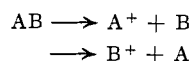ments suggests a charge competition reaction in their formation. This could not be the simple reaction of the type

$$AB \longrightarrow A^+ + B$$
$$\longrightarrow B^+ + A$$

because of the hydrogen content of the major C_7^+ and C_8^+ ions. There could be a more complex charge competition process which involved hydrogen loss as a secondary process. The C^{13} content of C_6^+, C_5^+ and C_4^+ ions show a remarkable similarity with relatively small tendency toward loss of C^{13} in processes responsible for the formation of these fragments. The statistical theory predicts rather specific dissociation mechanisms following paths of minimum energy and entropy and the production of stable products that resist subsequent decomposition reactions.

The cyclic $C_7H_9^+$ ion is expected to have more stability than a simple open chain which would undergo decomposition much more easily than a ring system. Furthermore since it is observed in high abundance, it is expected that it would be formed more readily from the parent species than lower molecular weight fragments and that it would then play the role of precursor of some of the lower molecular weight ion fragments. If one assumes that these ions are products of decomposition of a $C_7H_9^+$ intermediate in a set of consecutive decomposition reactions taking place subsequent to electron impact, then structures for $C_7H_9^+$ must be compatible with the C^{13} data. A C_7 ion with C^{13} randomly distributed in equivalent positions and

equal probability of bond rupture for the formation of C_4, C_5 and C_6 ions by bond rupture processes would produce a C_4^+ ion containing 47% C^{13}, C_5^+ containing 60% and C_6^+ containing 70%. The qualitative agreement between % of total C^{13} observed and calculated on the basis of random rearrangement and fragmentation suggests that while specific processes are responsible for C_9^+ and C_8^+, extensive rearrangements must take place in the formation of lower molecular weight species. If the assumption that $C_7H_9^+$ is the parent species of the lower molecular weight, C_6, C_5 and C_4 ions, then structures of the type a are disfavored for C_7H_9, since both equal probability of bond rupture in the formation of C_6 for example is improbable and the mechanism for random distribution of C^{13} among various positions is not obvious from this structure. Structures of type b and c are possible and have the advantage that they represent highly stabilized forms

a   b   c
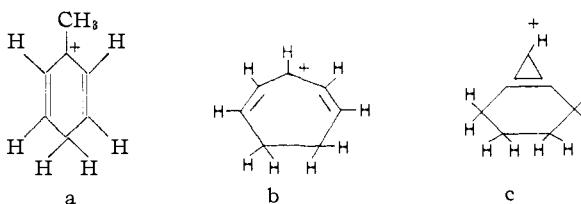
of $C_7H_9^+$, a condition required from consideration of the statistical theory of mass spectra for relatively abundant ions.

UPTON, L. I., NEW YORK

The Dipole Moments and the Conformations of Matridine and Related Compounds

BY BUNZO EDA, KYOSUKE TSUDA[1] AND MASAJI KUBO

The dipole moments of matridine, allomatridine, sparteine, α-isosparteine and related compounds were measured in benzene solutions. The dipole moment data indicate that in the allomatridine molecule, all the neighboring rings are trans-fused and that matridine has cis-fused rings. The moment of 2-methylperhydropyrido[3,4,5-i,j]quinolizine is close to that of allomatridine, indicating that the molecule of the former compound, like that of the latter, assumes a stable extended structure. The moment of α-isosparteine is in agreement with that calculated for the molecular structure determined by X-ray crystal analysis.

Introduction

When matrine and allomatrine are subjected to reduction with lithium aluminum hydride, they give matridine and allomatridine, respectively.[2] One of the present authors[3] has already succeeded in the total synthesis of allometridine, a stereoisomer of matridine. The conformational analysis of this isomeric pair of compounds has given a clue to the elucidation of the molecular structure of matrine,[4] an alkaloid first isolated from the root nodules of certain leguminous plants found in Japan. The present investigation was under-

taken in order to determine the conformations of these compounds from the measurements of dipole moments of matridine and related compounds.
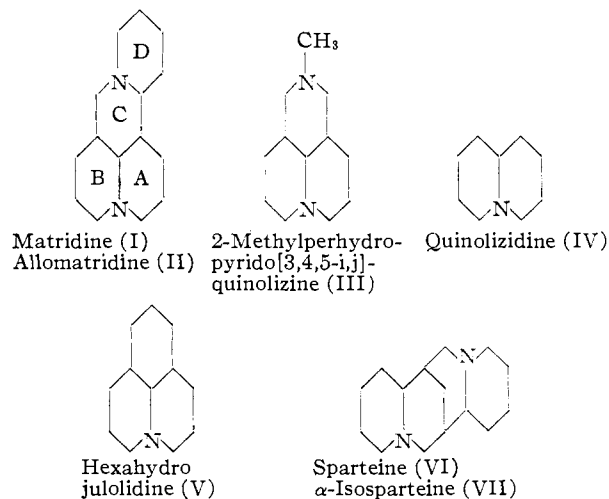
Materials

