[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, HOKKAIDO UNIVERSITY]

The Ultraviolet Absorption Spectra of Stereoisomeric 1,2,3,4,9,10,4a,9a-Octahydroacridines and Related Compounds[1]

BY TADASHI MASAMUNE

RECEIVED JANUARY 21, 1957

The near ultraviolet absorption spectra of *cis*- and *trans*-1,2,3,4,9,10,4a,9a-octahydroacridines and related stereoisomeric bases were measured in isoöctane, ether and alcohol. The absorption maximum of each *cis* isomer was situated at a longer wave length than that of the corresponding *trans* isomer in isoöctane and in ether; this shift was especially remarkable in alcohol. The solvent effect of alcohol on simple derivatives of aniline was examined and was found to be mainly attributable to the formation of hydrogen bonding between amine and alcohol, which depended upon the strength of the basicity and upon their steric configuration. This explanation was applied to the absorption spectra of four pairs of stereoisomeric tricyclic bases with success, it being emphasized that the formation of hydrogen bonding may be strongly influenced by the geometry of the bases. The ultraviolet absorption spectra of these bases were furthermore examined in 0.1 *N* hydrochloric acid and a characteristic peak was found to exist near 320 mμ.

Introduction

During the course of an investigation of the dehydrogenation of hydrogenated acridines,[2] it became desirable to study their ultraviolet absorption spectra in order to identify small amounts of dehydrogenated products. It was found that the absorption maximum of *cis*-1,2,3,4,9,10,4a,9a-octahydroacridine was situated at a longer wave length than that of the corresponding *trans*-base in alcohol. In the present work, the absorption spectra of those compounds were measured in isoöctane or in ether. The difference of absorption spectra of the stereoisomers in alcohol is believed principally due to the difference in solvation.

There are available many reports on the relation between geometrical form and absorption spectra of organic compounds.[3] However, no attention has been paid to the problem of whether or not the solvent effect on absorption spectra is affected by a difference in the molecular configuration of the solute. In the present article it will be shown that such a solvent effect does exist. For example, *trans*-tetrahydro-2,3-trimethylenequinoline exhibits a distinct blue shift in alcohol,[4] while the corresponding *cis* isomer shows a red shift in the same medium. A similar difference in solvation was observed in several other cases such as isomers of octahydroacridine and related compounds.

Experiments and Results

Materials.—The following stereoisomeric tricyclic bases were prepared by procedures described in the literature. Solid compounds were recrystallized to constant melting point from the solvents indicated and liquids were freshly redistilled before use: *cis*-hexahydrocarbazole,[5] m.p. 98–99° (alcohol); *trans*-hexahydrocarbazole,[5] m.p. 128–130° (alcohol); *cis*-octahydroacridine,[6] m.p. 71–72° (benzine); *trans*-octahydroacridine, m.p. 80–81° (petroleum ether); *cis*-tetrahydro-2,3-trimethylenequinoline,[7] oil, benzoyl derivative, m.p. 159–160° (acetone); *trans*-tetrahydro-2,3-trimethylenequinoline,[8] m.p. 66–68° (petroleum ether); *cis*-tetrahydro-2,3-pentamethylenequinoline,[8] oil, benzoyl derivative, m.p. 145–146° (alcohol); *trans*-tetrahydro-2,3-pentamethylenequinoline,[8] m.p. 59–60° (petroleum ether).

Ultraviolet absorption measurements were made using a Beckman quartz spectrophotometer, model DU; the following four solvents were used: ethanol, ether, isoöctane (dried over phosphorus pentoxide) and 0.1 *N* hydrochloric acid. The spectrum was examined at 0.5 mμ intervals near maximum and at 3 mμ intervals in another region of 215 to 350 mμ.

Basicity measurements were carried out at 15° according to the method of Thomson[9]: that is, because of the low solubility of the bases in water, solutions in 50% aqueous ethyl alcohol were used, and in view of uncertainty as to the value of K_w in those alcoholic solutions, the result was expressed as pK_a for the conjugated acids (calculated by means of the simple Henderson equation $pK_a = pH + (\text{salt})/(\text{base})$. Solutions were prepared as follows: in "50% alcohol" by dissolving *a* g. of the base in rather less than 10 cc. of ethanol, adding *b* cc. of 0.113 *N* aqueous

