups will be far severer in **8** than in **9**, because the C_9–O bond in **8** is shorter than the C_9–CH_2 bond in **9** while the difference between the Ar–O and Ar–CH_2 bond lengths does not seem to significantly affect this situation. Therefore the small barrier difference between **1a** and **5** may be understood by assuming that the sum of the eclipsing interactions between the aryl group and the *peri*-methyl group and those between the α -hydrogens and the *peri*-hydrogens in **9** do not largely exceed the eclipsing interaction between the aryl group and the *peri*-methyl group in **8**.

One may pose a possibility that the interconversion between the isomers might occur by configurational inversion at the oxygen atom by way of a transition state with a linear C–O–C arrangement, which is often called a lateral shift, rather than internal rotation about the C–O bond. Although we do not have experimental evidence at hand for or against the hypothesis, there seems an indication against it. Kawada and Iwamura reported that the energy barrier to interconversion between the "phase isomers" in bis(9-triptycyl) ether derivatives (**10**) are 42—44 kcal/mol.[13] They rejected the lateral shift as the mechanism of the interconversion, and thus the inversion barrier at oxygen should be higher than these values in **10**, and there is no reason to assume that the inversion barrier in **2** is largely different from those in **10**.[14]



10 X or Y = Cl

Molecular Mechanics Calculations. In order to confirm the rotamer assignment mentioned above by evaluating the relative energies of the rotamers and to have some insights into the molecular geometries of the rotamers, we performed molecular mechanics calculations on **2** and also on **3** for comparison, using the MM2 force field.[15] Several parameters were newly inputted in addition to those originally included in the program, which are given in the experimental section. Calculated total steric energies of the rotamers of **2** and **3** and their components are compiled in Table 4.

In both **2** and **3**, the *ap* rotamer is calculated to be more stable than ±*sc*, reproducing qualitatively the observation. The steric energy difference between the rotamers is fortuitously the same between **2** and **3**, but the component analysis shows that the contributing factors are different. In the oxygen compound **2**, the bending and torsion terms most contribute to the energy difference, both favoring the *ap* rotamer. In the methylene analog **3**, the torsion term strongly favors *ap*, while the van der Waals terms favor ±*sc*, partially compensating the contribution by torsion.

As the accurate values for the enthalpy and entropy differences between the rotamers could not be determined experimentally by the ^{1}H NMR studies, quantitative comparison between the experiment and the calculation is not straightforward. If it is assumed that the statistical factor of 2 for ±*sc* is the only contributor to the entropy difference, the populations of the *ap* rotamer are calculated from the steric energy difference of 1.18 kcal/mol to be 94% at −100 °C and 71% at 35 °C, which are compared with the observed values of 88% at −100 °C for **2** and 57% at 35 °C for **3**. Agreement seems fairly good.

The optimized geometries of *ap*-**2** and +*sc*-**2** are shown in Fig. 1. In both rotamers, the benzo bridge antiperiplanar to the *O*-methyl group is completely in a single plane together with the substituent(s) attached to it, and the benzo bridges flanking the *O*-methyl group and the *peri*-substituents attached to them bend away from the *O*-methyl group so as to relieve the steric congestion. No extraordinary bond lengths are found. The bonds connecting the benzo bridges to 9-C are somewhat longer (1.53—1.55 Å) than the normal sp^3-sp^2 carbon bond of 1.49 Å, and this feature is generally found in 9-substituted triptycene derivatives studied by X-ray crystallography.[16] The C_9–O–CH_3 angles are 113.7 and 113.4° in *ap*-**2** and ±*sc*-**2**, respectively, increasing by *ca.* 7° from the standard value of 106.8°.

In order to obtain the energy barrier to rotation about the C_9–OCH_3 bond in **2** by molecular mechanics calculations, dependence of the steric energy upon the dihedral angle C_{9a}–C_9–O–CH_3 was calculated by the "one-bond drive" technique. The transition state for the *ap*$\rightleftharpoons$±*sc* interconversion, in which the *O*-methyl group eclipses a *peri*-chlorine, was calculated to be 15.7 kcal/mol higher than the *ap* state. The calculated energy barrier is somewhat higher than the experimentally obtained one (11.9 kcal/mol). We must allow for the fact that highly strained transition states are usually difficult to be reproduced by using the parameters which are empirically determined so as to reproduce the energy and geometry of molecules in the ground state.

