EHT DEMONSTRATION OF IONIC STRUCTURE
OF 1-METHYL-3-CARBAMOYLPYRIDINIUM FLUORIDE
AND TETRAFLUOROBORATE*

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EHT calculations of the ion-pairs *I* and *II* confirm ionic character of the respective salt in accord with their behaviour in dilute aqueous solutions and spectral characteristics. These conclusions are supported by a study of the EHT energy changes due to motion of the ion X in the parallel plane located 200 pm above heterocyclic ring of the quaternary cation.

The EHT studies of pyridine hydrochloride and ionic salts of 1-methylpyridinium showed[1,2] that the Hückel approximation[3,4] can give a probable picture of localization of inorganic ion during its approach to heterocyclic ring of the corresponding cation. This interpretation is based on discussion of local minima position in the EHT energy curves or maps which, however, do not enable any calculation of overall stabilization energy of the ion-pair, which is inevitable consequence of approximative character of the mentioned method[1,2,5-7].

The aim of this work was to investigate applicability of the mentioned conclusions to quaternary nicotineamides ANA$^+$ X$^-$ which can be considered[8] acceptable quantum-chemical models of the prosthetic group of NAD$^+$ coenzyme.** As no suitable experimental data were found in literature concerning the two chosen nicotineamide salts *I* and *II*, we also describe one of alternative possibilities of their preparation from the quarternary iodide *III*.

EXPERIMENTAL

Temperature data are not corrected. The UV spectra were measured in aqueous solutions (c 10^{-4}M) using a Specord UV-VIS spectrophotometer (Zeiss, Jena) at 20°C. The IR spectra were measured with a Perkin–Elmer model 525 in Nujol suspensions.

1-Methyl-3-carbamoylpyridinium Fluoride (*I*)

Solution of 1·0 g substance[9] *III* in 25 ml water was precipitated to equivalence point with 5% aqueous solution of silver fluoride. The precipitated silver iodide was filtered off, washed with water thoroughly, and the filtrate was evaporated in vacuum at the temperatues below 30°C. The formed oily residue was transferred into a dessiccator over phosphorus pentoxide where it crystallized after several days. Yield of the colourless crystals of the fluoride *I* dihydrate was almost quantitative; on heating in a Boetius apparatus the substance decomposes at 119 to 130°C. For $C_7H_9N_2OF.2 H_2O$ (156·2) calculated: 43·75% C, 6·76% H, 14·57% N, 9·88% F; found: 43·78% C, 6·80% H, 14·52% N, 10·38% F. UV spectrum: λ_{max} 265 nm (log ε 2·63). IR spectrum. see Table I.

1-Methyl-3-carbamoylpyridinium Tetrafluoroborate (*II*)

Solution of 3·0 g substances[9] *III* in 50 ml water was precipitated to equivalence point with 5% aqueous solution of silver tetrafluoroborate, silver iodide was filtered off, washed with water, and the filtrate was evaporated in vacuum at 30°C. The dry residue was ground with mixture benzene–ether (1 : 1) whereupon it crystallized, and it was dried over phosphorus pentoxide in vacuum. Yield 2·5 g tetrafluoroborate *III*, m.p. 123 — 124°C (in Boetius apparatus). For $C_7H_9N_2OBF_4$ (223·9) calculated: 12·51% N; found: 12·41% N. UV spectrum: λ_{max} 266 nm (log ε 2·62); IR spectrum see Table I.

Thermal Analysis. Between 271° and 354°C the salt *II* undergoes decomposition accompanied by a defined mass decrease. For the process *II*—H_2O—BF_3—CH_3F calculated: 52·97%; found: 52·9%.

