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CYCLIC TETRAMERS OF CHIRAL AZIRIDINES. II.$^{1)}$
ISOLATION OF FOUR STEREOISOMERS

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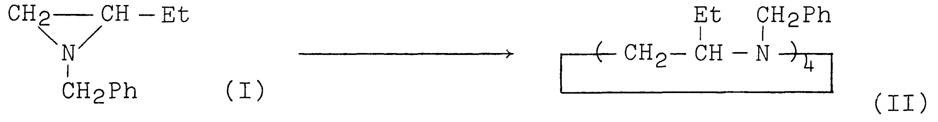
1-Benzyl-2-ethylaziridine (I) was oligomerized to give the cyclic tetramer (II). Four geometrical isomers are possible for II and all of them were isolated and characterized.

Synthesis of the cyclic tetramers (II) from 1-benzyl-2-ethylaziridine (I) was described in the preceding communication.$^{1)}$ Optically active I gave only one corresponding optically active tetramer II and no other isomers were found in the product. The formation of the sole isomer means that the ring cleavage of the aziridine takes place preferentially at the methylene-nitrogen linkage. In case of the racemic monomer, therefore, the cyclic tetramers to be obtained are the following four geometrical isomers (A~D).



$$\left[\left(CH_2-\underset{}{\overset{Et}{CH}}-\overset{CH_2Ph}{N}\right)_4\right]$$

Configuration	RRRR	SSSS	RRRS	SSSR	RRSS	RSRS
Isomer (II)	A_R	A_S	B_R	B_S		
	A		B		C	D

We now report synthesis and identification of these stereoisomers of the cyclic compound II. The racemic I gave a mixture of II (in 30 % yield) in a similar manner as described previously.$^{1)}$ Separation of the isomer A, B, C, and D was carried out by fractional recrystallization from an appropriate solvent, and/or by picking them up with tweezers under a low-power microscope. All the isomers which were isolated as the respective single crystals gave satisfactory elemental analyses. Various properties of the isomers are summarized in Table I with those of the optically active ones. Although their mass spectra were too similar to distinguish them one another even when they were taken under low voltage, the pmr spectra are exceptionally informative and reflect the configurational difference as shown in Fig. 1.

Isomer A shows the presence of one triplet at δ 0.97 for CH_3, two quartets

Table I. Properties of Cyclic Tetramers

Isomer	Mp (°C)	Point group	Crystal system	Lattice constant (Å)	Space group	Z
A_R	189	C_4	Tetragonal*	a=12.06, c=30.89	$P4_1$, $P4_3$	4
A_S	189	C_4	Tetragonal*	a=12.06, c=30.90	$P4_1$, $P4_3$	4
A	223	C_4	Monoclinic**	a=22.60, b=14.59, c=11.79 β=90.5°	$P2_1/a$	4
B	138	C_1	Triclinic	a=9.73, b=18.55, c=11.55 α=93.5°, β=106.3°, γ=75.3°		2
C	203	C_i	Triclinic	a=9.41, b=13.48, c=9.24 α=113.5°, β=102.0°, γ=64.0°		1
D	212	S_4	Tetragonal	a=27.70, c=12.50	$P4_2/n$	10

* Benzene molecule is contained, 1 : 1 ; $[\alpha]_D^{28}$ +242° and -240° (c 0.13, isooctane) for R- and S-forms, respectively.

** Isomer A has already been assigned as a mixture of an equal amounts of A_R and A_S.1)

for ring CH_2 centered at δ 2.05 and 3.04, and an AB quartet for benzyl CH_2 centered at δ 3.33. This means configurational and conformational homogeneity of four monomeric units. The relatively large splitting and the large difference in chemical shift of the ring and benzyl CH_2 signals reveal that the ring is in a fixed conformation. A prominent phenomenon is non-equivalence for CH_2 protons in the ethyl group. Spin-decoupling experiments with the spectrum proved that the triplet for CH_3 is not true one but a type of C nuclei in ABC_3 system which are coupled with each of geminal CH_2 protons in the ethyl group, and that two broad multiplets centered near δ 1.25 and 1.64 correspond to the protons of H_a and H_b in $-CH_aH_b-CH_3$, respectively. The two multiplets undergo coalescence into one multiplet at about 120°C. The high temperature needed for the coalescence shows that free rotation of the ethyl group was restricted remarkably by steric hindrance of benzyl group. This fact again suggests that the twelve-membered ring has an unflexible conformation owing to a steric requirement of the regularly arranged bulky C- and N-substituents.

