Restricted Rotation Involving the Tetrahedral Carbon. XXVIII. Barriers to Rotation about a C_{sp^3}–C(=O) Bond in 9-(1-Methoxycarbonyl-1-methylethyl)triptycenes[1,2]

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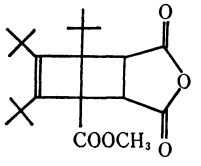
(Received June 30, 1979)

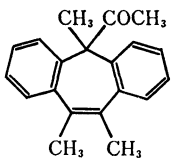
Restricted rotation about a C_{sp^3}–C(=O) bond in title compounds is found by ^1H NMR spectra of the *dl* forms. The barriers to rotation are obtained by the DNMR method to be *ca.* 15 kcal/mol. Infrared spectra which exhibit two conformations in the *dl* and the *meso* forms are also reported.

Rotational isomers of esters have been discussed with the use of vibrational spectra,[3] rotational spectra,[4] electron diffraction,[5] dipole moment,[6] and NMR spectra.[7] Infrared spectrum was a favorite technique for physical organic chemists and rotational isomerism about the C_{sp^3}–C(=O) bond of methyl chloroacetate was extensively studied by Josien.[8] The chloro group exerts large influences on the frequency and the intensity of the carbonyl stretching bands and makes it convenient to study by this method. Although the presence of two conformations of the ester group about a C_{sp^3}–C(=O) bond was deduced from the behaviors in the C–C–O stretching region of propionates and butyrates,[9] it has become possible to study the phenomenon from the C=O stretching region only recently.[10]

Since the rates of isomerization of rotamers are large, NMR spectra usually give information as a weighted mean of the possible rotamers. The rates of rotation may be made slow in the cases of sp^2-sp^2 bonds and there are numerous examples of this sort involving the carbonyl.[11] There had been only one example reported when we launched the project of synthesizing substituted 9-(1-methoxycarbonyl-1-methylethyl)triptycenes: Masamune *et al.* reported an exceptional case that a maleic anhydride adduct of methyl tri-*t*-butyl[4]-annulenecarboxylate (**1**) showed bifurcation of the methoxyl signal in ^1H NMR spectrum at −60 °C.[12] Although it is not an ester, restricted rotation about a C_{sp^3}–C(=O) bond has been found by NMR spectroscopy while our study has been in progress: Hart *et al.* concluded that the rotation of an acetyl group in compound **2** was frozen on the NMR time scale, because the two methyls in 4 and 5 positions of the cycloheptatriene system became nonequivalent at −12 °C.[13] Very recently, restricted rotation of bis(di-*t*-butylmethyl) ketone has been reported.[14]

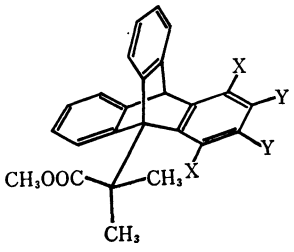


(1)

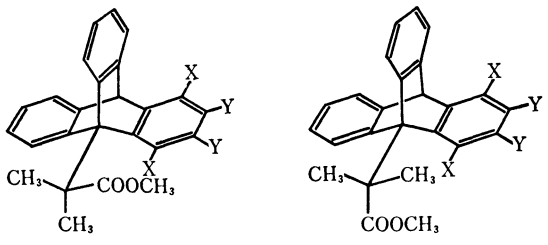


(2)

During the purification of 9-(1-methoxycarbonyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycene (**3**, X=Y=Cl) we have encountered a phenomenon that the methoxyl signal of this compound in ^1H NMR spectrum operating at 60 MHz appears as a broad band, if it is the *dl* form. In this paper, we wish to report a detailed investigation of the restricted rotation about a C_{sp^3}–C(=O) bond, triggered by finding the broadened band for the methoxyl group.



(*meso*-**3**)



(*dl*-**3**)

Experimental

Materials. The preparation of materials in this study has been reported elsewhere.[1] Pure samples of respective rotamers after separation by chromatography were used for the measurements.

^1H NMR Spectra. The spectra were obtained on a Hitachi R-20B spectrometer with a temperature variation accessory, operating at 60 MHz, unless otherwise specified. Chloroform-*d* was used as a solvent for compounds which showed coalescence of signals at the higher temperature, whereas chloroform-*d*–carbon disulfide (1 : 1) was a solvent for those which required deep cooling. Temperature was calibrated using the chemical shifts of methanol and ethylene glycol at the lower and the higher temperatures, respectively.

