

EHT STUDY OF 1-METHYLPYRIDINIUM FLUORIDE AND TETRAFLUOROBORATE

Josef KUTHAN, Vratislav SKÁLA and Stanislav BÖHM

*Organic Chemistry Department,
Prague Institute of Chemical Technology, 166 28 Prague 6*

Received February 9th, 1978

EHT method has been shown to predict correctly ionic character of 1-methylpyridinium fluoride and tetrafluoroborate (*I* and *II*, respectively) in accord with their spectral behaviour in dilute aqueous solutions. The energetically most favourable configuration of the ion-pairs *I* and *II* is represented by fixation of the anions above the plane of heterocyclic ring of the cation, but the EHT procedure does not fit the stabilization energy of ionic bond.

The EHT method proved¹ to give qualitatively correct interpretation of both ionic character of pyridine hydrochloride and mutual orientation of its ion-pair in crystal. With the aim to investigate further applicability of EHT for ion interactions we extended our quantum-chemical study to 1-methylpyridinium fluoride (*I*) and tetrafluoroborate (*II*). As the compounds *I* and *II* have not been described in literature yet, we attempted to prepare them. Results of these attempts and investigations are given in the present report.

EXPERIMENTAL

The UV absorption spectra were measured with a Specord UV-VIS spectrophotometer (Zeiss, Jena) in 10^{-4} M aqueous solution of *I* and *II*. The IR spectra were measured by the Nujol technique with a Perkin-Elmer apparatus model 525.

1-Methylpyridinium Fluoride (*I*)

Procedure A: Solution of 500 mg 1-methylpyridinium iodide² in 50 ml water was precipitated with 5% aqueous silver fluoride to the equivalence point determined potentiometrically. Precipitate of silver iodide was filtered off and the colourless filtrate was submitted to UV spectrophotometry to show the characteristic absorption curve of 1-methylpyridinium chromophore (λ_{\max} 258 nm, $\log \epsilon$ 2.68). All attempts to prepare the crystalline salt *I* by evaporation of water in vacuum at room temperature both in a rotary evaporator and in a dessicator over various dessiccants failed and gave always brown mixtures of decomposition products whose structure was not determined.

Procedure B: Solution of 500 mg 1-methylpyridinium iodide² in 50 ml acetonitrile was precipitated with saturated solution of silver fluoride in the same solvent. The precipitated solid was

collected by suction, thoroughly washed with the solvent, and dried over phosphorus pentoxide in vacuum. The microcrystalline almost colourless product did not melt up to 360°C. IR spectrum: ν_{\max} 672, 768, 1185, 1276, 1370, 1575, and 1628 cm^{-1} ; the starting iodide: ν_{\max} 672, 765, 1182, 1280, 1370, 1575, and 1628 cm^{-1} . For $\text{C}_6\text{H}_8\text{NF}\cdot\text{AgI}$ (347.9) calculated: 4.0%N, found: 3.7% N. On action of water the complex salt decomposes to silver iodide; after its removal by filtration the aqueous solution shows identical UV absorption curve as that from procedure A.

1-Methylpyridinium Fluoroborate (II)

Solution of 500 mg 1-methylpyridinium iodide² in 50 ml water was precipitated with 5% aqueous silver fluoroborate up to the equivalence point as in procedure A. After removal of silver iodide by filtration the filtrate showed a practically identical UV absorption curve as the aqueous fluoride I (λ_{\max} 259 nm, $\log \epsilon$ 2.64). Attempts to prepare the salt II in crystalline form by evaporation of the aqueous solution failed for the same reasons as those with the compound I. Due to insufficient solubility of silver fluoroborate in acetonitrile, the alternative route of preparation of II in this solvent could not be tried.

Calculations

The EHT calculations were carried out with an IBM 370/145 computer according to a modified version of a standard program with automatic generation of input geometries of EHT models from mere basic geometry and parameters. Under these circumstances the calculation of one eigen value lasted about 30 s. The used parametrization is seen in Table I. For the study of 1-methylpyridinium cation (MePy^+) the real geometry³ was used. However, configuration of methyl group was ideal as well as that of tetragonal BF_4^- ion with theoretical angles and the B—F bond lengths 143 pm.

RESULTS AND DISCUSSION

Reactions of 1-methylpyridinium iodide with silver fluoride and tetrafluoroborate gave dilute aqueous solutions of the salts I and II, respectively; their UV spectra

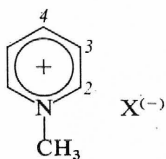
TABLE I

The Parameters Used

$IP(s)$ Ionisation potential of s orbital, $IP(p)$ that of p orbital, S.E. the Slater exponent.

Atom	$IP(s)$, eV	$IP(p)$, eV	S.E.
H	-13.60	—	1.300
C	-21.40	-11.40	1.625
N	-26.00	-13.40	1.950
F	-39.39	-20.86	2.600
B	-15.20	- 8.50	1.300

confirm that the chromophore of MePy^+ was not modified by formation of a covalent bond type C—F or N—F under the conditions of measurement (Fig. 1). Attempts to isolate the salts *I* and *II* in crystalline form failed due to not yet explained irreversible changes taking place after reaching certain higher limit concentrations in water.