TABLE 4. STERIC ENERGIES AND THEIR COMPONENTS BY MM2[a)]

	2			**3**		
	ap	±*sc*	Δ*E*	*ap*	±*sc*	Δ*E*
Total steric energy	30.87	32.05	−1.18	33.02	34.20	−1.18
Compression	3.44	3.46	−0.02	4.98	4.92	0.06
Bending	15.27	15.58	−0.31	17.14	17.18	−0.04
Stretch-bend	−0.27	−0.27	0.00	−0.26	−0.27	0.01
van der Waals						
1,4-	20.18	20.23	−0.05	19.63	19.52	0.11
other	−2.29	−2.33	0.04	1.28	0.83	0.45
Torsion	−7.41	−6.67	−0.74	−9.38	−7.66	−1.72
Dipole	1.95	2.05	−0.10	−0.37	−0.32	−0.05

a) in kcal/mol.

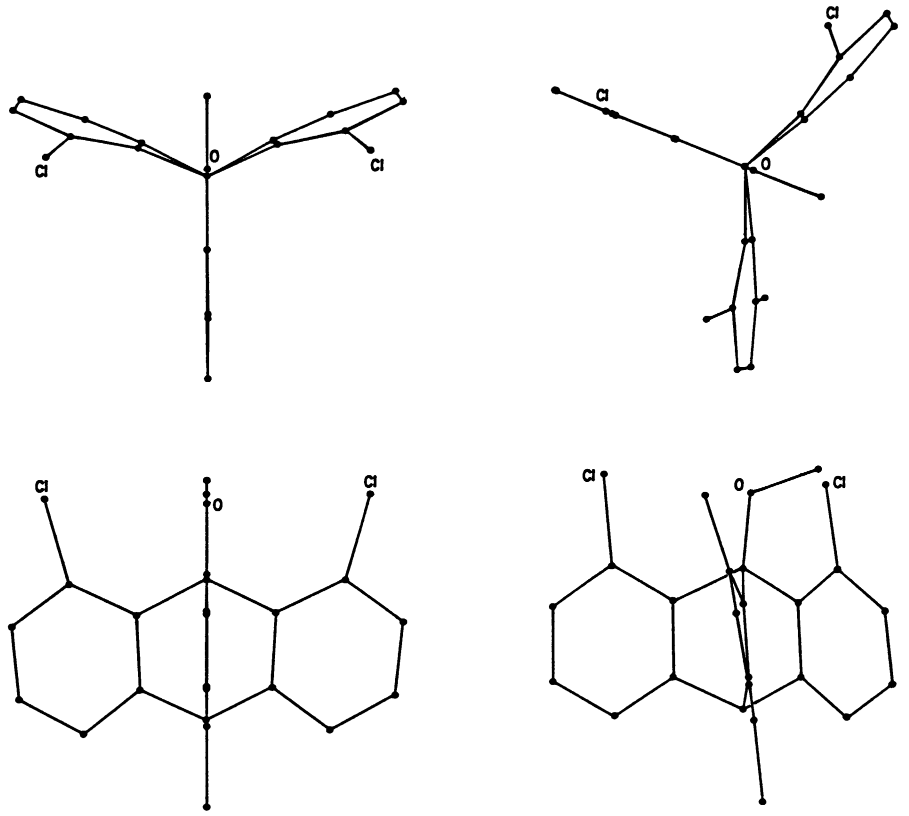


Fig. 1. The optimized geometries of *ap*-**2** and +*sc*-**2**. In each molecule, 9-C and 10-C are placed on the *z*-axis and 9a-C in the *xz* plane, and projections onto the *xy* (upper) and *yz* (lower) planes are shown. Hydrogens are not indicated.

The energy barrier to the direct $+sc\rightleftharpoons-sc$ interconversion, which is not experimentally obtained, was calculated to be 18.3 kcal/mol. As the *O*-methyl group eclipses the *peri*-methyl in the transition state, the higher barrier to this process than that to the $ap\rightleftharpoons\pm sc$ process may be reasonable.

More detailed and sophisticated molecular mechanics calculations on the potential surface of **2** are in progress and the results will be reported separately.

