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Stereospecific Syntheses and Acid Dissociations of 2,3-Diaminotetralins and 2,3-Diamino-*trans*-decalins[1]

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cis- and *trans*-2,3-Diaminotetralins and 2(*e*),3(*e*)-, 2(*e*),3(*a*)-, and 2(*a*),3(*a*)-diamino-*trans*-decalins were stereospecifically synthesized from 1,4-dihydronaphthalene and *trans*-Δ^2-octalin, respectively. The stepwise acid dissociation constants of the decalin derivatives were determined by potentiometric method and discussed in relation to their configurations.

In the course of investigations into steric effect on the chelate formation equilibria of complexane type ligands,[2,3] we required stereochemically pure samples of three kinds of 2,3-diamino-*trans*-perhydronaphthalenes. Since reasonable separation of the isomers was unlikely, we were obliged to synthesize each diamine separately *via* a stereospecific route, using a starting material of known stereochemistry. This paper deals with such routes and their applications to the synthesis of related *cis*- and *trans*-2,3-diamino-1,2,3,4-tetrahydronaphthalenes, as well as their proton dissociation behaviors in aqueous solutions.

*2,3-Diamino-*trans*-perhydronaphthalenes.* The three kinds of configurational isomers are denoted as *trans*-2(*a*),3(*a*)-,*cis*-2(*a*),3(*e*), and *trans*-2(*e*),3(*e*)-diamines. The sequences of their preparations are outlined in Scheme 1. Of the three routes, the first two are essentially the same as those reported by Swift and Swern.[4] The last one, however, required some modifications in order to control the number of inversions

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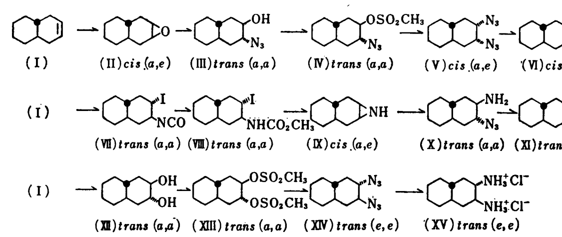
[1] Contribution No. 286 from the Department of Organic Synthesis, Kyushu University.

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

[3] Y. Yanagihara, T. Yano, H. Kobayashi, and K. Ueno, *ibid.*, **45**, 554 (1972).

[4] G. Swift and D. Swern, *J. Org. Chem.*, **32**, 511 (1967).



Scheme 1.

in the synthetic route. Our starting material for each synthesis was *trans*-octahydronaphthalene (I). Epoxidation of olefin (I) with perbenzoic acid gave *cis*-epoxide (II), which was ring-opened, with inversion, to *trans*-3(*a*)-azido-2(*a*)-ol(III) in a quantitative yield by the reaction with sodium azide in aqueous ethanol. Hydroxy function of the resulting azido-alcohol (III) was mesylated with methanesulfonyl chloride in pyridine to yield 3(*a*)-azido-*trans*-2(*a*)-perhydronaphthyl methanesulfonate (IV) in 86% yield. Sulfonate (IV) was treated with sodium azide in aqueous dimethylformamide to displace the methanesulfonate function, with inversion, to give oily *cis*-2(*e*), 3(*a*)-diazide (V) in 79% yield. It was then hydrogenated at room temperature over Adam's catalyst to yield the *cis*-diamine, which was immediately converted into *cis*-2(*e*),3(*a*)-diamino-*trans*-perhydronaphthalene dihydrochloride (VI) in 77% yield, melting above 250°C. Acetylation of the *cis*-diamine gave the bisacetyl derivative melting at 245—255°C.

On the other hand, iodine isocyanate, generated *in situ* from silver cyanate and iodine, was added olefin (I), and the resulting *trans*-iodoisocyanate (VII) was converted, without isolation, into *trans*-2(*a*)-iodo-3(*a*)-carbamate (VIII) in 32% yield. Highly purified carbamate (VIII) was ring-closed, with inversion, to *cis*-aziridine (IX) in 72% yield by warming with alcoholic potassium hydroxide. Aziridine (IX) was then converted into *trans*-2(*a*)-amino-3(*a*)-azide (X) in 72% yield by ring cleavage accompanied by inversion, with sodium azide in aqueous ethanol. Aminoazide (X) gave *trans*-2(*a*),3(*a*)-diamino-*trans*-perhydronaphthalene dihydrochloride (XI) in 27% yield by hydrogenation over Adam's catalyst at room temperature, followed by treatment with ethanolic hydrochloric acid. Dihydrochloride (XI) melted with decomposition above 200°C, while the bisacetyl derivative of the *trans*-diamine showed melting point at 245—250°C, which was very close to that of bisacetyl-*cis*-diamine. A mixed melting point test of both bisacetyl derivatives, however, showed considerable depression, mp 213—220°C.