a	*p*H	*b*	pK_a
Tetrahydroquinoline			
0.0276	4.60	1.05	4.72
.0272	4.60	1.05	4.73
.0311	4.70	1.05	4.71
.0385	4.80	1.05	4.65
		Mean	4.70
trans-Tetrahydro-2,3-trimethylenequinoline			
0.0285	4.17	1.00	4.50
.0400	4.45	1.00	4.43
		Mean	4.47
trans-Octahydroacridine			
0.0278	3.95	1.00	4.45
.0339	4.16	1.00	4.38
.0458	4.40	1.00	4.33
		Mean	4.39
trans-Tetrahydro-2,3-pentamethylenequinoline			
0.0299	4.06	1.05	4.64
.0403	4.46	1.05	4.62
		Mean	4.63
trans-Hexahydrocarbazole			
0.0325	4.18	1.25	4.66
.0290	4.39	1.00	4.70
.0351	4.50	1.00	4.60
		Mean	4.66

a	*p*H	*b*	pK_a
Dihydroindole			
0.0204	4.58	1.05	4.92
.0231	4.68	1.05	4.88
		Mean	4.90
cis-Tetrahydro-2,3-trimethylenequinoline			
0.0344	4.32	1.00	4.44
.0288	4.06	1.00	4.39
.0421	4.58	1.00	4.52
		Mean	4.45
cis-Octahydroacridine			
0.0528	4.19	1.00	4.02
.0352	3.94	1.00	4.12
.0318	3.86	1.00	4.09
.0317	3.83	1.00	4.06
		Mean	4.08
cis-Tetrahydro-2,3-pentamethylenequinoline			
0.0323	4.11	1.05	4.55
.0401	4.27	1.05	4.47
		Mean	4.51
cis-Hexahydrocarbazole			
0.0380	4.63	1.25	4.97
.0290	4.21	1.25	4.93
.0318	4.63	1.00	4.83
.0264	4.51	1.00	4.96
.0298	4.59	1.05	4.93
		Mean	4.92

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[1] Part X of "The Condensed Polynuclear Perhydro-Compounds Containing Nitrogen"; Part IX, T. Masamune, *Bull. Chem. Soc. Japan*, in press.

[2] T. Masamune and G. Homma, *J. Chem. Soc. Japan*, **77**, 1766 (1956).

[3] For excellent and comprehensive reviews see E. A. Braude in "Progress in Stereochemistry," ed. W. Klyne, Vol. I, Butterworth's Scientific Publications, London, 1954, p. 126.

[4] The shifts are with reference to isoöctane.

[5] J. Gurney, W. H. Perkin and S. G. P. Plant, *J. Chem. Soc.*, 2676 (1927).

[6] W. H. Perkin and S. G. P. Plant, *ibid.*, 2583 (1928); 438 (1926).

[7] W. H. Perkin and S. G. P. Plant, *ibid.*, 638 (1928).

[8] S. G. P. Plant and R. J. Rosser, *ibid.*, 1840 (1930).

[9] G. Thomson, *ibid.*, 1113 (1946).

TABLE I

NEAR ULTRAVIOLET ABSORPTION SPECTRA OF CYCLIC BASES IN VARIOUS SOLVENTS

Compound	Absorption maximum (mμ) and intensity (ε)[a]						
	Isoöctane	Ether	Alcohol	$\Delta\lambda_{eth}$	$\Delta\lambda_{alc}$	$\Delta\lambda_{sol}$	$\Delta\lambda_{iso}$
Dihydroindole	298 (2500)	302 (2610)	290.5 (2300)	4.0	−7.5	−11.5	
Tetrahydroquinoline	301 (2350)	303.5 (2650)	300 (2120)	2.5	−1.0	−3.5	
trans-Tetrahydro-2,3-trimethylenequinoline	298.5 (2320)	300 (2420)	295.5 (1980)	1.5	−3.0	−4.5	−8.5
cis-Tetrahydro-2,3-trimethylenequinoline	300 (2800)	303.5 (2380)	304 (1750)	3.5	4.0	−0.5	
trans-Octahydroacridine	300.5 (2050)	302.5 (2910)	300.5 (2100)	2.0	0.0	−2.0	−3.5
cis-Octahydroacridine	302 (2650)	304.5 (3580)	304 (2300)	2.5	2.0	−0.5	
trans-Tetrahydro-2,3-pentamethylenequinoline	301.5 (2460)	303 (2460)	300.5 (2170)	1.5	−1.0	−2.5	−3.5
cis-Tetrahydro-2,3-pentamethylenequinoline	303 (4540)	304 (2390)	304 (2690)	1.0	1.0	0.0	
trans-Hexahydrocarbazole	292.5 (2700)	293 (2920)	286.5 (1930)	0.5	−6.0	−6.5	−7.5
cis-Hexahydrocarbazole	295.5 (2970)	297.5 (3000)	293 (2200)	2.0	−2.5	−4.5	

[a] The figures in parentheses refer to molecular extinction coefficients.

