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RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. VIII.[1] ISOLATION OF THREE STABLE ROTAMERS ABOUT AN sp^3-sp^3 CARBON BOND

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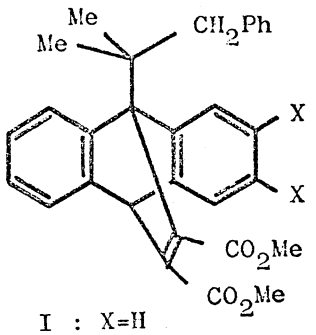
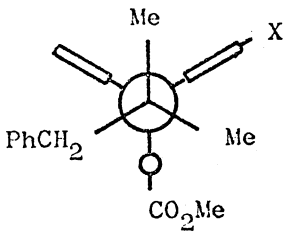
Each of the three possible rotational isomers formed by the rotation about a C-C single bond between the bridgehead tert-alkyl group and the skeleton of dimethyl 2,3-dichloro-9-(1,1-dimethyl-2-phenylethyl)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate is isolated. These compounds are found to be very stable at room temperature. Structural assignment is made by the NMR evidence.

Isolation of two rotational isomers of a triptycene-type compound I, dl and meso, at room temperature was reported from this laboratory.[2] Along this line, Iwamura succeeded in isolating C_2 (dl) and C_{2v} (meso) isomers of 9,10-bis(1-cyano-1-methylethyl)triptycene.[3] The existence of these stable isomers should be ascribed to the high barrier to rotation of the bridge-head tert-alkyl groups and the models of I may be shown by the Newman type projections Ia (and its enantiomer Ib) and Ic respectively. While resolution of the dl isomer is an interesting project, it may be substituted by an attempt at isolating three possible rotational isomers about an sp^3-sp^3 carbon bond. It is especially so if the resolution is time-consuming, laborious work. We now wish to report the successful isolation of such rotational isomers of compound II : IIa, IIb, and IIc.

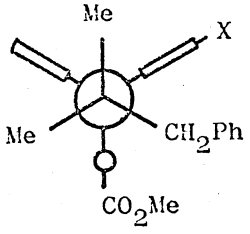
Addition of 1,1-dimethyl-2-phenylethylmagnesium chloride to 2,3-dichloroanthrone followed by dehydration with phosphorus pentoxide afforded 2,3-dichloro-9-(1,1-dimethyl-2-phenylethyl)anthracene (III)[4], mp 121-123°C, NMR (CCl_4, 60MHz): δ 1.73 (6H, s), 3.63 (2H, s), 6.9-8.3 (12H, m). Heating III with dimethyl acetylene-



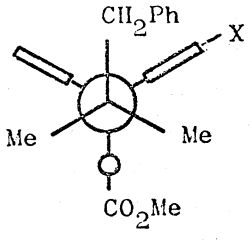
I : X=H
II : X=Cl



Ia : X=H
IIa : X=Cl



Ib : X=H
IIb : X=Cl



Ic : X=H
IIc : X=Cl

Table I NMR Data of the Isomers[a)]

Isomer	A		B		C	
Solvent / Protons[b)]	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
C-Me	1.80[c)]	1.63	1.77	1.67	1.71	1.72
		1.80	1.88	1.94	1.80	1.89
O-Me	3.74	3.33	3.74	3.33	3.68	3.28
	3.77	3.47	3.77	3.47	3.75	3.40
C-CH_2	3.60 q	3.80[d)]	3.50 q	3.77[d)]	3.69 q	3.49 q
	J=14.1Hz		J=14.1Hz		J=14.6Hz	J=14.4Hz
	$\Delta\nu$=15.6Hz		$\Delta\nu$=12.1Hz		$\Delta\nu$=8.7Hz	$\Delta\nu$=11.8Hz
10-H	5.49	5.44	5.49	5.44	5.49	5.44
1-H	7.76	7.75	7.99	8.04	8.05	8.05
8-H	7.9 m	7.9 m	7.7 m	7.7 m	8.0 m	8.0 m

a) Obtained for ca. 10%(w/v) solution at 34°C and 60MHz, and given in ppm relative to internal TMS. Singlet except otherwise noted. b) The aromatic protons other than peri-protons are not listed. c) Two methyls accidentally overlapped. d) Apparent singlet.