trans-2(*e*),3(*e*)-Diamine was prepared through a sequence involving simultaneous two inversions in contrast to the sequences leading to the other two isomers, which involved successive two inversions *via* three-membered ring intermediates. Olefin (I) was oxidized with performic acid to *trans*-2(*a*),3(*a*)-diol (XII) in 42% yield, followed by mesylating with methanesulfonyl chloride in pyridine to afford *trans*-2(*a*),3(*a*)-bismethanesulfonate (XIII) in 54% yield. Bissulfonate (XIII) was then treated with sodium azide in aqueous dimethylformamide to displace both sulfonate functions at the same time, with inversions. Resulting 2(*e*),3(*e*)-diazide (XIV) was, without further purification, hydrogenated over Adam's catalyst at room temperature, followed by treatment with ethanolic hydrochloric acid to give *trans*-2(*e*),3(*e*)-diamino-*trans*-perhydronaphthalene dihydrochloride (XV) in 29% yield.

Table 1. Acid dissociation constants of 1,2-diamines

Diamine	pK_{a_1}	pK_{a_2}
(VI) (*a*, *e*)[a]	6.36±0.01	9.93±0.01
(XV) (*e*, *e*)[a]	6.68±0.01	10.08±0.01
(XI) (*a*, *a*)[a]	6.97±0.01	9.97±0.01
cis-Cyclohexane-1,2-diamine[b]	6.41	9.99
trans-Cyclohexane-1,2-diamine[b]	6.72	9.89
Ethylenediamine[b]	7.48	10.18
Propane-1,2-diamine[c]	7.13	10.00
dl-Butane-2,3-diamine[d]	6.91	10.00

a) Measured at 25.0±0.1°C and $\mu=0.10$ (KNO_3).
b) Measured at 20°C and $\mu=0.1$ (KCl), G. Schwarzenbach and R. Bauer, *Helv. Chim. Acta*, **39**, 722 (1956).
c) Measured at 25°C and $\mu=0.5$ (KNO_3), F. Basolo, R. K. Murmann, and Y. T. Chen, *J. Amer. Chem. Soc.*, **75**, 1478 (1953).
d) Measured at 25°C and $\mu=0.5$ (KNO_3), F. Basolo, Y. T. Chen, and R. K. Murmann, *ibid.*, **76**, 956 (1954).

The apparent pK_a values of the conjugate acids (VI), (XI), and (XV) were measured potentiometrically in water at 25°C under an ionic strength of $\mu=0.1$ (KNO_3). The obtained values are summarized in Table 1 along with those of some related diamine hydrochlorides.

At the first dissociation step, the mutual field effect between the vicinal di-cation seems to be predominant in affecting the pK_{a_1} values of the three conjugate acids, since the inductive effect is considered to be equal among such isomeric systems to a first approximation. As expected from the order of the distance between the vicinal di-cation,[5] the isomer which shows the highest pK_{a_1} value is assigned to be the *trans*-(*a*,*a*)-diamine. The difference in pK_{a_1} values of the remaining two is of a similar extent, as observed between *cis*- and *trans*-cyclohexanediamine, and may be rationalized by steric hindrance among the axial ammonium and the axial hydrogens on the same six-memberes ring.[6] If this is the case, the isomer of the lowest

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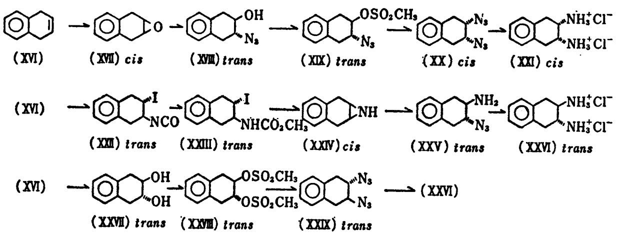
[5] Studies with Dreiding molecular models show that the nitrogen atoms in the *trans*-(*a*,*a*)-diamine are separated by approximately 3.7 Å, and those of *trans*-(*e*,*e*)- and *cis*-(*a*,*e*)-isomers by 2.8 Å.