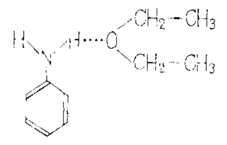
hydrochloric acid, then adding (12.5 − *a*) cc. of distilled water and making the volume up to 25 cc. with ethanol in a standard flask.

Results.—The values of λ_{max}, $\Delta\lambda_{ether}$ or $\Delta\lambda_{alc}$ (displacement of the λ_{max} in alcohol or ether relative to that in isoöctane) and $\Delta\lambda_{iso}$ (difference of λ_{max} between *cis* and *trans* isomers) of the near ultraviolet absorption spectra (Doub's "secondary" band)[10] of all the compounds included in this study are shown in Table I with data of their ϵ_{max}. The λ_{max} was estimated with reference to the intensity of absorption maximum, as λ_{max} was most easily measured and most often recorded to evaluate the solvent effect, which will be discussed in the following section. On the other hand, the values of λ_{max} and ϵ_{max} of absorption spectra of those bases in 0.1 *N* hydrochloric acid are given in Table III with basicity.

Discussion

The experimental results given in Table I may be summarized under the following two points. (1) The near ultraviolet absorption band of each *cis* compound of four pairs of stereoisomeric tricyclic bases was situated at a longer wave length than that of the corresponding *trans* compound. This red shift of the absorption maximum of each *cis* compound was observed in isoöctane and in ether; the effect was especially remarkable in alcohol. (2) In either *cis* or *trans* compounds, the absorption curve of each base in ether was found to be displaced always toward the visible side in isoöctane ($\Delta\lambda_{ether}$ positive). On the other hand, anomalous displacements were found in alcohol. In the case of *trans* isomers the absorption maximum shifted toward the shorter wave length ($\Delta\lambda_{alc}$ negative) or remained unchanged, while in the *cis* isomers the shift occurred toward the longer wave length side ($\Delta\lambda_{alc}$ positive), the only exception being *cis* hexahydrocarbazole. It is to be noted, however, that the blue shift of the *cis* compound of the latter was much less pronounced than that of the *trans* isomer.

The Solvent Effect on Near Ultraviolet Absorption Spectra.—Several papers,[11–13] have recently appeared in which solvent effects on organic spectra are correlated with various properties of the solute and the solvent. For example, Coggeshall and Lang[14] in dealing with the spectra of phenols have discussed effects due to the dipole–dipole interaction, to hydrogen bonding and to the polarization effect between solvent and solute. From among the above three effects Nagakura and Baba[15] directed special attention to the hydrogen bonding in explaining the shift of near ultraviolet absorption spectra of aniline in solutions. They observed that the solvent effect of ether upon the spectra was unusually large when compared with that in hexane. Their explanation of this abnormal behavior is as follows: On the formation of hydrogen bonds[16] shown in diagram (I), semi-ionic structures with the positive charge at the N atom come to have extra energies of stabilization.[17,18] Consequently the degree of electron migration from the N atom to the benzene ring increases, producing an abnormal red shift.



(I)

The red shifts of absorption ($\Delta\lambda_{ether}$ positive) in ether of all compounds examined in the present work (see Tables I and II) are found to be essentially the same as the results of Nagakura and Baba. This suggests that the observed shifts[19] for these compounds are due to the hydrogen bonding between the H atom of the imino group of the solute and the O atom of the solvent.

The spectroscopic behavior in alcohol is different from that in ether. In contrast to ethereal solutions, two types of hydrogen bonds are believed to be formed between amine and alcohol. One is formed between the H atom of the imino group and the O atom of alcohol, while the other is

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[10] L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

[11] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002, 1006 (1954).

[12] L. G. S. Brooker, G. H. Keyes, R. G. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt and F. L. White, THIS JOURNAL, **73**, 5332 (1951); L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, *ibid.*, **73**, 5350 (1951).

[13] H. E. Ungnade, *ibid.*, **75**, 432 (1953).

[14] N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

[15] S. Nagakura and H. Baba, *ibid.*, **74**, 5693 (1952).

[16] M. Tsuboi, *J. Chem. Soc. Japan*, **72**, 146 (1951); H. Tsubomura, *ibid.*, **73**, 841, 926 (1952).

[17] F. A. Matsen, THIS JOURNAL, **72**, 5243 (1950); C. Curran and G. K. Estok, *ibid.*, **72**, 4575 (1950). See also H. Baba, *Monogr. Res. Inst. Appl. Elec. Hokkaido Univ.*, **4**, 61 (1954).

[18] B. M. Wepster, *Rec. trav. chim.*, **72**, 661 (1953).