I, X = F
II, X = BF_4^-

Nevertheless the results of spectrophotometry of dilute aqueous solutions can be interpreted as a significant argument in favour of the formulas *I* and *II* having ionic bond between MePy^+ and F^- or BF_4^- , respectively.

Geometry of the ion-pairs $\text{MePy}^+ - \text{F}^-$ was investigated both in and outside of the plane of the heterocyclic ring. On the basis of these partial results we restricted ourselves to only out-of-plane interactions of the ion-pair $\text{MePy}^+ - \text{BF}_4^-$, the orientations of BF_4^- anion being, however, varied.

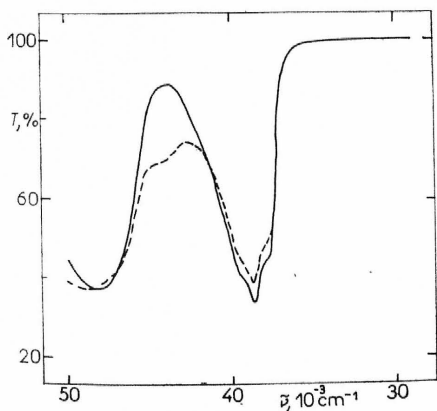


FIG. 1

Ultraviolet Spectra of Aqueous Solutions ($c = 1 \cdot 10^{-4} \text{M}$, $l = 1 \text{cm}$) of the Studied Compounds *I* and *II*

Compound *I* ———, compound *II* - - - - -.

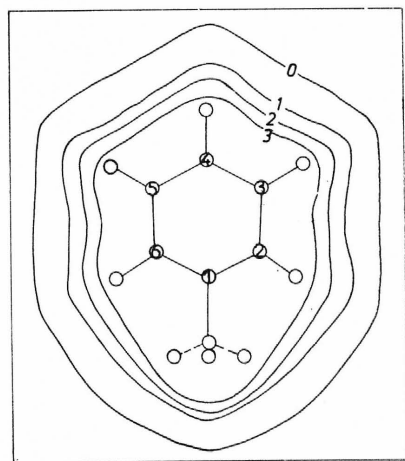


FIG. 2

EHT Energy Map of Ion-Pair *I* for the Anion F^- in Plane of Heterocyclic Ring

The contour line 0 corresponds to $E_{\text{tot}} = -840.0 \text{ eV}$; distance of the contour lines is 5 eV.

We found (as it was the case in our previous study¹, too) that EHT energy of the system leads to only local energy minima, and due to overall repulsive character it reaches convergently the value of sum of energies of the individual ions for the distance of the both partners about 500 pm. Therefore, interpretation is focused on the mentioned minima for which a favourable bonding overlap of MO's and AO's is presumed between the both ions.

Interaction of the ions in the fluoride I. If the anion F^- is located in the plane of the $MePy^+$ heterocycle, then the EHT energy shows no local minima. The situation is represented by the map in Fig. 2 where the zero isoline has the energy $E_{tot} = 840.0$ eV ($E_{MePy^+} + E_{F^-} = 840.26$ eV). Further three isolines correspond to a relatively steep energy increase $\Delta E_{tot} = E_{tot} - E_{MePy^+} - E_{F^-} = 5, 10, \text{ and } 15$ eV. The highest gradients obviously reflect non-bonding repulsions in the region of methyl group and those of the exocyclic C—H bonds, too. From these facts we conclude that only the forces of electrostatic nature not involved in EHT can operate within ion-pair I in planar arrangement.

In case of configuration having F^- anion out of plane of the heterocycle, we first investigated the energy sectional view cutting perpendicularly the atomic centres 1 and 4 and hence also the centre of gravity of positive charge of the ion $MePy^+$. Fig. 3 gives the corresponding EHT energy curves for various distances between the anion F^- and plane of the heterocycle $r = 150, 200, 250$ and 300 pm. The first two curves for the lowest r show the relatively deepest local minima approximately above the centre of the ring, the other two reflect then only a small effect of fading covalent interaction between the species $MePy^+$ and F^- . This fact can be well understood, as non-diagonal elements of the overlap matrix of the system for mutual orbital overlap of the both partners assume negligible values for $r > 250$ pm. With

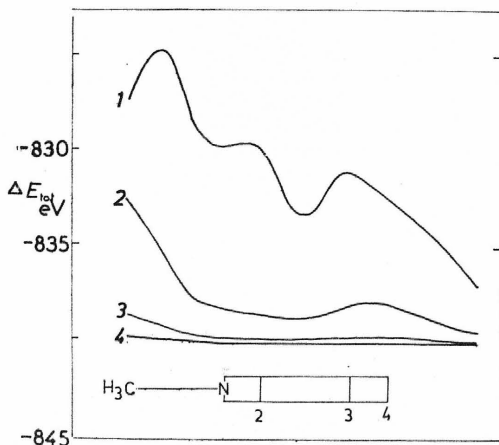


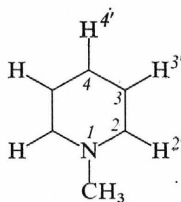
FIG. 3
Dependence of EHT Energy of the Ion-Pair I for the Anion F^- in the Plane Perpendicular to Plane of Heterocyclic Ring and Crossing the Positions 1 and 4