[6] The steric effect might act as a direct steric repulsion between ammonium hydrogen and the adjacent axial hydrogens, or as a buttressing effect of the axial hydrogens upon the axial ammonium group, causing a much shorter distance and consequently an increased field effect between the vicinal ammonium group in the *cis*-(*a*,*e*)-diamine than that of the *trans*-(*e*,*e*)-homologue. Alternately, such congestion around the axial ammonium function causes steric hindrance preventing solvation by polar solvent molecules which, otherwise, would stabilize the charged site by dielectric shielding: G. Schwarzenbach and R. Bauer, *Helv. Chim. Acta*, **39**, 722 (1956). Other workers also recognized and increased acidity of protonated amines in overcrowded steric environments: T. Sasaki, S. Eguchi, and T. Kiriyama, This Bulletin, **44**, 3410 (1971).

pK_{a_1} should be assigned to the *cis*-(*a*,*e*)-homologue. Assignations of the three conformational isomers are consistent with the consequences considered from their respective synthetic routes. Of the two conjugate cations in the *cis*-(*a*,*e*)-isomer, the axial ammonium dissociates preferentially to the equatorial function, and the assignment is compatible with the fact that the pK_{a_1} values of axial conjugate acids are smaller than those of the corresponding equatorial ones.[7] It seems also ascribable to the 1,3-diaxial steric hindrance that the *trans*-(*a*,*a*)-diamine shows a much lower pK_{a_1} value than ethylene diamine, the value being rather close to that of *dl*-butane-2,3-diamine in which the ammonium group is under considerable steric hindrance of the methyl group in the *guache* position.

In the second acid dissociation constants pK_{a_2} we expected rather large differences among the three isomeric diamines, depending upon the relative easiness of forming an intramolecular hydrogen bonding between the ammonium and the vicinal amino group. However, differences in the observed pK_{a_2}'s are very small as shown in Table 1. Each IR spectrum of the diamines measured at high dilution exhibits a sharp peak at 3380—3385 cm^{-1} and a broad peak at 3300 cm^{-1}, which are ascribable to a free amino group. Similarity of the spectra of the diamines, as shown in Fig. 2, indicates that intramolecular hydrogen bonding on the *trans*-(*e*,*e*)-diamine, though stereochemically quite possible, is unlikely to be formed even in a nonpolar solvent such as tetrachloroethylene.[8] Thus, the absence of intramolecular hydrogen bonding in the three isomeric diamine mono-cations, may be partly responsible for the resemblance in their second dissociation constants. However, the cause for their rather similar pK_{a_2} values, which were determined in aqueous media and found to be contrary to ones expected from a stereochemical standpoint, can be rationalized only with additional experimental data such as an equilibrium study in aqueous organic solvents.



Scheme 2.

2,3-Diamino-1,2,3,4-tetrahydronaphthalenes. The reaction sequences shown in Scheme 1 were then applied to the preparation of vicinal diamines having a tetralin skeleton as outlined in Scheme 2. Dihydrochloride (XXVI) of the *trans* isomer obtained from 1,4-dihydronaphthalene (XVI) *via* the aziridine (XXIV), was identical with the diamine dihydrochloride obtained from the same starting material (XVI) *via* the *trans*-diazide (XXIX). Two possible configurations of the *trans* vicinal diamine would be readily equilibrated on the flexible tetralin skeleton, so that they cannot be isolated separately, whereas the vicinal diamine groups on the rigid *trans*-decalin framework retain their configurations, two *trans* diamino isomers (XI) and (XV) being individually isolated. This also provides an evidence for the simultaneous displacement of the vicinal two sulfonate functions with azide groups, with inversions.

It should be noted that in the route leading to *trans*-diamine (XXVI), aziridine (XXIV) could be obtained only from the extremely purified iodocarbamate (XXII), otherwise the carbamate gave only naphthalene.

Experimental

trans-Δ^2-Octalin(I),[9] 2,3-epoxy-*trans*-decalin(II),[9] 2(*a*),3(*a*)-dihydroxy-*trans*-decalin(XII),[10] 1,4-dihydronaphthalene (XVI),[10] 2,3-epoxytetralin(XVII),[11] and *trans*-2,3-dihydroxytetralin(XXVII)[12] were prepared according to literature. Melting and boiling points were not corrected. Infrared spectra were determined with JASCO DS-301 and DS-403G spectrophotometers. NMR spectra were recorded with a Varian A-60 and JOEL JNM-PS-100[13] in heavy water solutions using *t*-butanol as an internal reference (at 72 Hz downfield from TMS) unless otherwise stated.

