Crystalline Adducts of Dicyclohexylamine with Di- and Triols

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It has been reported briefly in the literatures that dicyclohexylamine forms crystalline addition compounds with hydroxy compounds such as water1), ethanol1), cyclohexanols2) and cyclohexanediols2). An accidental observation of the formation of a white precipitate by mixing dicyclohexylamine with ethylene glycol urged the present authors to a more detailed study on the adducts.

When an acetone solution of dicyclohexylamine was mixed with some di- or tri-hydroxy compounds in the same solvent, immediate precipitation of very fine silky needles accompanied by an evolution of heat was observed. The crystals thus obtained could be easily recrystallized from acetone to give a pure adduct. The melting points, the analytical data of nitrogen and the composition of the adducts with various glycols are summarized in Table I.

It is to be noted that in spite of the remarkable change in the structure of glycols, the composition of the adducts with glycols was always in a ratio of 1 : 2. These results are inconsistent with those of Winans2) who reported the composition of the adducts with diols is 1 : 1 so far as he studied**.

The properties of the adducts with several kind of triols are listed in Table II together with its analytical data.

In these cases the molar ratio of the triol against the amine was found to be 1 : 3 excepting the case of glycerol in which it was found to be 2 : 3.

These adducts are readily soluble in common organic solvents and are especially easily recrystallized from acetone. The adducts are decomposed into the components by the addition of water. The most striking property of the

TABLE I. ADDUCTS OF DICYCLOHEXYLAMINE WITH GLYCOLS

Glycol	m. p.	N(%)		Molar ratio
	°C	Found	Calcd.	Glycol : Amine
Ethylene glycol	70	6.60	6.60	1 : 2
1,2-Propanediol	49∼49.5	6.28	6.39	1 : 2
1,3-Propanediol	53	6.32	6.39	1 : 2
1,4-Butanediol	68∼69	6.13	6.19	1 : 2
2,3-Butanediol	63.5∼64.5	6.11	6.19	1 : 2
1,3-Butanediol	below room temp	5.96	6.19	1 : 2
2(*cis*)-1,4-Butenediol	49.5∼51	6.14	6.22	1 : 2
2(*trans*)-1,4-Butenediol	68∼69	6.22	6.22	1 : 2
2-Butyne-1,4-diol	59.5	6.14	6.24	1 : 2
1,5-Pentanediol	39.5∼42	6.02	6.00	1 : 2
1,6-Hexanediol	59.5∼60.5	5.68	5.83	1 : 2
2,4-Hexadiyne-1,6-diol	68.5∼69	5.96	5.95	1 : 2
1,7-Heptanediol	58∼59	5.72	5.67	1 : 2
Diethylene glycol	25∼25.5	5.65	5.98	1 : 2
Hydrocinnamoin	151.5∼152	4.63	4.45	1 : 2
1,4-Di-(β-phenyl-α-hydroxyethyl)-benzene	78.5∼80	3.96	4.11	1 : 2

TABLE II. ADDUCTS OF DICYCLOHEXYLAMINE WITH TRIOLS

Triol	m. p.	N(%)		Molar ratio
	°C	Found	Calcd.	Triol : Amine
Glycerol	38.5∼39.5	5.75	5.77	2 : 3
1,2,4-Butanetriol	46∼47	6.44	6.46	1 : 3
(−)-1,2,5-Pentanetriol	27∼28	6.09	6.34	1 : 3
1,2,6-Hexanetriol	49∼50	6.04	6.20	1 : 3

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1) G. Fouque, *Compt. rend.*, **166**, 394 (1918).

2) G. F. Winans, *J. Am. Chem. Soc.*, **61**, 3591 (1939).

