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RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON.XXI. DIRECT OBSERVATION OF HINDERED ROTATION ABOUT A Csp^3-C(=O) BOND IN PERI-SUBSTITUTED 9-(1-METHOXYCARBONYL-1-METHYLETHYL)TRIPTYCENES BY ^{1}H NMR SPECTRA [1)]

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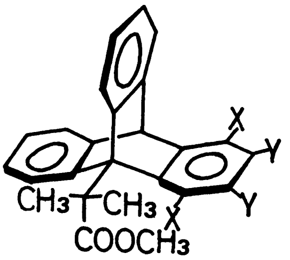
The methoxyl protons of the dl form of the title compound which carries a chloro group in one of the peri positions show a broad signal in ^{1}H NMR spectra at room temperature. The phenomenon is attributed to slow rotation about the C_α-C(=O) bond in the ester moiety by DNMR study. A similar phenomenon is observed with the dl form of the triptycene bearing a methyl group, but neither of the meso forms of triptycenes show splitting of the methoxyl signal. Activation parameters are obtained by total line-shape analysis.

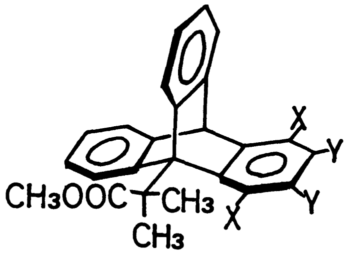
Rotational isomers of α-substituted acetate esters about the C_α-C(=O) bond have been detected by infrared spectroscopy, methyl chloroacetate being a typical example.[2)] It is only recent that the rotamers of such kind are detected in propionate or isobutyrate esters which carry only alkyl groups.[3)]

Due to its time scale, ^{1}H NMR usually provides information as a weighted mean of possible rotamers. Although some examples of observation of restricted rotation about a Csp^2-C(=O) bond have been reported in special cases,[4)] such examples due to restricted rotation about a Csp^3-C(=O) bond are rare. Anderson et al. attempted to observe such phenomenon with various carbonyl compounds by ^{1}H NMR spectroscopy in vain,[5)] whereas Masamune et al. reported such an observation with a maleic anhydride adduct of methyl tri-t-butyl[4]annulenecarboxylate.[6)] The latter reports that the methoxyl group gives two signals at -60°C with 1:3 intensity ratio but the barrier to rotation is not given.



dl 1 : X=Y=Cl

2 : X=CH$_3$,Y=H



meso 3 : X=Y=Cl

4 : X=CH$_3$,Y=H

We wish to report direct observation of hindered rotation of the methyl ester moiety in dl forms (1 and 2) of 1-substituted 9-(1-methoxycarbonyl-1-methylethyl)triptycene and kinetic parameters associated with the process. In contrast, the meso forms (3 and 4) showed only broadening of the signals in the ^{1}H NMR spectra at low temperatures.

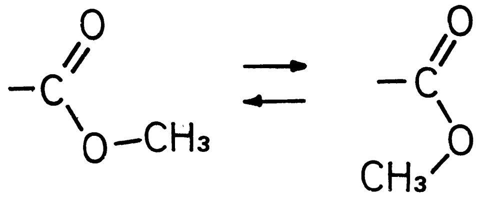
Diels-Alder addition of tetrachlorobenzyne, prepared from tetrachloroanthranilic acid, to 9-(1-methoxycarbonyl-1-methylethyl)anthracene[7)] afforded a mixture of dl- and meso-9-(1-methoxycarbonyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycene. Chromatography on alumina gave dl (1) and meso (3) form as stable entities at room temperature: dl form (1), mp 286-288°C; ^{1}H NMR ($CDCl_3$, 34°C) δ= 2.27 (s, 3H), 2.48 (s, 3H), 3.5-4.0 (broad, 3H), 6.09 (s, 1H), 6.9-8.0 (m, 8H): meso form (3), mp 200-202°C;[8)] ^{1}H NMR ($CDCl_3$, 34°C) δ=2.47 (s, 6H), 3.70 (s, 3H), 6.09 (s, 1H), 6.9-7.6 (m, 8H). A similar reaction with 1,4-dimethylbenzyne afforded dl (2) and meso (4) form of 9-(1-methoxycarbonyl-1-methylethyl)-1,4-dimethyltriptycene: dl form (2), mp 264-265°C; ^{1}H NMR ($CDCl_3$, 34°C) δ=2.29 (s, 6H),[9)] 2.43 (s, 3H), 2.52 (s, 3H), 3.73 (s, 3H), 5.62 (s, 1H), 6.73 (s, 2H), 6.8-7.9 (m, 8H): meso form (4), mp 203-204°C;[10)] ^{1}H NMR ($CDCl_3$, 34°C) δ=2.40 (s, 6H), 2.52 (s, 3H), 2.65 (s, 3H), 3.71 (s, 3H), 5.61 (s, 1H), 6.76 (s, 2H), 6.8-7.5 (m, 8H).

Since the methoxyl group in 1 gave a broad signal in ^{1}H NMR spectra, temperature of the measurement was changed. The signal was temperature dependent: it became sharp at high temperatures and split into two singlets at low temperatures (δ=3.58 and 3.90 in $CDCl_3$). The intensities of the two signals at the lower temperatures changed as summarized in Table 1 and the thermodynamic parameters are obtained as ΔH=0.4 kcal/mol and ΔS=2.0 eu.