*2(*a*)-Hydroxy-3(*a*)-azido-*trans*-decalin (III).* 2,3-Epoxy-*trans*-decalin(II) (14 g, 0.092 mol) was refluxed for 24 hr in 80% aqueous ethanol(200 ml) with sodium azide (7.4 g, 0.114 mol) and ammonium chloride (5.65 g, 0.114 mol). The reaction mixture was poured into water and extracted with ether. The ether layer was evaporated to give an oil which solidified gradually on cooling. Yield: 18.0 g, almost quantitative. Analytical sample was purified by sublimation under reduced pressure. Mp 36—38°C. IR: ν_{OH} 3310 cm^{-1}, ν_{N_3} 2120 cm^{-1}. Found: C, 62.14; H, 8.63; N, 20.69%. Calcd for $C_{10}H_{17}ON_3$: C, 61.59; H, 8.72; N, 21.54%.

*3(*a*)-Azido-2(*a*)-*trans*-decahydronaphthyl Methanesulfonate (IV).* Methanesulfonyl chloride (18 g, 0.158 mol) was gradually added to a solution of *trans*-azidohydrine(III) (18.0 g, 0.092 mol) in pyridine (100 ml) at 0—5°C with stirring for 3 hr. Stirring was continued for 1.5 hr without cooling. The reaction mixture was allowed to stand overnight at room temperature(14—25°C). The resulting solution was poured into water (1 liter) and the crystalline precipitate was recrystallized from methanol to give colorless needles(22 g, 86%). An analytical sample was purified by sublimation. Mp 56—58°C. IR: ν_{N_3} 2120 cm^{-1}, $\nu_{OSO_2CH_3}$ 800—1000 cm^{-1}. Found: C, 48.21; H, 6.97; N, 14.62%. Calcd for $C_{11}H_{19}N_3O_3S$: C, 48.35; H, 6.96;

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[7] J. Sicher, M. Tichý, F. Šipoš, M. Svoboda, and J. Jonáš, *Collection Czechoslov. Chem. Commun.*, **29**, 1561 (1964).

[8] The result is in line with the conclusion that in a series of monoprotonated diamines ($H_2N(CH_2)_nN^+H_3$) in acetonitrile, the intramolecular hydrogen bonding contributes very little to the increase of pK_a value of the diamines with $n=2$ or $n>5$. J. F. Coetzee and G. R. Padmanabjan, *J. Amer. Chem. Soc.*, **87**, 5005 (1965).

[9] W. S. Johnson, V. J. Bauer, J. L. Magrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *ibid.*, **83**, 606 (1961).

[10] H. B. Henbest, M. Smith, and A. Thomas, *J. Chem. Soc.*, **1958**, 3293.

[11] E. S. Cook and A. J. Hill, *J. Amer. Chem. Soc.*, **62**, 1995 (1961).

[12] R. Huisgen, E. Laschtuvka, I. Ugi, and A. Kammermeier, *Ann*, **630**, 128 (1960).

[13] Measured by Mr A. Kito at the Government Industrial Research Institute, Osaka, to whom the authors are very grateful.

N, 15.38%.

2(e),3(a)-Diamino-trans-*decalin Dihydrochloride (VI).* A mixture of the azidomethanesulfonate (IV) (35 g, 0.13 mol) and sodium azide (17 g, 0.26 mol) in 85% aqueous dimethylformamide (420 ml) was refluxed for 6 hr. The resulting solution was poured into water (1 l) and extracted with ether. Evaporation of the ethereal extract gave an oily diazide (23 g, 79%). Diazide (V) (23 g, 0.1 mol) was dissolved in absolute ethanol (150 ml) and hydrogenated in an autoclave, under 80 kg/cm^2 over Adam's catalyst (0.43 g) for 90 hr at room temperature. The resulting solution was acidfied with hydrochloric acid (100 ml) and the solvent was evaporated off. The residue was dissolved in water (200 ml) and washed with ether. The aqueous solution was treated with activated charcoal and evaporated off. The residual solid was recrystallized from water–ethanol to yield diamine dihydrochloride(19.3 g, 76.5%). Mp above 254°C. NMR(in D_2O):[14] 1.2—2.4 ppm(14H), 3.8—4.2 ppm(2H). Found: C, 49.66; H, 9.26; N, 11.62%. Calcd for $C_{10}H_{22}N_2Cl_2$: C, 49.79; H, 9.12; N, 11.62%. The bisacetyl derivative of (VI) had mp 246—250°C. Found: C, 66.60; H, 9.53; N, 10.94%. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.67; H, 9.52; N, 11.11%.