Calculation of Spectra and Kinetic Parameters. The ^1H NMR spectra at various temperatures were calculated with the use of a modified Binsch program[15] and the best fit of the calculated spectra with the observed was determined by visual fitting. The rate constants thus obtained were put into the Eyring equation to obtain kinetic parameters. The populations which were necessary for the calculation of the spectra

were obtained by using the thermodynamic parameters derived from the populations at low temperatures.

Infrared Spectra. The spectra were obtained on either a JEOL JIR-03F FT-IR or a JASCO DS-403G spectrometer. The samples were dissolved in either carbon tetrachloride or chloroform to make up *ca.* 10^{-3} mol/l solutions.

Results and Discussion

Assignment of the Spectra. The ^{1}H NMR spectra of *dl*-**3** (X=Y=Cl) at three temperatures are shown in Fig. 1. At a low temperature the methoxyl signal which had been broad at 34 °C split into a pair of sharp singlets, whereas the signal for the methoxyl at a high temperature was a sharp singlet. Methyl signals which had been a pair of singlets at room temperature split into a pair of doublets at the low temperature as well.

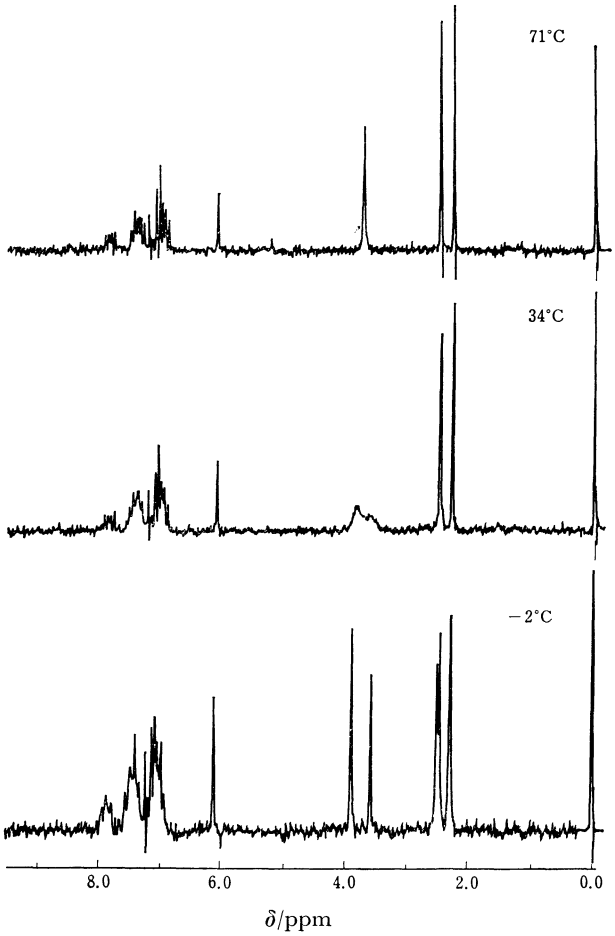
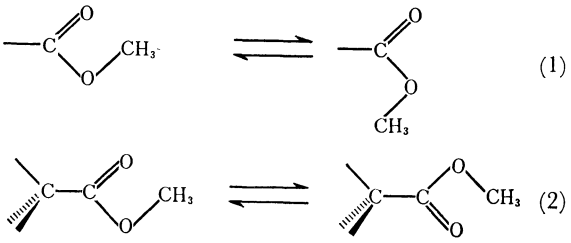


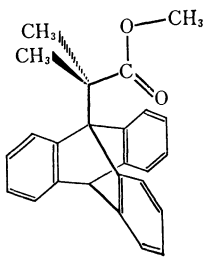
Fig. 1. ^{1}H NMR spectra of *dl*-**3** (X=Y=Cl) at three temperatures ($CDCl_3$, 60 MHz).

The temperature dependence of the spectra might be explained by two ways. One is to use the $Z \rightleftharpoons E$ conformational change (Eq. 1) and the other is the rotation about the C_{sp^3}–C(=O) bond (Eq. 2). The first possibility is unlikely, however. Esters are known to assume *Z* conformation in general and it is an exceptional case that the esters take *E* conformations. The *E* conformations are realized in esters which carry

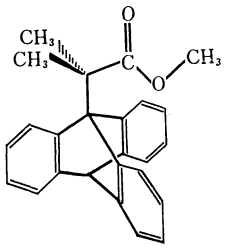


a small group as an acyl part and a large group as an alkoxyl part.[16] Since the compound in question carries a large acyl part and a small alkyl group, the possibility of the *E* conformation may be rejected.