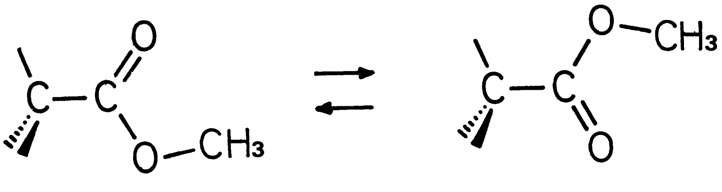
Table 1 Equilibrium Constants Determined by Intensities of Two Methoxyl Signals of the dl-Form of 9-(1-Methoxycarbonyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycene in $CDCl_3$

Temperature (°C)	K (=5/6)	Temperature (°C)	K (=5/6)
-25	1.13	10	1.25
-14	1.15	19	1.27
-2	1.18	22	1.28
5	1.22		

The assignment of structures corresponding to these two methoxyl signals poses problems. The first problem to be solved is identification of the rate process observed by DNMR. In principle, there are two possibilities which can cause the nonequivalence of the two methoxyl groups. On one hand, it is possible to postulate that E and Z forms of the ester are interchanging (eq. 1). On the other hand, it is also possible to attribute the phenomenon to the restricted rotation about the C_α-C(=O) bond in the ester which takes the Z conformation (eq. 2).

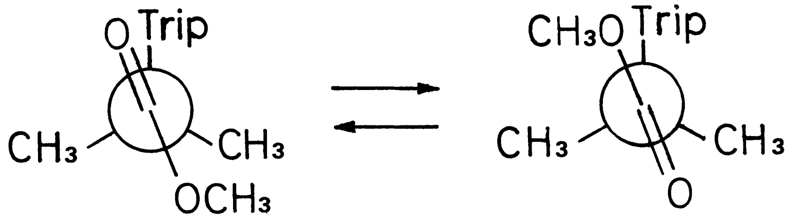


(1)



(2)

A possible answer to the question is that the process observed by the NMR spectra corresponds to the change of eq. 2, since the E conformation hardly exists in esters carrying a large alkyl group in the α-position of the acyl part:[3] the compound in question carries a large triptycyl group and two methyl groups in the α-position. Then we can attribute the phenomenon to the restricted rotation about the C_α-C(=O) bond, which makes a CH_3O-outside (5) and a CH_3O-inside (6) conformation distinguishable by the NMR method. Although carbonyl groups are known to take either an eclipsed or a staggered form relative to an α-substituent,[11] the steric requirement of the triptycyl group will force the ester group to take conformations shown.



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After assigning the rate process, we come to the second problem: which methoxyl signal does correspond to the CH_3O-inside conformation? We take advantage of the ring current effect of the benzene rings for the assignment of the conformation: the CH_3O-inside conformation is the one which gives the methoxyl signal at the higher field. Then the conclusion is the CH_3O-inside conformation is a little less stable than the CH_3O-outside conformation.

The same is true for the dl-form of the dimethyl compound (2): although the line broadening and the splitting (δ = 3.58 and 3.89 in $CDCl_3$) of the methoxyl signal occurred at lower temperatures, the CH_3O-outside conformation is a little more stable than the counterpart, ΔG being 0.2 kcal/mol at 34°C.

Total line shape analysis of the methoxyl signals was performed and kinetic parameters were obtained as shown in Table 2. It deserves mention that the meso forms showed broadening of the methoxyl signals but did not split at -79°C in $CDCl_3$-CS_2 (1:1). Although there is a possibility that the methoxyl signals due to the two conformations in the meso form are too closely located to resolve with the instrument (Hitachi R-20B spectrometer operating at 60 MHz), it is highly likely that the high barrier and consequently the splitting of the signals of the dl forms are caused by the steric hindrance given by the peri-substituent. The higher barrier to rotation of 1 than that of 2 is ascribed to attractive interaction between the chloro and the carbonyl group which stabilizes the ground state.12)

Table 2 Activation Parameters for Rotation about the C_α-C(=O) Bond (34°C)

X	Y	Process	ΔH‡ (kcal/mol)	ΔS‡ (eu)	ΔG‡ (kcal/mol)
Cl	Cl	5 → 6	13.7	-7.4	16.0
		6 → 5	14.1	-5.4	15.8
CH_3	H	5 → 6	10.9	-10.5	14.1
		6 → 5	11.2	-8.8	13.9

References and Notes

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8) This compound solidifies on further heating and melts at 286-288°C, probably because of isomerization to the dl form which is overwhelmingly stable.

9) The singlet signal is due to coincidence of the two chemical shifts under the conditions of the measurement. A 1-chloronaphthalene solution of this compound shows two singlets at 70°C.

10) This compound solidifies on further heating and melts at 264-265°C.

11) Eclipsed forms are successfully used for interpretation of microwave spectral data of CH_3CO compounds (CH_3CHO; R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., J. Chem. Phys., 26, 1695 (1957): CH_3COCH_3; R. Nelson and L. Pierce, J. Mol. Spectry., 18, 344 (1965): CH_3COF; L. Pierce and L. C. Krisher, J. Chem. Phys., 31, 875 (1959): CH_3COCl; K. M. Sinnott, J. Chem. Phys., 34, 851 (1961): CH_3COCN; L. C. Krisher and E. B. Wilson, Jr., J. Chem. Phys., 31, 882 (1959): $CH_3COCOOH$; C. E. Kaluza, A. Bauder, and Hs. H. Günthard, Chem. Phys. Lett., 22, 454 (1973)). However, there are some authors who have used staggered forms for explanation of the microwave data ($CH_3COCOOH$; K. M. Marstokk and H. Mollendal, J. Mol. Struct., 20, 257 (1974): CH_3COOCH_3; G. Williams, N. L. Owen, and J. Sheridan, Trans. Faraday Soc., 67, 922 (1971)).

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