** Winans prepared the adducts using petroleum ether or ether as solvent.

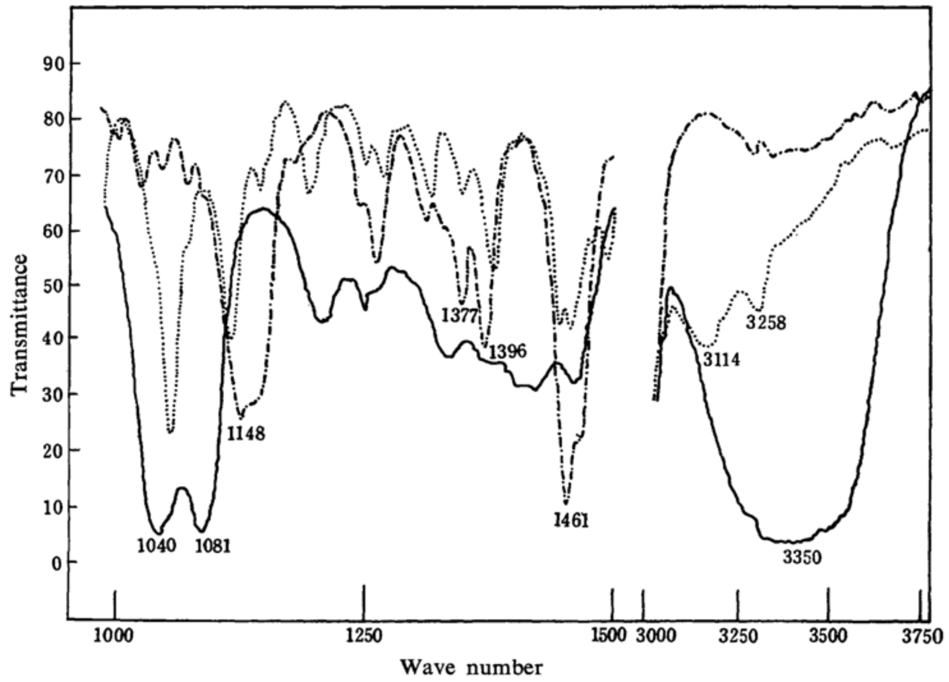

Fig. 1. The I. R. spectra of dicyclohexylamine (·-·-·), ethylene glycol (——) and the adduct with ethylene glycol (····).

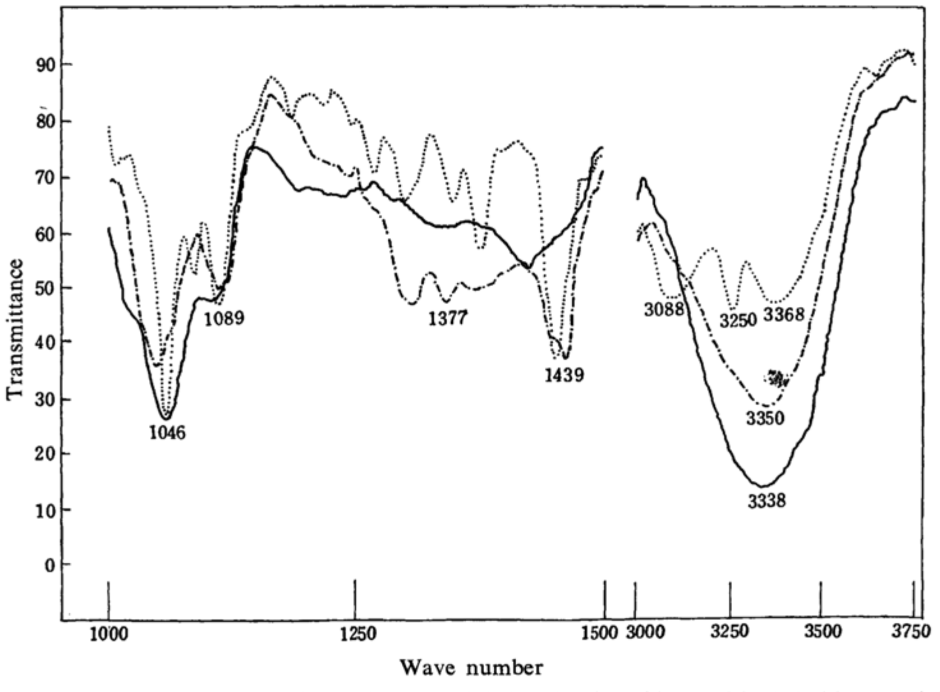

Fig. 2. The I. R. spectra of 1, 2, 4-butanetriol (——), the adduct with 1, 2, 4-butanetriol (····) and the adduct with glycerol (·-·-·).

adducts with diols is its tendency to sublime. When a crystalline adduct with a diol placed in an evacuated sealed tube is heated below its melting point, a rapid growth of beautiful silky needles on the cold wall of the tube can be observed.

The tendency of sublimation is characteristic of the adducts with glycols and can not be seen with the adducts with triols.