Although the process is now said to be represented by Eq. 2, there remain minor problems to be discussed. Carbonyl groups are in general to be more stable if they assume conformations in which a carbonyl group eclipses one of the single bonds involving the adjacent carbon.[17] The conformations written in Eq. 2 do not necessarily conform to this generality. We justify the conformations from two points, however. The first is that there is a report which successfully interpreted the microwave absorption data of methyl acetate by assuming a C=O staggered conformation.[18] In addition, large groups associated with the α-carbon in this compound and the triptycyl group will make regular conformations, which are otherwise stable, unstable. We call the conformations represented by Eq. 2 as CH_3O-inside and CH_3O-outside in this paper.



CH_3O-outside



CH_3O-inside

Another problem is the assignment of the NMR signals to the respective conformations. We take advantage of the ring current effects[19] of the benzene ring for the assignment. Since the methoxyl signal of methyl acetate is at δ 3.67, one of the two signals of *dl*-**3** (X=Y=Cl) is at a higher field and the other is at a lower field than that of the methyl acetate. Thus the methoxyl signal at the higher field corresponds to the CH_3O-inside conformation and the other at the lower field to the CH_3O-outside.

dl-**3** ($X=CH_3$, Y=H) showed a similar phenomenon except that the splitting of the methoxyl signal occurred at a lower temperature. The coalescence temperature was −4 °C, while that of *dl*-**3** (X=Y=Cl) was 34 °C.

Any of the *meso* forms of these compounds and **3** (X=Y=H) failed to show splitting of the methoxyl signals, although the temperature was lowered to −80 °C. Since they all showed broadening of the signals, spectra of **3** (X=Y=H) were examined at 200 MHz. They did not show splitting at −50 °C, however.

Table 1. Thermodynamic parameters for the equilibria(CH_3O-outside$\rightleftharpoons CH_3O$-inside) of *dl*-**3** in $CDCl_3$

X	Y	ΔH/kcal mol^{-1}	ΔS/eu	ΔG/kcal mol^{-1} at 25 °C
Cl	Cl	−0.43	−1.9	0.15
CH_3	H	−0.34	−1.8	0.18

Populations and Thermodynamic Parameters. The ^{1}H NMR spectra of *dl*-**3** were obtained at various temperatures and, from the integration of the spectra, the populations of the CH_3O-inside and CH_3O-outside conformations were obtained. Usual treatment of the data afforded the thermodynamic parameters shown in Table 1. The free energy difference at 25 °C is also included in the Table. The data suggest that the CH_3O-inside conformation is favored in terms of enthalpy while it is disfavored by entropy factors. And, as a whole, the CH_3O-outside conformation is slightly favored at 25 °C.

Table 2. $\nu_{c=o}$ absorptions of **3**

X	Y	Form	$\nu_{max}(\varepsilon)$ in CCl_4	$\nu_{max}(\varepsilon)$ in $CHCl_3$
H	H	—	1747 (450)	1739 (340)
			1720 (360)	1712 (190)
Cl	Cl	*dl*	1743 (630)	1734 (370)
			1725 (480)	1718 (310)
		meso	1747 (510)	1741 (410)
			1720 (280)	1714 (240)
CH_3	H	*dl*	1746 (390)	1739 (330)
			1717 (370)	1712 (260)
		meso	1748 (270)	1740 (390)
			1717 (220)	1709 (210)

Infrared absorptions due to the C=O stretching are tabulated in Table 2. Each conformer possesses two absorptions. The possibility of the bifurcation due to the Fermi resonance may be ruled out because the shift due to the solvent change, from carbon tetrachloride to chloroform, is very similar with the case of methyl acetate.[20] Thus the results support the existence of the CH_3O-inside and CH_3O-outside conformations deduced by the NMR spectra. We tentatively assign the absorptions at higher frequencies to the CH_3O-outside conformations and those at lower frequencies to the CH_3O-inside conformations because of the correspondence between populations and intensities. Bond dipoles are known to affect the C=O stretching frequencies and intensities[21] but the effects seem small here. The separation of the two bands is abnormally large in these compounds, compared with the ordinary