[19] Spectral shifts are measured by taking dilute solution of isooctane as the standard. No association of the solute appears to play an important role, since extremely diluted solution with 0.0001 *M* of the solute was employed in the present work.

TABLE II

NEAR ULTRAVIOLET ABSORPTION SPECTRA OF SIMPLE DERIVATIVES OF ANILINE IN VARIOUS SOLVENTS

Compound	Absorption maxima in solvent (mμ) Isoöctane	Ether	$\Delta\lambda_{eth}$	Alcohol	$\Delta\lambda_{alc}$	$\Delta\lambda_{sol}$	Basicity pK_a[a]
	287.5						
Aniline	284	290	—	286	—	−4.0	4.62
o-Toluidine	285	289	4.0	285.5	0.5	−3.5	4.39
m-Toluidine	288	292	4.0	287.5	−0.5	−4.5	4.69
p-Toluidine	294	296	2.0	290.5	−3.5	−5.5	5.12
3,4-Dimethylaniline	292	296	4.0	287	−5.0	−9.0	[b]
Methylaniline	294.5	297	2.5	295.5	1.0	−1.5	4.85
Ethylaniline	294.5	296	1.5	295.5	1.0	−0.5	5.11
Dimethylaniline	297.5	298.5	1.0	297.5	0	−1.0	5.06
o-Methyldimethylaniline	No max.	No max.	—	No max.	—	—	5.86

[a] These values were measured at 25° in aqueous solution by N. F. Hall and M. R. Sprinkle, THIS JOURNAL, **54**, 3469 (1932). [b] This value has never been measured, but the base is easily supposed to be stronger in basicity than *p*-toluidine on the basis of induction and resonance.

between the N atom of amine and the H atom of hydroxyl group. Solvent effects associated with the former are expected to produce the shift toward red the same way as in ethereal solutions. The situation becomes just the opposite in the latter case. With the formation of the latter type of hydrogen bond, the lone-pair electrons at the nitrogen atom will become displaced toward the hydrogen atom of alcohol. This displacement would increase the effective electron affinity of the nitrogen atom. Consequently, the magnitude of electron migration from the nitrogen atom into the benzene ring decreases, thus resulting in the blue shift of absorption maximum.

There are available several examples[20] which show the displacement of absorption spectra due to the hydrogen bonding of the latter type. Furthermore, it is known[21] that the solvent effect of this type is strengthened with increasing basicity of amines, if there is no steric hindrance; that is, excepting the cases when both the amino and hydroxyl groups cannot approach each other.

In order to obtain a clearer view on the relation of basicity and steric hindrance, the near ultraviolet absorption spectra of various simple derivatives of aniline were measured in isoöctane and in alcohol. The results obtained are given in Table II together with data on their basicity. In aromatic primary amines, which were supposed not to suffer from the steric hindrance, the degree of the displacement toward shorter wave lengths became greater with increasing basicity. This tendency will be seen at a glance at the values of $\Delta\lambda_{alc}$ or more clearly at those of $\Delta\lambda_{sol}$. Contrary to the above, the shifts toward the visible are produced in secondary amines. Moreover, no change of absorption maxima of tertiary amines occurs with variation of solvent ($\Delta\lambda_{alc}$ null).

The striking differences observed between the primary and tertiary (or secondary) amines might be explained as follows. The energy of the hydrogen bond is markedly less than the usual bond energy. Consequently, the existence of methyl groups on the N atom more strongly inhibits the formation of hydrogen bond with the use of the nitrogen atom concerned.

Further support of the above view may be found in the behavior of methylaniline, dihydroindole and tetrahydroquinoline given in Tables I and II. The blue shift of the absorption maximum in alcohol relative to that in isoöctane increases in the order of methylaniline, tetrahydroquinoline and dihydroindole. This order agrees with the order of decrease in steric hindrance of methylene groups. As was elaborated by Arnold[22] and others[23] the methylene group in five-membered ring offers less steric hindrance than that in a six-membered ring, while the latter offers less than that in an aliphatic normal chain.

The Influence of Conformation of Tricyclic Bases on their Near Ultraviolet Absorption Spectra.—Attempts were made to consider conformations of four pairs of stereoisomeric tricyclic bases and to explain why the near ultraviolet absorption spectrum of the *cis* compound should produce a smaller blue shift in alcohol as compared with that in isoöctane than that of the corresponding *trans* isomer ($\Delta\lambda_{alc}$ of *cis*-base − $\Delta\lambda_{alc}$ of *trans*-base, positive). A glance at the results given in Table I and the strength of basicity given in Table II will show for these displacements that there is no relationship with the strength of basicity. These shifts, therefore, have to be interpreted from the viewpoint of stereochemistry. As an example, the conformations of octahydroacridine will be discussed in the following.

