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Cyanomethylation Products of *dl*- and *meso*-Diphenylethylenediamines*

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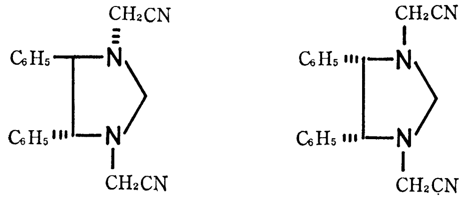
During the course of investigation of syntheses and chelating behaviors of complexane-type ligands, we found that *dl*-diphenylethylenedinitrirotetraacetic acid was obtained by carboxymethylation of *dl*-diphenylethylenediamine, and the *meso*-isomer gave 2-oxo-5,6-diphenylpiperazine-1,4-diacetic acid, but not the expected *meso*-dinitrirotetraacetic acid.[1]

Kroll and Gordon reported the synthesis of cyclohexane-*cis*-1,2-dinitrirotetraacetic acid from *cis*-1,2-diaminocyclohexane *via* a cyanomethylated intermediate.[2]

In order to obtain the corresponding tetraacetic acid *via dl*- and *meso*-diphenyl-*N*,*N*,*N'*,*N'*-tetrakis(cyanomethyl)ethylenediamines, cyanomethylation was attempted on the respective diamines using hydrocyanic acid and formaldehyde. However, the reaction products were not the tetrakiscyanomethylated compound, but the imidazolidine derivatives. In this paper we report on the structure with reference to the solvent effects in the proton chemical shifts of the compounds.

Results and Discussion

From the results of elemental analyses and spectroscopic data, the reaction products from *dl*- and *meso*-diphenylethylenediamines were found to be 4α,5β-diphenyl-1α,3β-bis(cyanomethyl)imidazolidine (I) and 4α,5α-diphenyl-1β,3β-bis(cyanomethyl)imidazolidine (II), respectively.



(I) (II)

Structure (I) and (II)

NMR spectral data of (I) and (II) in various solvents and at various temperatures are summarized in Table 1. The patterns of the NMR spectrum of (I) at −30°C are the same as those at 80°C except for slight shifts in signals.

It is of interest to note that two cyanomethyl protons show a quartet signal centered at 3.55 and 3.59 ppm with J=17.7 and 17.5 Hz in deuteriochloroform for (I) and (II), respectively. However, the protons in benzene solution show a singlet at 2.72 and a broad one at 2.77 ppm for (I) and (II), respectively. The results suggest that two cyanomethyl groups are equivalent in a magnetic field but not the two protons on each cyanomethyl group due to the asymmetric effect

TABLE 1. PROTON CHEMICAL SHIFTS OF (I) AND (II) IN VARIOUS SOLVENTS (δ, ppm)

Solute	Proton	$CDCl_3$	C_6H_6	C_6H_5Br	C_5H_5N
(I)	$-CH_2CN^{a)}$	$3.55^{b)}$ ($3.58^{c)}$)	$2.72^{b)}$ ($2.78^{d)}$)	$3.13^{b)}$ ($3.00^{d)}$)	$3.71^{b)}$ ($3.65^{d)}$)
	$>CH_2$	3.85 (3.89)	3.76 (3.75)	3.79 (3.79)	4.04 (4.00)
	$-\overset{|}{C}H$	4.28 (4.33)	3.78 (3.83)	4.03 (4.05)	4.38 (4.34)
	$-\overset{|}{C_6H_5}$	7.28 (7.33)			
(II)	$-CH_2CN^{a)}$	$3.59^{b)}$	$2.77^{b)}$	$3.18^{b)}$ ($3.22^{e)}$)	$3.81^{b)}$ ($3.71^{e)}$)
	$>CH_2{}^{a)}$	4.09	3.57	3.81 (3.86)	4.21 (4.21)
	$-\overset{|}{C}H$	4.29	3.99	4.12 (4.13)	4.48 (4.42)
	$-\overset{|}{C_6H_5}$	6.97			

a) The center of AB quartet pattern signals was taken as the chemical shift.
b) at 38°C. c) at −30°C. d) at 80°C. e) at 90°C.