dicarboxylate in toluene under reflux for 5 hr gave colorless crystals, mp 215.5-216.5°C (from THF-MeOH), in a high yield. Elemental analysis and NMR data (Table I and Figure I) revealed the product to be one of the rotational isomers of compound II : no other isomer was found in the product. This rotamer, tentatively named as Isomer C, was extremely stable at room temperature both in crystalline state and in solution, but slowly isomerized to give a mixture with the other rotamers (tentatively named as Isomers A and B) upon heating in o-dichlorobenzene at 150°C with a half-life of ca. 1 hr, although overlap of NMR signals prevented us from the quantitative kinetic study. Equilibration was reached in ca. 8 hr under the condition, and equilibrium composition of the isomers was A:B:C=3:3:2.

The equilibrated mixture was chromatographed on a silica gel column, and three isomers were eluted, in the order of A, B and C, with benzene as an eluent. Isomers A and B resisted to crystallization, although NMR confirmed their purity (Table I and Figure I). Both A and B gave the same equilibrium mixture as Isomer C did upon heating in solution.

Structural assignment of the isolated isomers was made as follows. Examination of chemical shifts of the peri-protons of Ia, Ic and a 9-tert-butyl analog IV revealed that IV shows a multiplet centered at δ 7.7, whereas Ia possesses two multiplets at δ 7.7 and 8.0 and Ic a multiplet at δ 8.0. These results may be summarized that replacement of a methyl group by a benzyl causes the deshielding of the nearby peri-proton(s) by ca. 0.3 ppm. Taking this into account and considering