Experimental

1,8-Dichloro-9-methoxyanthracene (4). To a stirred solution of 2.63 g (10.0 mmol) of 1,8-dichloroanthrone[17] in 200 mL of ethanol was added alternately in small portions a solution of 3.0 g of sodium hydroxide in 15 mL of water, and 6.0 mL of dimethyl sulfate. The solid formed was collected by filtration, washed with water and then with methanol, and dried in air, affording 2.30 g (83%) of **4**, mp 170—172 °C (from tetrahydrofuran). Found: C, 64.72; H, 3.36; Cl, 25.57%. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.01; H, 3.64; Cl, 25.58%. ${}^1H$ NMR ($CDCl_3$): δ=3.38 (3H, s), 7.2—8.2 (6H, m), 8.19 (1H, s).

8,13-Dichloro-9-methoxy-1,4-dimethyltriptycene (2). A solution of 3.30 g (20 mmol) of 3,6-dimethylanthranilic acid[18] in 30 mL of 1,2-dimethoxyethane was added dropwise in the course of 1 h to a boiling solution of 2.62 g (9.44 mmol) of **4** and 2 mL of isopentyl nitrite in 50 mL of dichloromethane. The mixture was heated under reflux for another 30 min and concentrated. The residue was chromatographed through an alumina column with benzene as the eluent. Recrystallization of the eluate from benzene gave 1.34 g (37%) of **2**, mp 279—281 °C. Found: C, 72.19; H, 4.59; Cl, 18.60%. Calcd for $C_{23}H_{18}Cl_2O$: C, 72.45; H, 4.76; Cl, 18.60%. The 400 MHz ${}^1H$ NMR spectrum of **2** at 25 °C in CD_2Cl_2 allows analysis of the aromatic proton signals: δ=6.635 and 6.669 (AB-q, J=7.8 Hz, 2,3-H_2), 7.061 (dd, J=7.1 and 7.9 Hz, 6,15-H_2), 7.081 (dd, J=1.2 and 7.9 Hz, 7,14-H_2), 7.312 (dd, J=1.2 and 7.1 Hz, 5,16-H_2).

Spectral Measurements. ${}^1H$ NMR spectra at ambient temperature were recorded on a Varian EM-390 spectrometer operating at 90.0 MHz. Variable temperature ${}^1H$ and ${}^{13}C$ NMR spectra were obtained on a JEOL GX-400 spectrometer operating at 399.65 and 100.53 MHz, respectively. Temperatures were read as digital outputs from the variable temperature accesory and are not corrected.

Computer Simulation. Theoretical spectra were obtained on a HITAC M-280H computer system at the Computer Center of the University of Tokyo (CCUT) using a modified version of the DNMR3 program by Binsch.[19] Three pairs of signals due to the 1-, 4-, and *O*-methyl groups were simulated at each temperature and the most consistent value of rate constant was chosen.

Molecular Mechanics Calculations. The calculations were performed on the HITAC M-280H system using the MM2 program in the CCUT Program Library (code name: Y4/TC/MM2). The force field in the program has been modified by Professor E. Ōsawa from the original program[15] in order that the four-fold torsional potential term (V_4) is considered. Any necessary modification of the calculation procedure accompanying the incorporation of the V_4 terms has been properly taken into account in the program. As the force field does not contain the parameters concerning C_{arom}–Cl bonds, several parameters were newly added. For the compression and bending force constants, those obtained for tetrachloroethylene were used.[20] For the torsional parameters involving the aromatic chlorine, the corresponding hydrogen parameters in the program were diverted. New parameters are shown below together with modifications for C_{arom}–C_{arom} bonds. The atom type numbers represent as follows; 1: sp^3-carbon, 2: aromatic carbon, 5: hydrogen, 12: chlorine.

Compression	K_s/mdyn†/Å	l_0/Å
2 — 2	8.067	1.3937
2 —12	2.66	1.715

Bending	K_b/mdyn Å/rad^2	t_0/deg
2—2—12	0.400	120.0

Torsion	V_1	V_2	V_3	V_4/kcal/mol
1—2—2—12	0.0	16.4	0.0	−2.3
2—2—2—12	0.0	16.4	−1.06	−2.3
5—2—2—12	0.0	16.4	0.0	−2.3

The authors are grateful to Professor E. Ōsawa for helpful discussion on the molecular mechanics calculations, and to Dr. G. Izumi of Nippon Kayaku Co., Ltd. for the measurements of 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra.

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† 1 dyn = 10^{-5} N.