DETERMINATION OF THERMODYNAMIC FUNCTIONS BY MEANS OF INFRARED SPECTROSCOPY. II.*

"AXIAL" AND "EQUATORIAL" HYDROGEN BONDS

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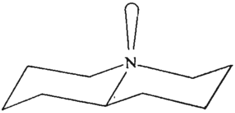
Received March 23rd,

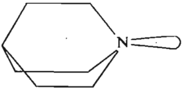
The values were obtained of the association constants K_{25} and of the thermodynamic func ΔG_{25}, ΔH, and ΔS of the hydrogen-bond formation in ternary systems quinuclidine–phe C_2Cl_4 and quinolizidine–phenol–C_2Cl_4; the H-bond properties were studied in depend on different spatial arrangement of the lone pair of the N atom. Quinuclidine which has equat ly situated electron pair, exhibits a higher $-\Delta H$ value of the interaction with phenol in com son with quinolizidine the lone pair of which is oriented axially.

Spatial arrangement of the lone pair of the nitrogen atom in molecules of saturated heteroc bases has been studied by means of chemical methods[1,2] or, more frequently, by using the di moment measurements[3], as well as NMR[4] and infrared[5] spectra.

In this paper, the effect of different arrangements of the lone pair in molec of quinolizidine (*I*) (expected to be axial[6]) and quinuclidine (*II*) (equatorial**) on formation of H bonding with phenol in tetrachloroethylene*** were studied. It been found that quinolizidine with more sterically hindered lone electron pair weaker base.



I



II

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* Part I: This Journal *34*, 2390 (1969).

** It is considered insignificant that six-membered rings in quinuclidine are in the boat f

*** This solvent was used in order to avoid chemical reactions of the bases with solvents.

EXPERIMENTAL

Quinolizidine was set free from its perchlorate (m.p. 148·5—150°C) by KOH, dissolved in diethyl ether and after drying the solution with solid KOH and evaporation of solvent it was distilled under reduced pressure. Quinuclidine was obtained from its hydrochloride in a similar way; the crystalline sample was purified by repeated sublimation *in vacuo*. Phenol and tetrachloroethylene were thoroughly purified and dried before use. Infrared spectra were measured with a Zeiss (Jena) spectrophotometer, model UR-10, by using the procedures and equipment described earlier[1]. The proton-donor and proton-acceptor concentrations were ~0·003 and ~0·013 mol . l^{-1}, respectively. The calculation of association constants (at 5, 15, 25, 35, and 45°C) was based on the assumption of a 1 : 1 stoichiometry of the complex formed. The accuracy of the ΔH scale was checked by determining ΔH values of the complex formation between acetonitrile and phenol in CCl_4; the values obtained ($-4{\cdot}14$ and $-4{\cdot}22$ kcal mol^{-1}) agree well with previous findings[1]. The accuracy of ΔH and ΔS values does not exceed 2·5 and 4%, respectively.

RESULTS AND DISCUSSION

Both the quinuclidine and quinolizidine[6] molecules are rigid with lone electron pair of the nitrogen atom in equatorial and in axial positions, respectively. Both are very strong bases (compare the values of $-\Delta H$ as well as pK_a in Table I).

Supposing the H-bonds are colinear* with the spatial orientation of the lone-pair, quinolizidine** should give rise to a complex with an "axial" whereas quinuclidine with an "equatorial" hydrogen bond. When considered to be a "substituent" of the six-membered cyclohexane-like ring, the axial hydrogen bond should be more sterically hindered. Quinolizidine, being this case, cannot then realize its basicity as easily as the quinuclidine does. The lower basicity*** of quinolizidine (expressed in ΔG, ΔH and pK_a values, see Table I) is in agreement with this assumption; the ΔS of both bases is undistinguishable with respect to the experimental error of its estimation. Let us now compare the values of thermodynamic functions of the compounds studied with those of structurally similar and well investigated triethylamine.

The steric effects become more important in this molecule with hindered internal rotation. This molecule possesses a similar ΔH value† as quinuclidine, but it shows a higher value of ΔS which means that the rather large basicity of triethylamine cannot be fully realized. The steric hindrance in triethylamine manifests itself also in the fact that this compound reacts 700 times slower with isopropyl iodide than

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* The phenyl group of phenol is not taken into account in this model.

** The hydrogen bond formation is assumed not to shift the equilibrium of the *cis/trans* forms of quinolizidine towards the *cis* form.

*** The values of association constants[7] describing the formation of the same complex are about 56% of those obtained by us. Nevertheless, in the scale presented, the steric effect of a 3(a)methyl group can easily be discovered.

† Tetrachloromethane was used for studying the complex formation of trimethylamine instead of tetrachloroethylene. It is expected that ΔH and ΔS values estimated for the same complex in both solvents will not differ substantially from each other.

quinuclidine[10]. Similar results can be derived from the data describing the methanol-1-azabicyclo-2,2,1-heptane and methanol–triethylamine complex formation. Both compounds have identical values of ΔH but differ in ΔS values.

TABLE I

Thermodynamic Functions of Hydrogen Bond Formation between Phenol (Methanol) and Some Nitrogen Bases

Compound	Proton-donor	Solvent	$-\Delta H$ kcal mol^{-1}	$-\Delta S$ cal $grad^{-1}$. mol^{-1}	$-\Delta G_{25}$[a] kcal mol^{-1}	K_{25}[a] l mol^{-1}	pK_a
Quinolizidine[b]	C_6H_5OH	C_2Cl_4	7·4	16·3	2·6	78	10·19 ± 0·07[c]
Quinuclidine[b]	C_6H_5OH	C_2Cl_4	8·6	16·9	3·6	409	10·58[d]
Triethylamine	C_6H_5OH	CCl_4	8·35 ± 0·5[e]	20 ± 1·7[e]	2·5[e]	—	10·87[f]
1-Azabicyclo-[2,2,1]heptane[g]	CH_3OH	CCl_4	5·2	12·5	—	—	—
Triethylamine[g]	CH_3OH	CCl_4	5·2	15·3	—	—	—

[a] Values related to 25°C; [b] mean values of two independent measurements; [c] lit.[2]; [d] lit.[8]; [e] lit.[9]; [f] lit.[10]; [g] lit.[11].

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Translated by the author (M. H.).