Conformations of Octahydroacridine.—Tetrahydroquinoline is regarded as an analog of tetralin with substitution of nitrogen for carbon at position 1 and consequently with only slight distortion of the ring. Arguments similar to those given in the case of tetralin by Barton[24] and others[25] may, therefore, be applicable to derivatives of tetrahydroquinoline. Since 1,2,3,4,9,10,4a,9a-octahydroacridine is regarded as a 2,3-tetramethylene derivative of tetrahydroquinoline, its *trans* isomer may be assigned a conformation with the tetra-

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[20] G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955); T. Kubota, *J. Pharm. Soc. Japan*, **74**, 831 (1954).

[21] M. Tsuboi, *J. Japan. Chem.*, **7**, 611 (1953).

[22] R. T. Arnold and P. N. Craig, THIS JOURNAL, **72**, 2728 (1950); R. T. Arnold and J. Richter, *ibid.*, **70**, 3505 (1948); R. T. Arnold and P. N. Craig, *ibid.*, **70**, 2791 (1948); R. T. Arnold and E. Rondestvedt, *ibid.*, **68**, 2176 (1946); **67**, 1265 (1945).

[23] R. Adams and D. C. Blomstrom, *ibid.*, **75**, 2375 (1955); M. Orchin and C. Golumbic, *ibid.*, **71**, 4151 (1951).

[24] D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chemistry & Industry*, 21 (1954).

[25] E. J. Corey and R. A. Sneen, THIS JOURNAL, **77**, 2505 (1955).

methylene group equatorial in positions 2 and 3 of tetrahydroquinoline. A conformation with both the substituents axial can be excluded by steric considerations. There may, moreover, be considered two conformations concerning the nitrogen atom, as represented in diagrams II and III, respectively, one having the lone-pair electrons in the quasi-axial position and the other in quasi-equatorial. In contrast to piperidine analogs in which the latter is considered to exist predominantly,[26] it is assumed that tetrahydroquinoline has another conformation (the former type) with the lone-pair electrons in quasi-axial position. There is an evidence for the above assumption: on account of the overlap between the π-orbits of the benzene ring and the p-orbital of the nitrogen atom, the structure with the electrons in quasi-axial position should be stabilized. Further support may be found in the existence of the "secondary" absorption band of octahydroacridine and other aromatic amines treated in this study, in the decrease in basicity as compared with aliphatic amines, and in also several chemical reactions.[27]

Two conformations are possible for *cis*-octahydroacridine, as shown in diagrams IV and V, since those having the lone-pair electrons in quasi-axial position are excluded from consideration. In conformation IV, the methylene group at C_3 exists in an axial position and that at C_2 in equatorial one, whereas in V their positions are reversed.

In the former, the tetramethylene group produces steric compression over the p-orbital of a nitrogen atom whereas in the latter, the substituent shields the quasi-axial hydrogen atom at C_4. Little attention has been directed to steric influence due to the lone-pair electrons. This appears to be less than the steric hindrance caused by the hydrogen atom. By the above reason conformation IV may be inferred to be more predominant than the latter. On the basis of these likely assumptions it seems reasonable to assign conformations II and IV for *trans*- and *cis*-octahydroacridines,[28] respectively. Similar interpretation may be developed to assign conformations for *trans* and *cis* isomers of tetrahydro-2,3-trimethylenequinoline and of tetrahydro-2,3-pentamethylenequinoline.

The Difference $\Delta\lambda_{sol}$.—In order to account for the solvent effect in alcohol more definitely, the concept $\Delta\lambda_{sol}$ will be proposed, being defined as $\Delta\lambda_{alc} - \Delta\lambda_{ether}$. Since the size of the ether molecule is almost the same as that of the alcohol molecule, the value of $\Delta\lambda_{ether}$ is considered to indicate the solvent effect afforded only by hydrogen bonding between the H atom of the imino group and the O atom of the alcohol. Consequently, the term $\Delta\lambda_{sol}$ displays the solvent effect resulting from only hydrogen bonding between the N atom of the amine and the H atom of the alcohol. Examination of Table I shows that the term $\Delta\lambda_{sol}$ was particularly small in each of three *cis* derivatives of tetrahydroquinoline. This means that no hydrogen bonding is formed between the N atom of amine and the H atom of alcohol. The conformations of these *cis* isomers suggested in the previous paragraph are in good agreement with these facts: tri-, tetra- or pentamethylene substituent dominates so much space over the p-orbital of the nitrogen atom that the polymethylene groups will obstruct the proximity of ethanol molecules and will thus block the formation of hydrogen bonding.