Calculations

The quantum-chemical calculations were carried out with a standard program EHT using a computer IBM 370/145. The geometry of 1-methyl-3-carbamoyl-cation MeNA$^+$ was the same as in ref.[10], for BF$_4^-$ anion ideal tetragonal arrangement was chosen with the B—F bond lengths 143 pm. Orientation of the ion-pair MeNA$^+$—X$^-$ in the coordinate system is given in Fig. 1. The

TABLE I

Comparison of Positions of Some Absorption Maxima in IR Spectra of Nujol Suspensions of the Salts *I* to *III*

Compound	$\tilde{\nu}_{max}$, cm^{-1}									
I	—	—	—	900	978	1 210	1 375	1 450	1 615^a	1 680^b
II	518^c	525^c	563^c	898	965	1 205	1 395	1 445	1 618^a	1 682^b
III	—	—	—	893	950	1 210	1 375	1 452	1 682^a	1 682^b
NaBF$_4$	515^c	523^c	548^c	—	—	—	—	—	—	—

^{a} δ(NH); ^{b} ν(C=O); ^{c} ν(BF).

used parameters are summarized in Table II, the non-diagonal elements of **H**-matrix were expressed by the Wolfsberg–Helmholtz approximation[4].

RESULTS AND DISCUSSION

The spectral characteristics of the salts *I* and *II* indicate that the both are ionic compounds. From Table I it is obvious that their IR spectra show absorption bands in the region 890 to 1700 cm^{-1}, their position being only little affected by character of the anion X$^-$. Besides that overall appearance of the absorption curve is similar for all the compounds *I* to *III* in this region, which can be interpreted by existence of the MeNA$^+$ ion in all the cases. Further evidence of ionic nature of the salt *II* in solid state comes from identification of three characteristic absorption maxima of tetrafluoroborate anion in the region 510 to 570 cm^{-1}. Besides that IR spectrum of the substance *I* in the region 1600 to 4000 cm^{-1} agrees with the finding that a hydrate is present (ref.[11]). The ionic nature of the salts *I* and *II* is further supported by UV spectra of their aqueous solutions. From Fig. 2 it is seen that the extinction curves of the both salts *I* and *II* are almost identical and exhibit a characteristic chromophoric system of quarternary nicotineamide ions ANA$^+$ (ref.[12]).
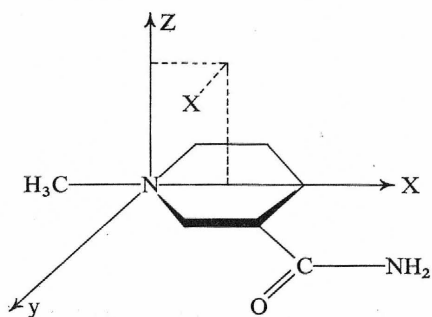

FIG. 1

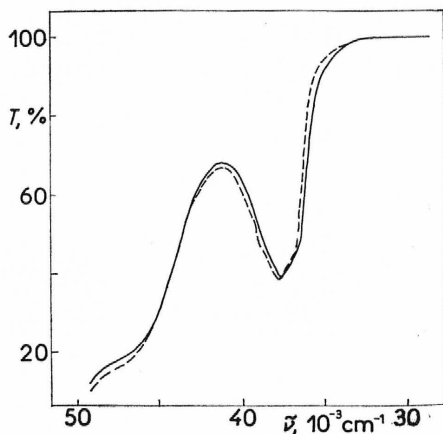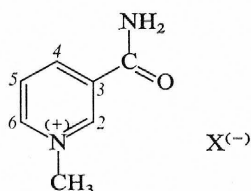Orientation of Ion-Pair MeNA$^+$X$^-$ in Carthesian Coordinate System

FIG. 2

Electronic Spectra of Compounds *I* and *II* in Aqueous Solution
        Compound *I* ———, compound *II* -----,
$c = 1 . 10^{-4}$M, $l = 1$ cm.

$$I, X = F$$
$$II, X = BF_4$$
$$III, X = I$$

In our study the planar conformation of MeNA$^+$ cation was used in all cases, as it is energetically the most favourable in the EHT conformational analysis[10], and, on the other hand, it is in accord with the available experimental knowledge[13,14] about structure of the ion type ANA$^+$ in crystalline state. Thus the EHT calculation of the ion-pairs *I* and *II* was based on the principle of "supermolecule", *i.e.* solution of secular equations derived from AOs of the whole system regardless of their correspondence to the individual ionic partners. The above-mentioned conformation of amide group in MeNA$^+$ cation was considered constant for simplicity, and thus the EHT energy of the system (E_{tot}) was followed as exclusive function of x, y, z coordinates of the anion X$^-$ (Fig. 1). Under these circumstances behaviour of E_{tot} was similar to that of the simpler pyridinium cations[1,2], particularly the argument $E_{tot} > E_{MeNA^+} + E_{X^-}$ was valid[1], the latter two quantities being EHT energies of the isolated ions.