Methyl-2(a)-iodo-trans-*decalin-3(a)-carbamate (VIII).* *trans*-Δ^2-Octalin (I) (7 g, 0.05 mol) and iodine (12.7 g, 0.05 mol) were dissolved in dry ether (120 ml) at 0—5°C and silver cyanate[15] (12 g, 0.075 mol) was added in one portion with stirring. After continuous stirring for 2 hr, an additional silver cyanate (6 g) was added. The resulting light yellow mixture was then kept under stirring for further 15 hr with cooling at 0—5°C. It was filtered and the filtrate was evaporated to dryness. The residue, dissolved in absolute methanol (100 ml), was refluxed for 3 hr and kept standing overnight to give colorless needles (5.4 g, 32%), which were recrystallized from methanol. Mp 134.5°C. IR: ν_{NH} 3280 cm^{-1}, $\nu_{C=O}$ 1690 cm^{-1}. Found: C, 42.67; H, 6.11; N, 4.05%. Calcd for $C_{12}H_{20}NO_2I$: C, 42.73; H, 5.93; N, 4.15%.

2,3-Imino-trans-*decalin (IX).* A solution of potassium hydroxide (7 g) in water (15 ml) was added into a solution of the methylcarbamate (VIII) (8 g, 0.024 mol) in ethanol (60 ml). After being refluxed for 2 hr, the reaction mixture was poured into water (700 ml). The aqueous mixture was extracted with ether and the ethereal extract was evaporated off to give (IX) (2.6 g, 72%). An analytical sample was purified by sublimation. Mp 42—47°C. IR: ν_{NH} 3170 cm^{-1}. Found: C, 78.40; H, 11.06; N, 8.65% Calcd for $C_{10}H_{17}N$: C, 79.54; H, 11.26; N, 9.27%.

2(a)-Amino-3(a)-azido-trans-*decalin Hydrochloride (X).* A solution of (IX) (10 g, 0.07 mol), sodium azide (9.15 g, 0.14 mol), and ammonium chloride (7.56 g, 0.14 mol), in ethanol (160 ml) and water (40 ml) was refluxed for 24 hr, and then poured into water. The aqueous mixture was adjusted to be slightly alkaline and extracted with ether. The ethereal extract was evaporated off to give an oil (10.8 g, 84%) which was subjected to hydrochlorination to yield (X). Hydrochloride (X) was recrystallized from ethanol–ether for an analytical sample. Mp 190—197°C. IR: (free HCl) ν_{NH_2} 3320 cm^{-1}, ν_{N_3} 2120 cm^{-1}. Found: C, 52.11; H, 8.27; N, 24.04%. Calcd for $C_{10}H_{19}N_4Cl$: C, 52.06; H, 8.24; N, 24.30%.

2(a)-3(a)-Diamino-trans-*decaline Dihydrochloride (XI).* Aminoazide compound (X) (10.8 g, 0.055 mol) was hydrogenated in a similar manner to that described for VI. Yield, 5.2 g (39%). Mp 197—230°C (decomp.). NMR (in D_2O):[14] 1.2—2.2 ppm (14H), 4.00 ppm (2H). Found: C, 47.55; H, 9.15; N, 11.03%. Calcd for $C_{10}H_{22}N_2Cl_2\cdot 0.7H_2O$: C, 47.30; H, 9.24; N, 11.05%.

The bisacetyl derivative of XI had mp 245—250°C. Found: C, 66.37; H, 9.40; N, 10.86%. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.67; H, 9.52; N, 11.11%.

2(a),3(a)-Dihydroxy-trans-*decalin(XII).* Into a mixture of 99% formic acid(110 g) and 30% hydrogen peroxide (13 g), was gradually added *trans*-Δ^2-octalin (I) (13.6 g, 0.1 mol) at 40—45°C with stirring and the stirring was continued for 9 hr. After the remaining performic acid was decomposed with sodium sulfite, formic acid was removed by evaporation and the residue was refluxed together with ethanol (50 ml) and sodium hydroxide (15 g) in water (30 ml) for 5 hr. The resulting mixture was acidified and again evaporated under reduced pressure. The residual precipitate was washed with water and recrystallized from benzene. Yield was 15.7 g. Mp 164—165.5°C. (lit,[9] 163—164°C). IR: ν_{OH} 3280 cm^{-1}. Found: C, 70.62; H, 10.56%. Calcd for $C_{10}H_{18}O_2$: C, 70.58; H, 10.58%.

trans-*Decahydro-2(a),3(a)-naphthalene Bismethanesulfonate (XIII)* was prepared from XII (12.8 g, 0.076 mol) in a similar manner to that for IV. Methanesulfonate (XIII) was purified by repeated recrystallization from methanol. Yield, 23 g (93%). Mp 129—130°C. IR: $\nu_{OSO_2CH_3}$ 800—1000 cm^{-1}. Found: C, 43.85; H, 6.86%. Calcd for $C_{12}H_{22}O_6S_2$: C, 44.17; H, 6.75%.

