Confirmation of the Structures of 2-Acetoxy-5-methoxy- and 5-Acetoxy-2-methoxy-7-methoxycarbonyl-triptycenes by Means of Electric Dipole Moments

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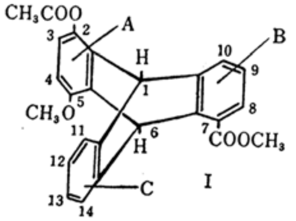
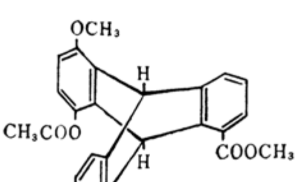
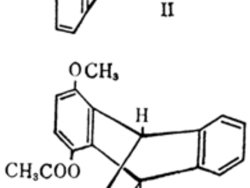
The monomethylation, followed by the acetylation, of 2, 5-dihydroxy-7-methoxycarbonyltriptycene, which was derived from 2, 5-diacetoxy-7-methoxycarbonyltriptycene,[1] afforded two isomers, I (m. p. 269~270°C) and II (m. p. 279~280°C). The deacetylation of I and II yielded the corresponding hydroxy-methyl ethers. Only the hydroxy-methyl ether derived from II shows a weak infrared absorption due to an intra-molecular hydrogen bond, indicating the proximate spatial positions of the hydroxyl and methoxycarbonyl groups. On the basis of this evidence, the structures shown below have tentatively been assigned to these compounds.[2]



I



II



III

In order to confirm the structures of I and II, the present authors have measured the electric dipole moments of I and II in *p*-dioxane at 25°C, together with that of 2-acetoxy-5-methoxy-triptycene (III, m. p. 274~275°C) as a reference substance.

The polarization data of these compounds are summarized in Table I. The notations ε, v, n, ω, $p_{2\infty}$, P_2, R_D, and μ represent the dielectric constant, the specific volume, the refractive index, the weight fraction of the solute, the specific polarization, the molecular polarization, the molecular refraction for the sodium D line, and the dipole moment respectively. The dielectric data were analyzed according to the Halverstadt-Kumuler's method, and the dipole moments were obtained on the assumption that distortion polarizations are equal to $1.05\times R_D$.[3]

The estimation of the molecular dipole moments of I, II, and III was carried out on the basis of the following fundamental assumptions: 1) the additivity of the vectors of the group moments,[4] and 2) the D_{3h} symmetry of the triptycene skeleton. The values and directions of the group moments used in the calculation are given in Table II. With regard to the substituents at the 2- and 5-positions, the following three possible configurations (a, b, and c) were taken into consideration: a) both the methoxyl and acetoxyl groups lie in the same plane as that of the aromatic ring A, and the substituent groups take the cis-configuration because of the steric hindrance of the hydrogen atoms at the 1- and 6-positions;[5] b) both the methoxyl and the acetoxyl groups lie on a plane perpendicular to the plane of the aromatic ring A, and the substiuent groups take the cis- or trans-configuration; and c) the methoxyl group takes a coplanar position

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[1] A. Sonoda, F. Ogura, and M. Nakagawa, This Bulletin, 35, 853 (1961).

[2] F. Ogura and M. Nakagawa, unpublished work. The details of the synthesis, the spectral properties and the optical rotatory dispersion of these compounds will be reported elsewhere.

[3] R. J. W. LeFèvre, "Dipole Moments," Methuen and Co., London (1948), p. 17.

[4] C. P. Smyth, "Dielectric Behavior and Structure," McGraw Hill, New York (1955), p. 253.

[5] E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York (1955), p. 408.

TABLE I. POLARIZATION DATA IN DIOXANE AT 25°C

	I	II	III
ε	$2.2120+2.95\omega$	$2.2053+1.95\omega$	$2.2053+2.08\omega$
v	$0.97274-0.181\omega$	$0.97277-0.210\omega$	$0.97277-0.175\omega$
n^2	$2.01642+0.436\omega$	$2.01642+0.468\omega$	$2.01642+0.482\omega$
$p_{2\infty}$	0.7034 cc.	0.5402	0.5749
P_2	281.7 cc.	216.3	196.8
R_D	111.8 cc.	111.2	99.0
μ	2.84±0.14D	2.21±0.13	2.13±0.11

TABLE II. VALUES AND DIRECTIONS OF GROUP MOMENTS

Group	Moment (D)	Direction
Methoxycarbonyl ($\mathrm{CH_3\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}}$)	1.83	70° with the bond between the carbon of 7-position and the carbonyl carbon.
Methoxyl ($\mathrm{CH_3\text{--}O\text{-}}$)	1.25	55° with the bond between the carbon of 5- or 2-position and the oxygen atom.
Acetoxyl ($\mathrm{CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-}}$)	1.52	129° with the bond between the carbon of 2- or 5-position and the oxygen atom.

with the aromatic ring A, whereas the acetoxyl group lies on the plane perpendicular to the latter plane. Concerning the methoxycarbonyl group on carbon 7, it was assumed that the group takes a coplanar configuration with the aromatic ring B to attain the maximum mesomeric effect. Since two conformations seem to be possible, i. e., the conformation with the closest distance between the carbonyl oxygen and the hydrogen atom at the 6-position and that with the greatest distance between the above-mentioned two atoms, the notations bearing asterisk (a*, b*, c*) are employed to indicate the latter conformation. The calculated results are given in Table III. The values of the dipole moments based on the configuration b and b* are the root mean square values of the four possible configurations and turn out to be identical. The values based on c and c* are those of the two possible configurations.

TABLE III. CALCULATED DIPOLE MOMENTS (D)

Configuration	I	II	III
a	2.92	2.09	1.68
a*	2.83	1.95	1.68
b, b*	3.27	2.55	2.29
c	2.98	2.18	2.29
c*	3.53	2.87	2.29

These calculations lead to the conclusion that the dipole moments of I are always greater than those of II for all probable configurations and that discrimination between I and II is, therefore, possible. The most satisfactory agreement with the observed values is obtained in the case of the configuration c which is supported also by the electronic spectral information on I and II.[2)]

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