Matridine (I) and allomatridine (II) were prepared by the method described in a previous paper.[2] The melting points were 56–57° and 76–78°, respectively. 2-Methylperhydropyrido[3,4,5-i,j]quinolizine (or 9-methyl-9-azahexahydrojulolidine) (III) and quinolizidine (or norlupinane) (IV) were synthesized according to the procedure already reported.[5] The former crystallized with one molecule of water and showed a melting point of 74–75°. On drying over phosphorus pentoxide, the crystals turned into an oily anhydrous compound, which was used for dipole moment measurements. The compound IV was purified by recrystallization of its hydrobromide. The free base was an oil boiling at 184°. Hexahydrojulolidine (V) was prepared by

(1) Institute of Applied Microbiology, University of Tokyo.

(2) E. Ochiai, S. Okuda and H. Minato, J. Pharm. Soc. Japan, 72, 781 (1952).

(3) K. Tsuda and H. Mishima, Pharm. Bull., 5, 285 (1957).

(4) R. H. F. Manske and H. L. Holmes, "The Alkaloids," Vol. III, Academic Press, Inc., New York, N. Y., 1953, p. 178.

(5) K. Tsuda, S. Saeki, S. Imura, S. Okuda, Y. Sato and H. Mishima, J. Org. Chem., 21, 1481 (1956).

the method of Protiva and Prelog.[6] The racemic compound, which was obtained with a greater yield than that of the *meso* form, was converted into its picrate having a melting point of 183° and was purified by recrystallization. The free base distilled at the bath temperature of 100–105° under a reduced pressure of 4 mm. Sparteine of *l*-form (VI) was prepared from a commercial sample of sparteine sulfate, the boiling point being 188° under a reduced pressure of 18 mm. When it was subjected to isomerization[7] with aluminum chloride as a catalyst, α-isosparteine (VII) was formed. Recrystallization from its solution in the mixture of acetone

Matridine (I)   2-Methylperhydro-   Quinolizidine (IV)
Allomatridine (II) pyrido[3,4,5-i,j]-
                    quinolizine (III)

Hexahydro   Sparteine (VI)
julolidine (V)   α-Isosparteine (VII)

and water gave crystals of α-isosparteine monohydrate having the melting point of 105°. Although sublimation under a reduced pressure yielded an anhydrous compound, the hydrate was employed for the dipole moment measurements, because the anhydrous preparation was liable to be colored.

Experimental Method and Results

The measurements were carried out at 25° on dilute solutions in benzene. The dielectric constants were measured by means of a heterodyne beat apparatus provided with a platinum cell.[8] For each solute, determinations were made on solutions of four different concentrations appropriately chosen below about 2 weight per cent. except in the case of compound VII, which was studied at three concentrations less than 0.8%. The graphical plots of the dielectric constant as well as the density of solutions against the concentration in weight per cent. gave linear dependence within experimental errors. The slopes of these straight lines were evaluated by the least squares method and the molar polarizations of the solutes were calculated by a method similar to that introduced by Halverstadt and Kumler,[9] differing in that densities were used rather than the specific volumes. The sum of electronic and atomic polarizations of each of these compounds was approximated with the calculated molar refraction for the D line.

The results are shown in Table I, in which ϵ_1 and d_1 denote, respectively, the dielectric constant and density of the solvent; α and β are, respectively, the changes of the dielectric constant and density of the solution with the weight fraction of the solute; other notations have their usual significances.

The use of α-isosparteine monohydrate may, indeed, make it a matter of considerable difficulty to evaluate the moment of the anhydrous compound. However, one of the present authors[10] has experienced a similar problem in the determination of the dipole moments of anhydrous and hydrated tropolone methyl ether. In this case, the square of the observed moment of the hydrated compound was found to be almost equal to the sum of the squares of the observed mo-

(6) M. Protiva and V. Prelog, *Helv. Chim. Acta*, **32**, 621 (1949). See also N. J. Leonard and W. J. Middleton, THIS JOURNAL, **74**, 5114 (1952).

(7) F. Galinovsky, P. Knoth and W. Fischer, *Monatsh. Chem.*, **86**, 1014 (1955).

(8) Y. Kurita and M. Kubo, THIS JOURNAL, **79**, 5460 (1957).