On the other hand, the three *trans* isomers are supposed to suffer steric hindrance to only a slight degree in the formation of hydrogen bonding between the N atom of the amine and the H atom of the alcohol, as shown by negative values of the term $\Delta\lambda_{sol}$ given in Table I. It is to be noted that the value of $\Delta\lambda_{sol}$ in *trans*-tetrahydro-2,3-trimethylenequinoline (-4.5 mμ) was smaller than that in the other two *trans* isomers (-2.0 and -2.5 mμ), being consistent with the observation[22] by Arnold and his associates as mentioned above.

Conformations of hexahydrocarbazole will be discussed next. As it is well known that cyclohexane fused with a five-membered ring consists mainly of the chair form,[29] conformation VI will be suitable to be assigned for *trans*-hexahydrocarbazole and VII or VIII for the *cis* isomer, each corresponding to those, II, V and IV, of octahydroacridine. The conformation VI is formed when each of two equatorial hydrogen atoms on the two adjacent carbon atoms of cyclohexane is substituted by amino and phenyl radical of aniline, respectively. In conformation VII, the *cis* isomer has a configuration with the amino and phenyl radicals in the equatorial and axial position of adjacent carbon atoms of cyclohexane, respectively, whereas in conformation VIII they are in axial and equatorial position, respectively. Similar argument to that described in the case of *cis*-octahydroacridine cannot be applied to the stability between conformations VII and VIII. However, it will be reasonable to consider that *cis*-hexahydrocarbazole consists chiefly of conformation VII, because the p-orbital of nitrogen atom is screened with the tetramethylene group in conformation VIII but, on the contrary, conformation VII hardly suffers steric hindrance as is also true in the case of the *trans* isomer. Examination of Table I indicates that the value of $\Delta\lambda_{sol}$ of *cis*-hexahydrocarbazole was not very different from that of the *trans* isomer, as expected from a consideration as above outlined.

The Difference $\Delta\lambda_{ether}$.—In addition to the term of $\Delta\lambda_{sol}$, the values of $\Delta\lambda_{ether}$ must, therefore, be discussed in order to elucidate the difference of absorption maxima of the *cis* and *trans* isomers of tricyclic bases in alcohol, and the following will be proposed as an explanation. The positive values of $\Delta\lambda_{ether}$ are due mainly to the formation of hydrogen bonding between the H atom of the imine and the O atom of the ether. It seems to require a carbon atom at the β-position in relation to the nitrogen atom (called β-carbon) or a hydrogen atom attached to the carbon (called β-hydrogen) to display a serious steric influence on the proximity

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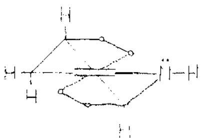
(26) D. H. R. Barton, *Quart. Revs.*, **10**, 73 (1956).

(27) J. Hartwell and A. W. Schrecker, THIS JOURNAL, **73**, 2909 (1951).

(28) This argument does not exclude the existence of structures other than II and IV, which possibly exist at room temperature. But it is assumed that these structures, II and IV, are more important than others for the analysis of absorption spectra.

(29) E. L. Eliel and C. Pillar, THIS JOURNAL, **77**, 3600 (1955).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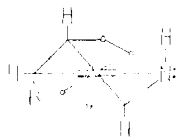
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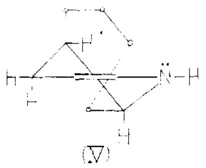
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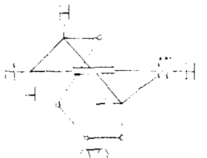
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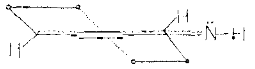
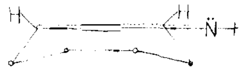
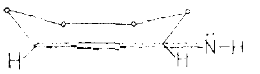

(VI)


(VII)


(VIII)

of the ether molecule. In each of conformations II and IV of *cis*- and *trans*-octahydroacridines, a quasi-equatorial hydrogen atom of an imino group runs almost parallel to the equatorial β-hydrogen atom, and those atoms with the nitrogen atom and β-carbon atom lie approximately coplanar with the benzene ring. The latter steric relation was extended to both *cis* and *trans* isomers of tetrahydro-2,3-pentamethylenequinoline with slight change due to transformation from a six-membered ring to a seven-membered ring. Therefore, in each of the two pairs both the *cis* and *trans* isomers are able to form the hydrogen bonding with ether molecule to the same degree, and as the result the difference of $\Delta\lambda_{\text{ether}}$ between isomers is supposed to be almost nothing.