2(e),3(e)-Diamino-trans-*decalin Dihydrochloride (XV).* Methanesulfonate (XIII) (19.7 g, 0.06 mol) dissolved in 85% aqueous dimethylformamide (210 ml) was refluxed for 5.5 hr together with sodium azide (16.0 g, 0.25 mol). Reaction mixture was treated subsequently in a similar manner to that for VI. The oily diazidodecalin was separated as a fraction soluble in petroleum ether (100 ml, boiling region 38—43°C). Yield, 8.6 g (64%). Without further purification, the product (XIV) was hydrogenated over Adam's catalyst in absolute ethanol (100 ml) at room temperature under 100 Kg/cm^2 for 72 hr. The resulting ethanol solution was acidified with hydrochloric acid, ethanol being removed by evaporation. The residue was dissolved in water and washed with ether. The final aqueous solution was evaporated and the residue was recrystallized from water–ethanol to yield diamine dihydrochloride(XV) (2.7 g, 28.5%). Mp 265—270°C. NMR(in D_2O):[14] 1.2—2.4 ppm (14H), 3.6—3.8 ppm (2H). Found: C, 49.44; H, 9.10; N, 11.20%. Calcd for $C_{10}H_{22}N_2Cl_2$: C, 49.79; H, 9.10; N, 11.62%.

The bisacetyl derivative of XV had mp above 290°C. Found: C, 66.49; H, 9.55; N, 11.08%. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.67; H, 9.52; N, 11.11%.

trans-*3-Azido-2-hydroxytetralin (XVIII).* 2,3-Epoxytetralin (XVII) (27.3 g, 0.187 mol) dissolved in 80% aqueous ethanol (380 ml), was refluxed for 24 hr together with sodium azide (15 g, 0.23 mol) and ammonium chloride (12.3 g, 0.23 mol). The reaction mixture was poured into water (1 liter) and a cystalline precipitate was recrystallized from benzene–petroleum ether. The yield was nearly quantitative. Mp 66—67°C. IR: ν_{OH} 3300 cm^{-1}, ν_{N_3} 2124 cm^{-1}. Found: C, 63.58; H, 5.83; N, 22.08%. Calcd for $C_{10}H_{11}N_2O$: C, 63.49; H, 5.82; N, 22.02%.

trans-*3-Azido-2-tetrahydronaphthyl Methanesulfonate (XIX).* *trans*-Azidohydrin (XVIII) (40.8 g, 0.217 mol), dissolved in pyridine (155 ml) was treated with methanesulfonyl chloride in a similar manner to that for III. The yield was nearly quantitative. An analytical sample was recrystallized from methanol. Mp 76—76.5°C. IR: ν_{N_3} 2120 cm^{-1}, $\nu_{OSO_2CH_3}$

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[14] The proton signal in D_2O was used as a reference and set at 5.0 ppm downfield from TMS.

[15] R. G. Neville and J. J. McGee, "Inorganic Syntheses" Vol. 8, p. 23 (1966) McGraw-Hill, New York.

820—980 cm^{-1}. Found: C, 49.14; H, 4.94; N, 15.42%. Calcd for $C_{11}H_{13}N_3O_3S$: C, 49.43; H, 4.87; N, 15.73%.

cis-*2,3-Diazidotetralin (XX).* A mixture of azidomethanesulfonate (XIX) (17 g, 0.064 mol) and sodium azide (8.5 g, 0.13 mol) was treated in a similar manner to that for V, to give the oily product (XX) (7.5 g, 54.5%). IR: $\nu_{\mathrm{N_3}}$ 2120 cm^{-1}.