(9) I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

(10) Y. Kurita, S. Seto, T. Nozoe and M. Kubo, *Bull. Chem. Soc. Japan*, **26**, 272 (1953).

TABLE I

DIPOLE MOMENTS OF MATRIDINE AND RELATED COMPOUNDS IN BENZENE SOLUTIONS AT 25°: $\epsilon_1 = 2.273$, $d_1 = 0.8715$

Cmpd.	α	β, g./cc.	$P_{2\infty}$, cc.	MR_D, cc.	μ (D)
I	0.272	0.1420	79.1	71.1	0.63
II	.813	.1259	104.5	71.1	1.27
III	.957	.1017	93.7	59.0	1.30
IV	.305	.0209	54.4	43.4	0.74
V	.306	.0660	67.0	55.2	0.76
VI	.358	.1265	84.3	71.1	0.80
VII·H₂O	1.705	.1448	153.0	74.8	1.95 (0.65[a])

[a] Calculated for anhydrous α-isosparteine.

ment of the anhydrous compound and the moment of water. Accordingly, it was presumed that in very dilute benzene solutions, the hydrate dissociated into its component parts, or at least the moments of the component parts in a hydrated molecule oriented in the external field as if they were in separate molecules. With this presumption applied to α-isosparteine monohydrate, the moment of α-isosparteine μ_{anhydr} could be calculated from the observed moment of the hydrate μ_{hydr} as $\mu_{hydr}{}^2 = \mu_{anhydr}{}^2 + \mu_{H_2O}{}^2$, where the dipole moment of water μ_{H_2O} was assumed to be equal to 1.84 D. as in the gaseous state. The resulting value of μ_{anhydr} is given in Table I in parentheses.

Discussion

Assuming that the valency angle of nitrogen is equal to that of carbon and that all the six-membered rings take a chair form, one can conceive twelve conformations possible for the structure I or II, a pair of optical isomers being counted as one conformation. This is because the system of condensed rings A, B and C may take four conformations

a   b   c   d
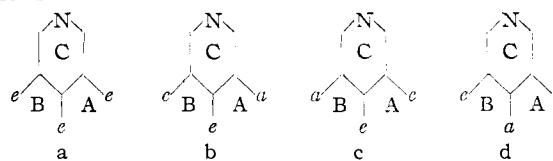
and the two rings C and D may join with each other in three different ways.
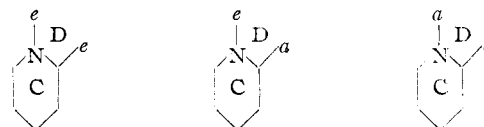
Here, e and a stand for equatorial and axial bonds, respectively. However, there are good reasons for believing that the two rings C and D are *trans*-fused.[3] This condition reduces the possible conformations to one-third, the resulting four conformations being as

a   b   c   d
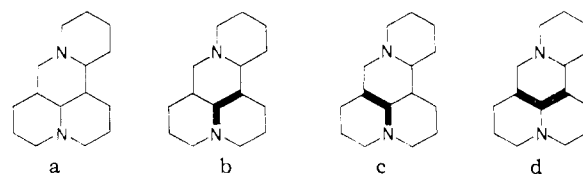
Here, a bold line indicates that the two rings on either side of the line are *cis*-fused, while a fine line belonging to two rings signifies that these rings are *trans*-fused. Accordingly, matridine and allomatridine are presumed to correspond to two of these four conformations, respectively.

The moments of these compounds are, to a first approximation, the resultant of two group moments located at the N < C_3 portions of the respective molecule. The two group moments are parallel to each other in the conformation a, whereas they make a tetrahedral angle α with each other in the three other conformations b, c and d. The N < C_3 group moment μ_0 can be approximated with the moment of quinolizidine 0.74 D. or that of hexahydrojulolidine 0.76 D. rather than with that of trimethylamine 0.86 D.[11] Allomatridine having a moment nearly twice as great as that of quinolizidine must therefore be represented by the conformation a, while matridine having a moment nearer to $2\mu_0 \cos^{1/2}\alpha = 1.15\mu_0$ than to $2\mu_0$ must correspond to one of the conformations b, c and d. One of the present authors[3] already has advanced an argument that compounds of allomatrine series have the structure a and those of matrine series the structure d from the considerations on the relative stability of matridine and its isomer as well as on the reactions of matrine and allomatrine with cyanogen bromide, of matridine and allomatridine with methyl iodide, and also of potassium matrinate and potassium allomatrinate with methyl iodide. The present results afford a definite evidence in favor of this conclusion. Quite recently, Bohlmann and collaborators[12] published a paper, in which they reported that they arrived at the same conclusion. Their argument is founded on other reactions than those studied by one of the present authors[3] and on the infrared absorptions of matrine and $\Delta^{5(\text{or }6)}$-dehydromatridine in the wave number range 2700–2800 cm.$^{-1}$ showing features characteristic of a trans-fused quinolizine ring. The moment of 2-

(11) R. J. W. Le Fèvre and P. Russel, Trans. Faraday Soc., 43, 374 (1947).