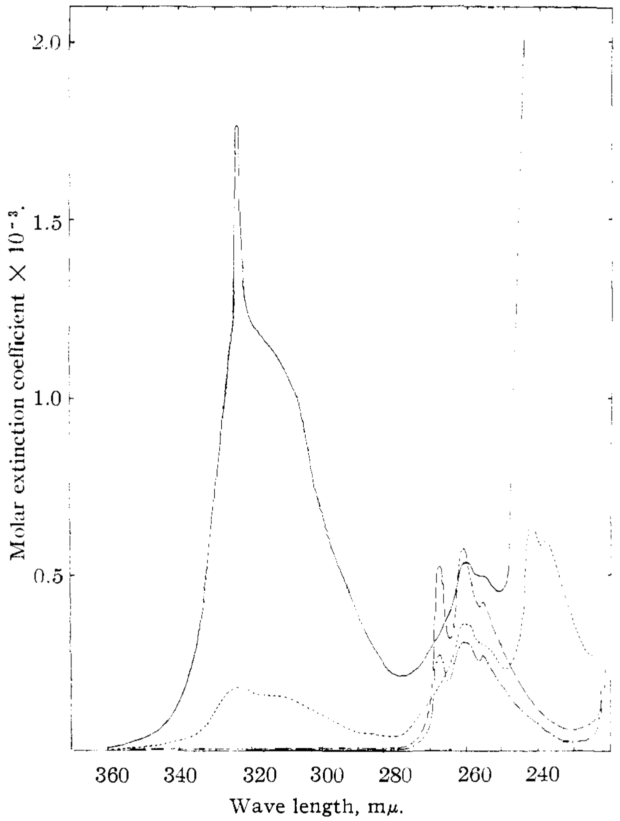


Fig. 1.—Ultraviolet absorption spectra of tricyclic bases in 0.1 *N* hydrochloric acid, concn. $M \times 10^{-3}$: — — —, *cis*-hexahydrocarbazole; —·—·—, *trans*-hexahydrocarbazole; - - - - - -, *cis*-octahydroacridine; ———, *trans*-octahydroacridine.

On the other hand, the position is different in the other two pairs of stereoisomers where a five-membered ring combines with a six-membered ring. While the above-mentioned relation comes to each of two *trans*-isomers of those bases, each of two *cis*-isomers behaves differently: that is, each β-carbon atom, and more important each β-hydrogen atom, is forced out of coplanarity with tetrahydroquinoline or dihydroindole, because each atom of a five-membered ring is coplanar. As a result, it would be expected that the approach of an ether molecule toward the hydrogen atom of imino group is easier in each *cis* isomer, and the value of ($\Delta\lambda_{\text{ether}}$ of *cis* isomer − $\Delta\lambda_{\text{ether}}$ of *trans* isomer) is expected to be positive. The values of $\Delta\lambda_{\text{ether}}$ given in Table I were found to fit in with these considerations.

One might conclude that the experimental results given in Table I are in good agreement qualitatively with what might be expected from both the conformational analysis for tricyclic bases and the inferences on the solvent effect of alcohol developed by division into terms of $\Delta\lambda_{\text{ether}}$ and of $\Delta\lambda_{\text{sol}}$. This inference of the solvation of alcohol may be extended with some reason to simple derivatives of aniline included in Table II; it may be pointed that the effect caused by the hydrogen bonding between the N atom of the aromatic amine and the H atom of the alcohol is large and depends remarkably on steric hindrance as well as on strength of basicity; however, on the contrary, that between the amino H and the alcohol O is comparatively small and is probably influenced only by steric hindrance and not by basicity.

Ultraviolet Absorption Spectra of Tricyclic Bases in 0.1 *N* Hydrochloric Acid and their Basicity.—It is well known that the absorption spectra of derivatives of aniline in acidic solution agree closely with the spectrum of benzene.[30] This rule was recognized in stereoisomeric hexahydrocarbazoles in this study. But absorption spectra of the other three pairs of stereoisomers of tricyclic bases exhibited characteristic peaks at longer wave lengths (near 320 mμ), as shown in Fig. 1 and in Table III. Especially, *trans*-octahydroacridine displayed an absorption peak with extraordinary strong intensity in this region. While a rational explanation could not be offered for these phenomena, which probably result from distortion of the benzene ring by ring formation of substituents, attention should be drawn to the association of intensity of those

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(30) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