Isomer D belongs to the point group S_4, which has seldom been observed in organic compounds.2) For symmetry reasons the spectrum appears only one set of the signals for the four monomeric units. The higher field shift of CH_3 signal suggests that the group is held above or below the phenyl ring in N-benzyl group. Magnetic non-equivalence of the methylene protons in ethyl group is observed more clearly than that of isomer A, and the coalescence in the two multiplets of CH_2 has not observed even at 150°C. This indicates the higher resistance to rotation of the ethyl group compared with that of isomer A. The low-field shift of the

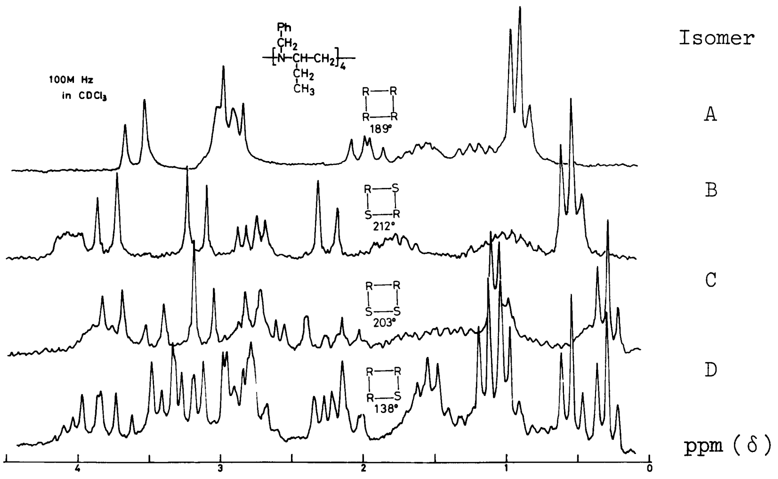


Fig. 1. Pmr spectra of the isomers of cyclic tetramer II.

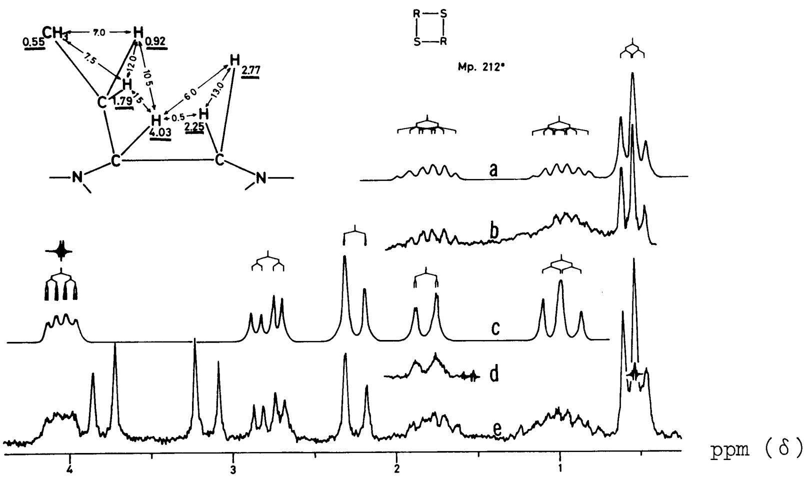


Fig. 2. Comparison of 100-MHz pmr spectra of C-substituent and ring protons of isomer D. At the top, a schematic summary of the coupling constants (Hz) and chemical shift (δ, underlined) used for the simulation is shown: (a) and (c) simulated spectra; (b) and (d) spin-decoupled spectra; (e) observed spectrum, N-benzyl CH_2 resonance centered at δ 3.47 as AB quartet.

methine proton (δ 4.05) may be ascribed to a kind of steric compression effect. Possibly this phenomenon is an evidence of crowding in space with regularly arranged groups. In order to confirm the description and to obtain a complete set of vicinal and geminal coupling constants, the spectra experimentally obtained are compared with the simulated ones in Fig. 2. Although no decoupled signal on H_a with CH_3 was obtained, because of their close chemical shifts, an expected signal must be similar to the signal at δ 0.92 in (c). This isomer seems to be in a more restricted conformation than that of isomer A in solution.

Isomer C does not contain any equivalent groups owing to the absence of required C_n, but has a pair of enantiotopic groups. Two sets of signals are virtually observed in the spectrum.

Isomer B which is an asymmetric molecule, contains neither equivalent groups nor enantiotopic ones. The spectrum, therefore, indicates four different sets of signals and is too complex to analyse precisely but they are in no contradiction.

The conformations of these isomers, with the data mentioned above and the aid of the information of ball-and-stick models, are considered to be a crown type ring geometry for isomer A, a boat type for isomer D, and a chair conformation for isomer C. The consideration will be confirmed by the complete estimation of the coupling constants and a Karplus-type function for the dihedral angles.

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