(12) F. Bohlmann, W. Weise and D. Rahtz, Angew. Chem., 69, 642 (1957).

methylperhydropyrido[3,4,5-i,j]quinolizine is close to that of allomatridine, indicating that the molecule of the former compound, like that of the latter, assumes a stable extended structure.

The conceivable conformations for sparteine and α-isosparteine[13] are the following six, of which iii, v and vi can be ruled out from the considerations of steric hindrance.
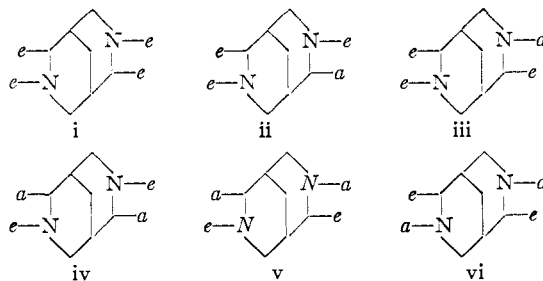
Like the skeletons of matridine and allomatridine, the frameworks of sparteine and α-isosparteine can be accommodated in the diamond lattice and it is easy to see that the two N < C_3 group moments make a tetrahedral angle with each other in conformations i, ii and iv. The observed moments for the two compounds agree with any of the three possible conformations. The X-ray crystal analysis carried out by Przybylska and Barnes[14] on α-isosparteine monohydrate has shown that α-isosparteine has the structure shown by i. Accordingly sparteine must have either the conformation ii or iv. Although dipole moment data alone are unable to make a choice between these two alternatives, one may tentatively assign the conformation ii to sparteine, leaving iv for β-isosparteine.

(13) Reference 4, p. 156.

(14) M. Przybylska and W. H. Barnes, Acta Cryst., 6, 377 (1953).

CHIKUSA, NAGOYA, JAPAN

The Stereochemistry of Base-catalyzed Epoxidation

BY HERBERT O. HOUSE AND ROLLAND S. RO[1]

RECEIVED NOVEMBER 30, 1957

The cis and trans isomers of 3-methyl-3-penten-2-one have been prepared. Each isomer, when allowed to react with alkaline hydrogen peroxide, yielded 3-methyl-trans-3,4-epoxy-2-pentanone thereby demonstrating that the epoxidation is not stereospecific. Appropriate experiments in a deuterium-containing medium demonstrated that the base-catalyzed epimerization of β-methyl-trans-benzalacetophenone oxide to the cis isomer and the reverse process involved a carbanionic intermediate.

The epoxidation of olefins with peracids is known to proceed stereospecifically, the configuration of the epoxide produced being the same as the configuration of the starting olefin.[2–4] However, this method of epoxidation is usually not applicable to α,β-unsaturated ketones since the reaction of such olefins with peracids either yields enol esters, the products of a Baeyer–Villiger reaction, rather than

α,β-epoxy ketones[2,5] or occurs very slowly if at all.[6,7] For this reason the general procedure for the epoxidation of α,β-unsaturated ketones con-

(1) Alfred P. Sloan Postdoctoral Fellow, 1957–1958.

(2) S. Winstein and R. B. Henderson in R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 1.

(3) D. Swern, Chem. Revs., 45, 1 (1949).

(4) D. Swern, Org. Reactions, 7, 378 (1953).

(5) C. H. Hassall, ibid., 9, 73 (1957).

(6) Although certain α,β-unsaturated esters have been epoxidized by the use of peroxytrifluoroacetic acid [W. D. Emmons and A. S. Pagano, THIS JOURNAL, 77, 89 (1955)], we are unaware of any instances where this reagent has been employed successfully with α,β-unsaturated ketones. In one instance [P. L. Julian, E. W. Meyer and I. Ryden, ibid., 72, 367 (1950)] a steroidal α,β-unsaturated ketone was reported to yield an epoxide when treated with perbenzoic acid. The suggestion was made [E. Wenkert and M. Rubin, Nature, 170, 708 (1952)] that this type of epoxidation might be general but no experimental evidence has been provided to support this suggestion.

(7) H. O. House and D. J. Reif, THIS JOURNAL, 79, 6491 (1957).