cis-*2,3-Diaminotetralin Dihydrochloride (XXI).* Diazide (XX) (7.5 g, 0.035 mol) in absolute ethanol (100 ml) was hydrogenated in a similar manner to that for VI. Dry hydrogen chloride was passed into the resulting ethanol solution at 0—5°C to give a colorless precipitate, which was recrystallized from water–ethanol to yield diamine dihydrochloride (XXI) (7 g, 85%). Mp 243°C. NMR(in D_2O): 2.05 ppm (4H), 2.97 ppm (2H), 6.06 ppm (4H). Found: C, 51.17; H, 6.93; N, 11.73; Cl, 29.4%. Calcd for $C_{10}H_{16}N_2Cl_2$: C, 51.06; H, 6.83; N, 11.90; Cl, 30.2%.

trans-*Methyl-2-iodo-3-tetrahydronaphthylcarbamate (XXIII).* 1,4-Dihydronaphthalene (XVII) (13 g, 0.1 mol) and iodine (25.4 g, 0.1 mol) were dissolved in dry ether (170 ml) at 0—5°C. To this solution was added silver cyanate (15 g, 0.1 mol) in one portion. The mixture was stirred for 24 hr and filtered. The filtrate was evaporated to dryness. The solid residue was dissolved in absolute methanol (300 ml), and refluxed for 3 hr. The solution was treated with sodium thiosulfate in order to remove the remaining iodine and then evaporated to about 100 ml. The concentrated solution was poured into water (3 l) to give precipitate which was recrystallized from methanol. Mp 138—140°C. IR: ν_{NH} 3320 cm^{-1}, $\nu_{\mathrm{C=O}}$ 1700 cm^{-1}. Found: C, 43.23; H, 4.33; N, 4.12%. Calcd for $C_{12}H_{14}NO_2I$: C, 43.50; H, 4.23; N, 4.23%.

cis-*2,3-Iminotetralin (XXIV).* A solution of potassium hydroxide (18 g) in water (35 ml) was added into a solution of methanesulufonate (XXIII) (20 g, 0.06 mol) in ethanol (170 ml). After being refluxed for 2 hr, the reaction mixture was concentrated to about 100 ml and poured into water (300 ml). The aqueous mixture was extracted with ether and the ethereal extract was evaporated and distilled to give an oil (5 g, 57%) boiling at 70—80°C/0.17 mmHg, which solidified immediately. Mp 72°C. IR: ν_{NH} 3238 cm^{-1}. Found: C, 81.81; H, 7.52; N, 9.12%. Calcd for $C_{10}H_{11}N$: C, 82.75; H, 7.59; N, 9.66%.

trans-*3-Azido-2-aminoteralin Hydroazide (XXV).* A mixture of imine (XXIV) (5 g, 0.036 mol), sodium azide (11.5 g, 0.174 mol) and ammonium chloride (9.5 g, 0.147 mol) in 80% aqueous ethanol (220 ml) was refluxed for 17 hr, and then poured into water. A solid product was obtained by extraction of the aqueous mixture with ether, followed by evaporation to dryness. Recrystallization from methanol gave the product melting at 88°C. Yield, 5.5 g (68%). IR: $\nu_{\mathrm{N_3}}$ 2040 and 2140 cm^{-1}, (free HN_3) $\nu_{\mathrm{N_3}}$ 2110 cm^{-1}, $\nu_{\mathrm{NH_2}}$ 3320 and 3380 cm^{-1}. Found: C, 52.21; H, 5.70; N, 42.36%. Calcd for $C_{10}H_{13}N_7$: C, 51.94; H, 5.63; N, 42.42%.

trans-*2,3-Diaminoteralin Dihydrochloride (XXVI). trans*-3-Azido-2-aminotetralin (XXV) (4.5 g, 0.025 mol) was hydrogenated and was worked up in a similar manner to that for *cis*-diamine (XXI). Yield, 3.2 g (57%). Mp 270°C. NMR(in D_2O): 2.00 ppm (4H), 2.75 ppm (2H), and 6.07 ppm (4H). Found: C, 51.11; H, 6.93; N, 11.67%. Calcd for $C_{10}H_{16}N_2Cl_2$: C, 51.06; H, 6.83; N, 11.90%.

*1,2,3,4-Tetrahydro-*trans*-2,3-naphthalene Bismethanesulfonate (XXVIII). trans*-Glycol (XXVII) (21.1 g, 0.13 mol) was mesylated in a similar manner to that for III and XIII, to give the bismethanesulfonate (XXVIII) (39.4 g, 95%) which was recrystallized from methanol. Mp 138°C. IR: $\nu_{\mathrm{OSO_2CH_3}}$ 825—1000 cm^{-1}. Found: C, 44.65; H, 5.05%. Calcd for $C_{12}H_{16}O_7S_2$: C, 44.95; H, 5.02%.