The existence of intermolecular polymeric association due to hydrogen bond in hydroxy compounds is well known, and the presence of this type of hydrogen bonds in ethylene glycol and in 1, 2, 4-butanetriol was revealed by the presence of a very broad absorption at 3350 and 3338 cm^{-1} in the infrared spectra of these alcohols as illustrated in Figs. 1 and 2. The diol and the triol also show a broad and strong absorption in the range of 1300～1440 cm^{-1} presumably arising from deformation of the associated hydroxy group or the streching of C–O of the associated hydroxy group. Also the infrared spectrum of dicyclohexylamine shows a broad absorption in the region of 3100～3500 cm^{-1} indicating the presence of associated N–H group. On the other hand, the infrared spectrum of the adduct with ethylene glycol showed two absorption peaks at 3114 and 3258 cm^{-1} instead of the broad absorption band of the glycol at 3350 cm^{-1} (Fig. 1).

Remarkable change in absorption was also observed in the range of 1300～1440 cm^{-1}. The broad absorption in the spectrum of ethylene glycol in this region disappeared in the spectrum of the adduct.

These spectroscopic evidences indicate that the formation of amine-glycol adduct is attributed to the formation of new strong intermolecular O—H···N hydrogen bonds destroying the original polymeric intermolecular hydrogen bonds which exist in ethylene glycol and in dicyclohexylamine. These arguments are consistent with the fact that the amine-diol adducts are easy to sublime. The formation of such a type of an "addition compound" in solution has been pointed out by several investigators[3]. The absorption band at ca. 3326 cm^{-1} in the infrared spectrum of the system of alcohol-amine-solvent was attributed to the formation of an amine-alcohol complex by Baker et al.[3c]

The situations are somewhat different in the cases of the adducts with triols. As illustrated in Fig. 2, the infrared spectrum of 1, 2, 4-butanetriol clearly indicates the presence of polymeric intermolecular hydrogen bonds in the triol. However, the infrared spectrum of the adduct with the triol exhibits three absorptions in the range of 3000～3400 cm^{-1} (3368, 3250 and 3088 cm^{-1}). Also the adduct with glycerol shows a broad and intense absorption at 3350 cm^{-1} (Fig. 2). These broad absorptions at 3368 or 3350 cm^{-1} seem to indicate the presence of remaining intermolecular polymeric hydrogen bonds in these amine-triol adducts. It is reasonable to conclude that some part of hydrogen bonds is used to associate the amine-triol adduct with each other, giving them the nature of non-sublimation.

Another point of interest in the physical property of the adducts is the oscillation of the melting points. As illustrated in Fig. 3, zigzag lines were obtained when the melting points of the adducts with α,ω-diols and α,β,ω-triols were plotted against the number of carbon atoms. These results indicate that the melting points of the series of an even number of carbon atoms are higher than those of the odd number series. The same phenomenon has been recognized in several homologous series of aliphatic compounds such as n-paraffins and α,ω-dicarboxylic acids.

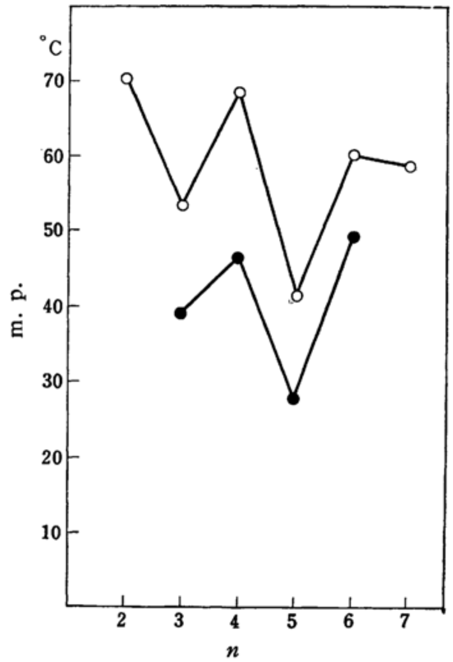

Fig. 3. The melting points of the adducts with α,ω-diols and α,β,ω-triols.

○—○ $HO\cdot(CH_2)_n\cdot OH$

●—● $HO\cdot CH_2\underset{OH}{CH}\cdot(CH_2)_{n-2}\cdot OH$

The molecular weight determination of the adducts with ethylene glycol, 1, 4-di-(β-phenyl-α-hydroxyethyl)-benzene and 1, 2, 6-hexanetriol were carried out by means of cryoscopic and

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[3] (a) M. Freymann, *Compt. rend.*, **204**, 261 (1937).
(b) J. Errera and H. Sack, *Trans. Faraday Soc.*, **34**, 728 (1938).
(c) J. W. Baker, M. M. Davies and J. Gannt, *J. Chem. Soc.*, **1949**, 24.