TABLE 2. DIFFERENCE BETWEEN THE SHIFTS IN SOLVENTS AND IN $CDCl_3$ at 38°C (Hz)[a)]

Solvent	(I)			(II)		
	$-CH_2CN$	$>CH_2$	$-\overset{|}{\underset{|}{C}}H$	$-CH_2CN$	$>CH_2$	$-\overset{|}{\underset{|}{C}}H$
C_6H_6	+49.5	+ 5.5	+29.9	+48.7	+31.1	+18.0
C_6H_5Br	+25.2	+ 3.4	+13.9	+24.0	+17.6	+ 9.9
C_5H_5N	−10.1	−11.3	− 6.0	−14.0	− 7.6	−11.3

a) Positive: high-field shift. Negative: low-field shift.

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[1] N. Okaku, Y. Toyota, Y. Moriguchi, and K. Ueno, This Bulletin, **40**, 2326 (1967).

[2] H. Kroll and M. Gordon, *Ann. N.Y. Acad. Sci.*, **88**, 341 (1960).

of the imidazolidine ring nitrogen to which the cyanomethyl group attached, while in a benzene solution the asymmetric effect of nitrogen was suppressed owing to the association of the benzene molecule to the solute molecule.

A singlet signal at 3.85 ppm and a quartet one centered at 4.09 ppm with J=3.4 Hz for (I) and (II), respectively, can be attributed to the methylene protons interposed between two nitrogens on the ring. The methine protons appeared as a singlet at 4.28 and 4.29 ppm for (I) and (II), respectively.

The solvent-induced shift for protons are shown in Table 2. The solvent affected the methine proton to a greater extent than the methylene proton on the ring for (I), whereas the methylene protons in (II) were more affected than the methine proton. The difference was considered to be due to the fact that the benzene molecule is associated to the solute molecule in a different manner for (I) and (II) because of the different configurations of (I) and (II).

Superimposed proton signals for each pair of the substituents on the imidazolidine ring of (I) and (II), and splitting of the methylene protons interposed between two ring nitrogens of (II) indicated C_2 and σ symmetries effectively in NMR time scale for (I) and (II), respectively. Study with a molecular model showed significant steric hindrance between the phenyl and the cyanomethyl groups, favoring *trans* configuration for the substituents concerned.

A question remains whether cyanomethylation took place after the imidazolidine ring was formed[3] or a tricyanomethylated diamine once formed liberated hydrocyanic acid to form the imidazolidine ring.[4] The actual reaction conditions suggest that the former process is more probable.

Experimental

Chemical shifts were measured on a Varian A-60 spectrometer using TMS as an internal reference. The concentrations of the sample solution were approximately 10%.

Material. *dl*- and *meso*-Diphenylethylenediamines were synthesized from benzaldehyde according to the method in literature.[5-7]

4α,5β-Diphenyl-1α,3β-bis(cyanomethyl)imidazolidine (I). An aqueous 36% formaldehyde (1.4 g, 0.019 mol) and 0.93 g (0.019 mol) of sodium cyanide were added successively to a cold solution of 1.34 g (0.0047 mol) *dl*-diphenylethylenediamine dihydrochloride in 1.2N hydrochloric acid and the resulting mixture was kept in a pressure bottle. The mixture was allowed to stand for 3 days at room temperature. The precipitate obtained was recrystallized from methanol. $\nu_{C\equiv N}$, 2220 cm^{-1}; mp 130—131°C, yield 60%.

Found: C, 75.49; H, 5.99; N, 18.54%. Calcd for $C_{19}H_{18}N_4$: C, 75.50; H, 5.96; N, 18.54%.

4α,5α-Diphenyl-1β,3β-bis(cyanomethyl)imidazolidine (II) was synthesized in a similar manner to that described above. A methanol soluble fraction of the product was recrystallized from ethanol. $\nu_{C\equiv N}$, 2230 cm^{-1}; mp 163—164°C, yield 36%.

Found: C, 75.32; H, 5.83; N, 18.87%.

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[3] For example: T. Yano, H. Kobayashi, and K. Ueno, This Bulletin, **43**, 3167 (1970).

[4] Unpublished data.

[5] I. Lifschitz and J. G. Bos, *Rec. Trav. Chim. Pays-Bas*, **59**, 173 (1940).

[6] S. Tripett, *J. Chem. Soc.*, **1957**, 4407.

[7] W. H. Mills and T. H. H. Quibell, *ibid.*, **1935**, 839.