TABLE III

NEAR ULTRAVIOLET ABSORPTION SPECTRA OF TRICYCLIC BASES IN 0.1 *N* HYDROCHLORIC ACID

Compound	Absorption maxima (mμ) and intensity (ε)[a]				Basicity,[b] pK_a
trans-Tetrahydro-2,3-trimethylenequinoline	324 (57)	267 (268)	260 (572)	244 (269)	4.47
cis-Tetrahydro-2,3-trimethylenequinoline	324 (266)	266 (267)	259 (310)	243 (850)	4.45
trans-Octahydroacridine	324 (1760)		261 (536)	242 (3000)	4.39
cis-Octahydroacridine	324 (176)		261 (360)	242 (650)	4.08
trans-Tetrahydro-2,3-pentamethylenequinoline	321 (920)		260 (380)	241 (2690)	4.63
cis-Tetrahydro-2,3-pentamethylenequinoline	321 (260)		261 (355)	242 (1080)	4.51
trans-Hexahydrocarbazole		268 (276)	261 (310)	256 (265)	4.66
cis-Hexahydrocarbazole		268 (522)	261 (576)	256 (419)	4.92

[a] The figures in parentheses refer to molecular extinction coefficient. [b] The basicity was measured at 15° in 50% aqueous alcohol.

absorption spectra with basicity. In each of four pairs cited in Table III, absorption maxima agree within the limit of 1 mμ, but those intensities were different among stereoisomers. Each of the bases possessing absorption bands of higher intensities was found to be a stronger base than the corresponding isomer. This correlation might be assumed because the strength of basicity of aromatic amines is closely associated with the resonance state of benzene, but no generalization would be safe from the few examples treated in this study. The problem will be kept under further investigation.

Acknowledgments.—The present research was conducted under the supervision of Professor Harusada Suginome, President of Hokkaido University. The author is also indebted to Professor Ken-iti Higasi for his help in revising the manuscript. Thanks are due to Mr. Seiya Suzuki for help with some of the measurements.

SAPPORO, JAPAN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, IOWA STATE COLLEGE]

The Preparation and Dichromate Oxidation of Certain 6-Substituted Phenanthridines

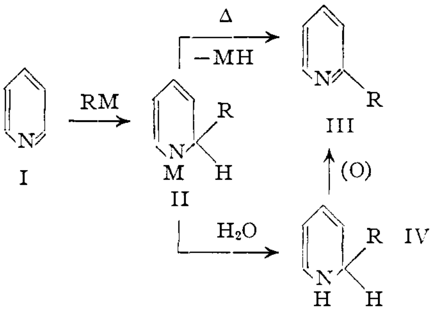
BY HENRY GILMAN AND JOHN EISCH

RECEIVED MARCH 7, 1957

The preparation of 6-substituted phenanthridines and their 5,6-dihydro derivatives by the organometallic alkylation of phenanthridine has been examined. It was found that not only do organolithium compounds (*n*-butyl- and *o*-tolyllithium) attack phenanthridine readily, but active Grignard reagents such as benzylmagnesium chloride can also add to the azomethine linkage. Finally, even ordinary Grignard reagents such as *n*-propylmagnesium bromide alkylate this heterocycle if the reaction time is protracted.

The dichromate oxidation of 6-*n*-propyl- and 6-*n*-butylphenanthridines gave, in addition to phenanthridinone, the corresponding 6-acylphenanthridines. This reaction is suggested not only to be diagnostic for 6-alkylphenanthridines but also to be a preparative method for 6-acylphenanthridines.

Although the aza-aromatic heterocycles previously studied, pyridine, quinoline and isoquinoline, are readily alkylated by organolithium compounds,[1] they react with organomagnesium compounds only with difficulty.[2] To obtain even mediocre yields, workers have resorted to such stringent reaction conditions as autoclave technique, higher-boiling solvents or dioxane media. The course of the reaction, however, seems quite analogous for organolithium and organomagnesium compounds, *i.e.*, addition of RM (M = Li, MgX) to the nitrogen heterocycle in a 1,2- or 1,4-manner. The interaction of pyridine (I) and an organometallic compound (RM) may be viewed as typical[3]



The resulting adduct II may either split out MH to give III thermally, or the dihydro compound IV obtained upon hydrolysis may be dehydrogenated.

Recent investigations have demonstrated that dibenzopyridines such as phenanthridine exhibit a high order of reactivity toward allylmagnesium

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(1) K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931).

(2) For a general review of the interaction of Grignard reagents with aza-aromatic heterocycles, see M. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1257 *et seq.*

(3) The predominating isomer from the reaction between pyridine and organolithium compounds is the 2-isomer, whereas the action of benzylmagnesium chloride leads in small yield to a 4:1 mixture of 4-benzyl- and 2-benzylpyridines (R. A. Benkeser and D. Holton, THIS JOURNAL, **73**, 5861 (1951)). With allylmagnesium bromide the main product has been shown to be 4-allylpyridine; smaller amounts of 2-allypyridine which may have been formed could not be isolated (ref. 4).