TABLE III. DISSOCIATION OF THE ADDUCTS IN SOLUTION

Alcohol component in adduct	Molecular weight			Degree of dissociation, %
	Calcd.	A.	B.	
Ethylene glycol	424	206 207	225	$\alpha_1=100$ or $\alpha_2=50$
1,4-Di-(β-phenyl-α-hydroxyethyl)-benzene	680	—	240	$\alpha_2=100$
1,2,6-Hexanetriol	677	—	214	$\alpha_3=100$ or $\alpha_4=70$

A. Cryoscopic method in benzene.

B. Isothermal distillation method in acetone solution.

isothermal distillation methods. The results summarized in Table III indicate the dissociation of the adduct in the solution. These results present no evidence on the nature of dissociation, but the calculated degree of dissociation is tabulated in Table III assuming the following types of dissociation.

$$\text{Diol}\left\{\begin{array}{l}(\text{amine})_2(\text{diol}) \overset{\alpha_1}{\rightleftarrows} (\text{amine})(\text{diol})+(\text{amine}) \\ \text{or} \\ (\text{amine})_2(\text{diol}) \overset{\alpha_2}{\rightleftarrows} 2(\text{amine})+(\text{diol})\end{array}\right.$$

$$\text{Triol}\left\{\begin{array}{l}(\text{amine})_3(\text{triol}) \overset{\alpha_3}{\rightleftarrows} (\text{amine})(\text{triol})+2(\text{amine}) \\ \text{or} \\ (\text{amine})_3(\text{triol}) \overset{\alpha_4}{\rightleftarrows} 3(\text{amine})+(\text{triol})\end{array}\right.$$

As stated above, the formation of crystalline adduct with dicyclohexylamine is quite general for primary or secondary diols and triols, but it was found that the tertiary glycols such as 2,4-dimethyl-2,4-butanediol and 1,1′,4,4′-tetraphenyl-1,4-butynediol give no crystalline adducts. 2-Amino-ethanol, 1,8-terpin and (−)-menthol also gave no crystalline product even at the temperature in a refrigerator. The last two examples are remarkable as structurally related cyclohexanol itself gave a well defined adduct of m.p. 56∼57°C with the composition of 1 : 1 (N, found: 4.87; calcd. for 1 : 1-adduct: 4.98%). These findings seem to suggest that the formation of crystalline adduct is influenced by the steric environment around the hydroxyl group.

Experimental***

Preparation of the Adducts.—A mixture of diol (1 mol.) and acetone (equal volume) was added to a solution of dicyclohexylamine (2 mol.) in acetone (equal volume). The mixture was kept for several hours in a refrigerator to complete the crystallization. The crystals formed were filtered and recrystallized from acetone. The molar ratio 1 : 3 (triol : amine) was used in the cases of the preparation of the adducts with triols.

Sublimation under reduced pressure was found as an excellent method of purification of the adducts with diols.

Measurement of the Infrared Spectra.—The spectrometer used was a Hilger H 800. The spectra of the hydroxy compounds and the amines were measured by the method of liquid film. The spectra of the adducts were measured employing KBr-disk method.

Determination of the Molecular Weight.—*(1) Cryoscopic method.*

a) Adduct with ethylene glycol: 0.01385 g.
Benzene: 2.637 g.
$\Delta T=0.130$°C. Mol. wt., 206

b) Adduct with ethylene glycol: 0.03859 g.
Benzene: 2.637 g.
$\Delta T=0.378$°C. Mol. wt., 207

(2) Isothermal distillation method. — A Signer molecular weight apparatus as modified by Clark was used using benzophenone as the standard and acetone as the solvent.

a) Adduct with ethylene glycol: 0.02878 g.
Benzophenon: 0.01220 g.
Final volumes: standard solution, 0.65 ml.
adduct solution, 1.24 ml.
Mol. wt., 225

b) Adduct with 1,2,6-hexanetriol: 0.00905 g.
Benzophenone: 0.00836 g.
Final volumes: standard solution, 1.12 ml.
adduct solution, 1.04 ml.
Mol. wt., 214

c) Adduct with 1,4-di-(β-phenyl-α-hydroxyethyl)-benzene: 0.01196 g.
Benzophenone: 0.01449 g.
Final volumes: standard solution, 1.00 ml.
adduct solution, 0.92 ml.
Mol. wt., 240

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*** All melting points are not corrected.