TABLE II

Parametrization in the EHT Method

Atom	$-I_s$, eV	$-I_p$, eV	Slater exponent	Charge
H	13·6	—	1·3	1·0
B	15·2	8·5	1·3	3·0
C	21·4	11·4	1·625	4·0
N	26·0	13·4	1·950	5·0
O	32·3	14·8	2·275	6·0
F	39·389	20·86	2·600	7·0

Configuration of Fluoride I

Preliminary calculations for $z = 0$ (*i.e.* planar configuration of the ion-pair *I*) showed that isolines of the energy map $E_{tot} = f(x, y)$ do not give any local minima during approach of anion F^- to the heterocycle (positions 2, 4 and 6) or to N—H bonds of the amide group. Therefore, this planar situation was not studied to any more detail. With respect to the finding[1,2] that, in principle, the EHT method) cannot calculate stabilization energies of overall ionic attraction of two opposite ions, the investigation was restricted to the arrangement in which F^- and MeNA$^+$ are located in two parallel planes, their distance being $z = 200$ pm. This distance was chosen with respect to the effective volume[15] of F^- anion, 136 pm, and to previous experience in a similar study[2]. The corresponding complete energy map of the ion-pair *I* is given in Fig. 3. For its construction E_{tot} eigen values were used which were obtained for the coordinates x and y within -250 to 550 pm and within -425 to 300 pm, respectively, the calculation steps being 25 pm in the both cases. The map exhibits two local minima, a deeper one above the heterocycle, somewhat closer to the nitrogen atom, and the other one in close vicinity of the other nitrogen atom (amide group). Although energy difference of these two extremes is not too high, (~ 0.3 eV), the former minimum is considered physically more justified for configuration of the ion-pair *I*. This conclusion is supported by the fact that the used Hückel approximation of E_{tot} calculation reflects, in principle, only the effects of orbital overlap (covalent interaction) and hardly takes into account the interaction of point charges between the both ions MeNA$^+$ and F^-. Configuration of the second local minimum necessitates a close approach of negative particle to nitrogen atomic centre carrying a relatively high negative charge[16], and consequently this process will be made less favourable
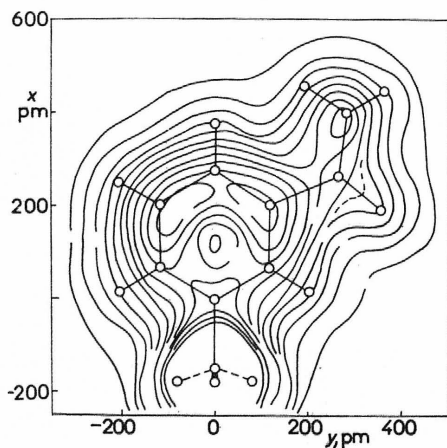

FIG. 3

EHT Energy Map of Ion-Pair *I* with Distance $z = 200$ pm

The level 0 corresponds to -1153.0 eV; the level distances 0.2 eV.

by an additional electrostatic repulsion higher than in the case of the former local minimum which is more distant from negatively charged atomic centres of the heterocycle. The configuration of the ion-pair I corresponding to the deeper extreme thus indicates ionic character of the bond between the particles $MeNA^+$ and F^- in accord with the found spectral properties of the fluoride I. Figure 3 also shows noteworthy energy maxima determining the regions in which motion of the F^- ion is extremely unfavourable energetically. According to expectation a very intensive maximum corresponds to localization of atomic centres of the methyl group, the other two being located near the carbon centres at 3 and 5 positions which (according to both EHT and CNDO/2 calculations) carry partial negative charges[16].