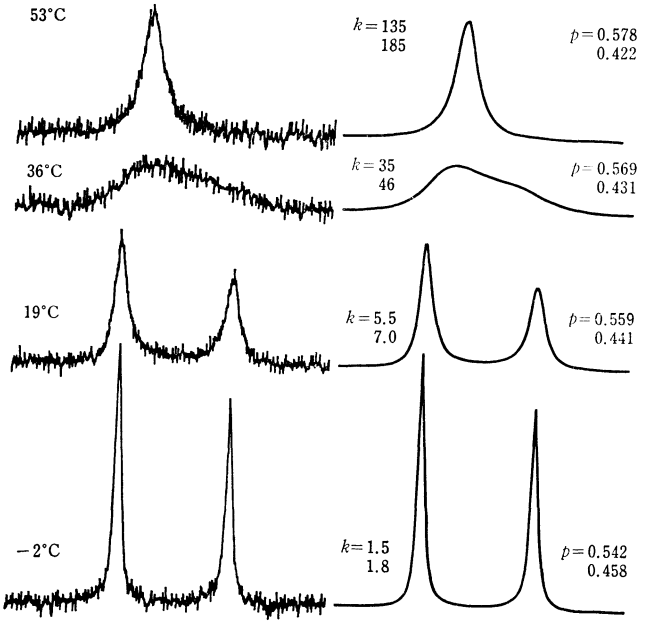


Fig. 2. Observed (left) and calculated (right) spectra of *dl*-**3** (X=Y=Cl) at four temperatures. The upper numbers of *k*'s correspond to the rates of CH_3O-inside →CH_3O-outside processes and the lower the CH_3O-outside→CH_3O-inside. The upper numbers of *p*'s correspond to populations of the CH_3O-outside conformation and the lower the CH_3O-inside conformation.

esters, probably due to the steric effect of the conformations concerned.

Barriers to Rotation. An example of the results of band shape simulations is shown in Fig. 2. The populations calculated by the thermodynamic values in Table 1 were used as constants and the rates of forward rotation were varied in the calculation. The rates of backward rotation are determined by the rates of forward rotation and the population automatically. The kinetic parameters obtained by this method are tabulated in Table 3.

The parent compound **3** (X=Y=H) and the *meso* forms of **3** failed to give split signals even at low temperatures. Therefore, it is not possible to perform the total line shape analysis. However, since the lines due to methoxyl and methyl groups show line broadening at low temperatures, it is possible to obtain rough estimates of barriers to rotation, by assuming the chemical shift differences. It may be argued that the chemical shift differences might be very small in these series, although the barriers are high. We rule out this possibility from the fact that *dl*-**3** (X=Y=Cl), δ 3.58 and 3.90, and *dl*-**3** (X=CH_3, Y=H), δ 3.58 and 3.89, give almost

Table 3. Kinetic parameters for rotation about the C_{sp^3}–C(=O) bond in *dl*-**3** in $CDCl_3$

X	Y	Process	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ eu	$\Delta G^{\ddagger}$(25 °C) kcal mol^{-1}
Cl	Cl	CH_3O-out→CH_3O-in	13.7	−7.4	15.8
		CH_3O-in→CH_3O-out	14.1	−5.4	15.7
CH_3	H	CH_3O-out→CH_3O-in	10.9	−10.5	14.0
		CH_3O-in→CH_3O-out	11.2	−8.9	13.8

the same chemical shift differences. If the chemical shift difference were affected by the peri-substituents, the change in the peri-substituent would have resulted in a larger difference. Assuming that the chemical shift difference of the two forms of *meso*-**3** (X=Y=Cl) is the same with that of *dl*-**3** (X=Y=Cl) and that populations are 50: 50, we can use Eq. 3 for estimating the rates of rotation.[22]

$$k = \left\{\frac{\pi}{2}(\Delta\nu)\right\}^2 \Big/ \left(\frac{1}{T_2'} - \frac{1}{T_2}\right) \qquad (3)$$

where $1/T_2'$ is obtained from the line width at a given temperature and $1/T_2$ from that where exchange is fast. Thus ΔH^*, ΔS^*, and ΔG^* at 25 °C were obtained as 4.2 kcal/mol, −21.8 eu, and 10.7 kcal/mol, respectively. *meso*-**3** (X=CH_3, Y=H) and **3** (X=Y=H) gave similar values. Although the reliability of these values is limited, these may be used as a first approximation in discussion.

The barriers obtained thus far indicate that, in order to exhibit high barriers to rotation, it is necessary to have a peri-substituent. Barriers to rotation are determined by the relative energies of the ground and the transition states. Since no special stabilization or destabilization of the ground state is apparent, the high barriers for the *dl* form may be attributed to the peri-substituent which gives a strong repulsion in the transition state of rotation to raise the transition state. Close examination of the data in Table 3 reveals that *dl*-**3** (X=Y=Cl) gives higher barriers to rotation than *dl*-**3** (X=CH_3, Y=H) in spite of the fact that the van der Waals radius of the methyl group is larger than the chloro. This may be ascribed to the attractive interaction between the carbonyl moiety and the chloro group[23] which are located closely with each other.

We wish to thank people in Brucker for the measurement of the ^{1}H NMR spectra at 200 MHz. Our thanks are also due to the Ministry of Education for a Grant-in-Aid for Scientific Research.

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