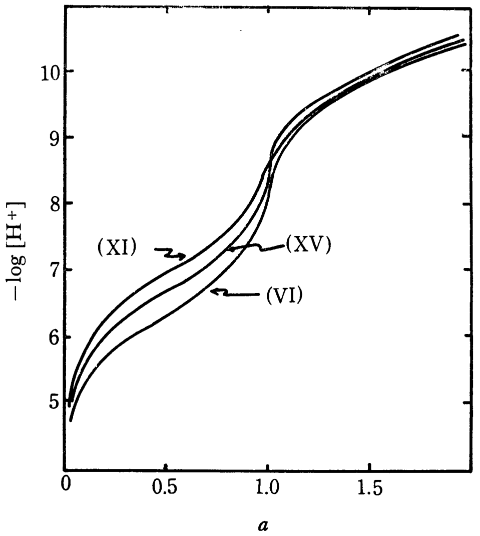

Fig. 1. Titration curves of diaminodecalins. Concn of ligands: 2×10^{-3} M.

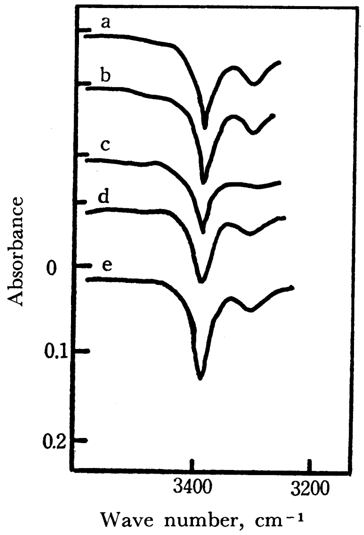

Fig. 2. N-H streching vibration of diamines in dilute C_2Cl_4 solutions (1×10^{-3} M).

a) *cis*-2(*a*),3(*e*)-diamine, b) *trans*-2(*e*),3(*e*)-diamine
c) *trans*-2(*a*),3(*a*)-diamine, d) *cis*-diaminotetralin
e) *trans*-diaminotetralin

trans-*2,3-Diazidotetralin (XXIX).* Bismethanesulfonate (7.4 g, 0.023 mol) was refluxed in a mixture of dimethylformamide (60 ml) and water (10 ml) for 5 hr together with sodium azide (5.1 g, 0.091 mol), to afford diazide (XXIX) (2 g, 40%), which was recrystallized from methanol. Mp 55°C. IR: $\nu_{\mathrm{N_3}}$ 2120 cm^{-1}. Found: C, 56.49; H, 4.75; N, 39.20%. Calcd for $C_{10}H_{10}N_6$: C, 56.07; H, 4.67; N, 39.25%. Hydrogenation of the diazide (6 g, 0.03 mol) followed by subsequent working up yielded diaminodihydrochloride (XXVI) (4.5 g, 68%).

Determination of Acid Dissociation Constants. The potentiometric measurements were carried out at 25°C and under a constant ionic strength ($\mu=0.100$) with potassium nitrate, using a Horiba pH meter model P equipped with 1026 glass and 2010 calomel electrodes. The pH-meter reading was calibrated under the same titration conditions by referring to the hydrogen ion concentration calculated from the acetic acid–potassium hydroxide titration system.

Calculation. The titration curves of diamine dihydrochlorides are shown in Fig. 1, from which the dissociation constants were calculated according to the standard procedure by Schwarzenbach *et al.*[16] as typical dibasic acids. The result for the present diamines are summarized in Table 1 along with the values of related compounds.

Infrared Spectra in Highly Diluted Solutions. Sample solutions were prepared as follows. To a solution of 20 mg of diamine hydrochloride in 0.5 ml of water were added three drops of 50% aqueous potassium hydroxide. The resulting alkaline solution was extracted with two 1.5 ml portions of tetrachloroethylene which had been purified by passing through a column of activated alumina. The combined extract was dried over anhydrous sodium sulfate. IR spectra were measured with matched pairs of 1.0, 5.0, and 10.0 cm quartz cells using a JASCO-DS-403G spectrophotometer at room temperature. Concentrations of the solutions were in the range 2×10^{-2}—6×10^{-4} M, where intermolecular association of these compounds can be neglected. The results are shown in Fig. 2.

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16) G. Schwarzenbach, A. Willi, and R. O. Bach, *Helv. Chim. Acta*, **30**, 1303 (1947).