As the behaviour of the $MeNA^+$ ions as a model for NAD^+ represents an object of our steady interest, we tried to draw some conclusions from the map in Fig. 3 concerning possible rationalization of calculations of similar interactions with other types of X^- anions. This plan is not insignificant, if it is realized that precise construction of the mentioned map necessitated (in spite of relative calculation simplicity of EHT method) all in all 990 values E_{tot}. From character of the energy contour lines in Fig. 3 it can be judged that for obtaining approximate x, y coordinates of the local extremes it would be possible to restrict the calculations of the ion-pair I to EHT energy sections crossing the positions 1 and 4, or 2 and 5, or 3 and 6 of the heterocycle, or possibly another two sections along $C-N(H_2)$ and $C=O$ bonds,
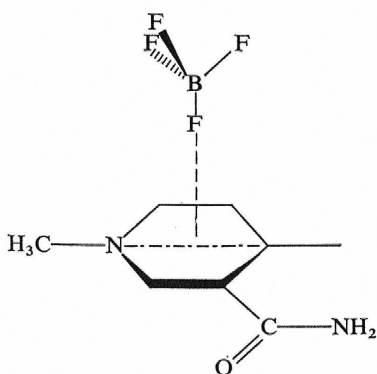

FIG. 4

Orientation of Ion-Pair II

The distance of the nearest F atom from the plane of the heterocyclic ring is $z = 200$ pm.

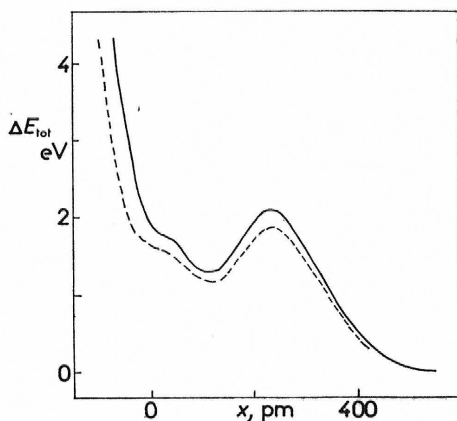FIG. 5

Comparison of EHT Electronic Energies for Ion-Pairs I and II Depending on Parameter x ($y = 0$ pm, $z = 200$ pm)

Compound I——, compound II-----.

if the situation near the amide group were interesting. This more economical approach was used partially in the following sections of this report, and it is being used at present in our further studies on ionic interactions of MeNA$^+$ cation.

Configuration of Tetrafluoroborate II

In previous communication[2] it was shown that mutual action of the complex anion BF_4^- and 1-methylpyridinium cation can (within the EHT method satisfactorily be expressed by the curves of interaction of one to three fluorine atomic centres of the whole BF_4^- particle, the configuration corresponding to positions of F^- ion. Due to relative complex geometry of the ion-pair II, we limited ourselves to a test as to whether the mentioned approximation is acceptable in this case, too, *i.e.* whether ionic structure of the more complex case II can be inferred from behaviour of F^- anion in the EHT model of the ion-pair I. Fig. 4 shows the mutual configuration of the both ionic partners chosen for this purpose. Therein only one fluorine atomic centre of BF_4^- ion is placed in parallel plane at the distance 200 pm from the plane of the heterocycle, and the corresponding EHT energy curves should be acceptably approximated by the respective curves of the ion-pair I. Figure 5 compares the dependences $E_{tot} = f(x)$ of the energy section of the respective map crossing 1 and 4 positions for the two ion pairs I and II. Obviously the both dependences are almost identical, hence ionic structure of the tetrafluoroborate II can be considered (from the viewpoint of the original presumptions) to be correctly interpreted within possibilities of simple EHT. The configuration of the ion-pair II given in Fig. 4 (having the nearest fluorine centre located above the heterocycle in the sense of the position of the local energy minimum in Fig. 5), of course, need not be the energetically most favourable mutual orientation of the both particles MeNA$^+$ and BF_4^- even within the EHT approach. However, we did not find it useful to investigate these problems in more detail.

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