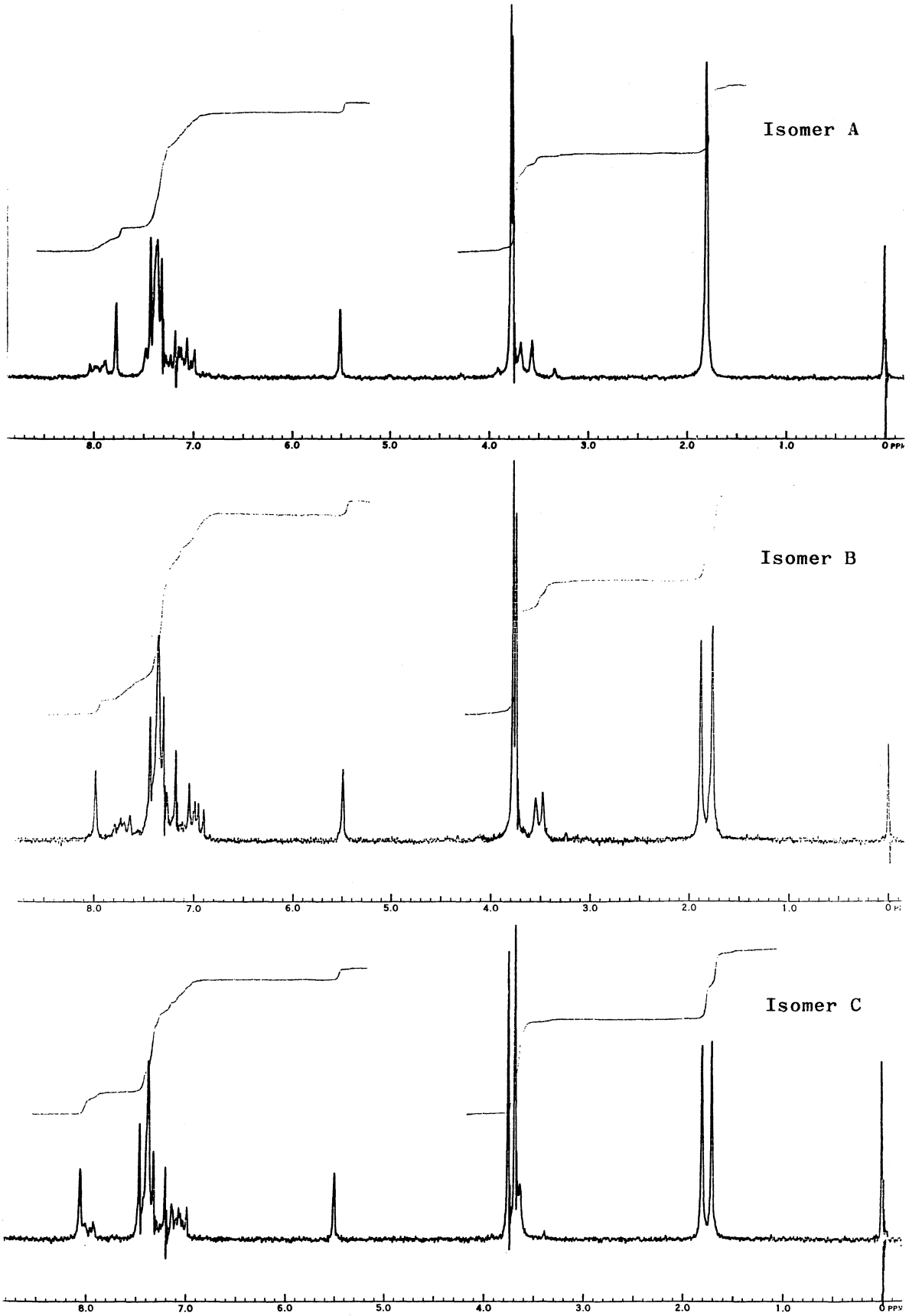


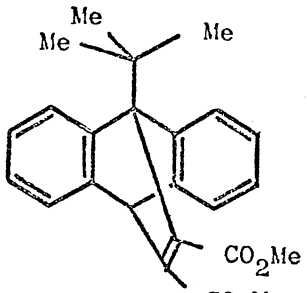
Figure I NMR Spectra of the Isomers ($CDCl_3$, 60MHz).

Table II Predicted Chemical Shifts of the peri-Protons.[a)]

Isomer / Proton	IIa	IIb	IIc
1-H	7.7 s	8.0 s	8.0 s
8-H	8.0 m	7.7 m	8.0 m

a) Given in ppm relative to TMS.

that substitution of a hydrogen atom by a chlorine in an aromatic ring does not significantly affect the chemical shift of the aromatic protons[5)], appearance of the peri-proton signals in the three rotamers was predicted as shown in Table II. Comparison of the predicted values with the observed spectra made it possible to assign structures IIa, IIb and IIc to isomers A, B and C, respectively.



IV

The sole formation of Isomer IIc in the synthesis is of interest. Considering the transition state of the reaction the formation of IIc requires a conformation of the anthracene derivative in which bulkier benzyl group occupies the farthest position from the entering acetylenedicarboxylate moiety. This stereoselectivity is in accord with the previous observation in the synthesis of compound I[2)], but will require further study for generalization and/or rationalization.

After establishing the assignment of the conformations, the equilibrium composition of A:B:C=3:3:2 can be compared with that of compound I : dl:meso=3:1. Since the dl isomer of I corresponds to A and B in compound II and the meso to C, the equilibrium composition of I and II can be said to be very close with each other. The two chlorine atoms in compound II seem to play only a minor role in the thermodynamic equilibrium.

References.

1) The preceding paper: F. Suzuki, M. Ōki, and H. Nakanishi, Bull. Chem. Soc. Japan, 46, 2858 (1973).
2) M. Ōki and G. Yamamoto, Chem. Lett., 1972, 45.
3) H. Iwamura, Chem. Commun., 1973, 232.
4) Satisfactory elemental analyses were obtained for new compounds.
5) H. Spiesecke and W. G. Schneider, J. Chem. Phys., 35, 731 (1961).

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