Distance of F^- from the ring plane: r , 1 150 pm, 2 200 pm, 3 250 pm, 4 300 pm.

respect to the generally accepted⁴ effective volume of F^- anion 136 pm the curve for $r = 200$ pm is considered most interesting. Overall energy situation in the plain so remote from that of the heterocycle is demonstrated in the EHT map in Fig. 4. Steepness between the isolines is not (except for the region of methyl group) so marked as in Fig. 3. A local minimum can, however, be seen approximately above the centre of the cyclic system, which can be ascribed to the most favourable spatial localization of the F^- particle from the viewpoint of orbital overlap. On the contrary, the energy maxima above the methyl group and near the CC bond between 3 and 4 positions can be considered to be quite unlikely positions for F^- . The energy contour lines of the ion-pair *I* seem roughly to follow magnitude of EHT electron charges in an isolated $MePy^+$ ion. The fact that no local minimum is present near any carbon centre indicates absence of covalent σ bond between the both partners. Table II gives a comparison of the calculated atomic charges of the isolated ions $MePy^+$ and F^- as well as those of the ion-pair *I* formed by placing F^- in minimum of the map in Fig. 4. Obviously no significant shift of electron density from negative to positive partner occurs, which contradicts the idea of even slight CT-complex of π type⁵. In this respect the situation is analogous to that of pyridine hydrochloride¹.

TABLE II

Comparison of EHT Atomic Charges in the Isolated Ions $MePy^+$ and F^- with those in the Ion-Pair *I*



Position	Q_{MePy^+, F^-}	Q_I
1	0.033	0.029
2	0.315	0.332
3	-0.057	-0.062
4	0.068	0.054
2'	0.026	0.026
3'	0.035	0.035
4'	0.021	0.021
CH ₃	0.238	0.242
F	-1.000	-0.998

Generally, EHT calculation of the compound *I* stand in accord with the finding concerning its ionic behaviour in dilute aqueous solutions.

Interaction of ions in the tetrafluoroborate II. As anion BF_4^- is known⁶ not to form covalent bonds with usual cations, a possible energy minimum above the centre of the cation in the ion-pair of salt *II* can be considered to be another test for verification of applicability of EHT for representation of ionic relation between the both partners. Therefore, we restricted our study to only those EHT models of the ion-pair *II* in which the anion BF_4^- is placed above the plane of the cation MePy^+ . Within these restrictions we investigated three configurations *A*, *B*, and *C* (Fig. 5). One fluorine atomic centre in *A* and three equivalent fluorine centres in *B* and *C* were fixed at the distance of $r = 200$ pm above the plane of the heterocyclic ring. Figure 6 compares EHT energy curves for perpendicular section intersecting the positions 1 and 4 and those of all mentioned configurations of the ion-pair *II* and fluoride *I*. The clearest situation is that of the configuration *A*. A local minimum can be seen here which is located in the same place as that of the ion F^- . On the contrary, a similar minimum of the configuration *B* represents obviously location of one fluorine atom near position 4, whereas that of *C* means location of F near position 1, which stands in accord with coordinates of fluorine atom centres in Fig. 5. The deepest local energy minimum ($\Delta E_{\text{tot}} = 1.17$ eV) corresponds to the configuration *A* which should, therefore, be most preferred energetically, even though the corresponding minima in *B* and *C* are not much higher ($\Delta E_{\text{tot}} = 2.62$ and 2.03 eV, respectively). In this context it is noteworthy that X-ray diffraction analysis of pyridinium salts with SbF_6^- and PF_6^- anions⁷ showed orientation analogous to configuration *B*, the geometry of the interacting anion being, of course, different.

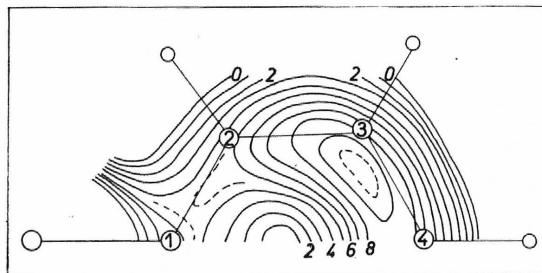


FIG. 4

EHT Energy Map of the Ion-Pair *I* for the Anion F^- Located 200 pm Above the Heterocyclic Ring Plane

The contour line 0 corresponds to $E_{\text{tot}} = -839.0$ eV; distance of individual contour lines are 0.1 eV.

The presumption that EHT curve of the perpendicular section cutting the 1 and 4 positions is (for the configuration *B*) really a consequence of fixation of free fluorine atomic centres of BF_4^- anion above the plane of MePy^+ cation is supported by further energy characteristics in Fig. 7. It is shown here that addition of the curves of three

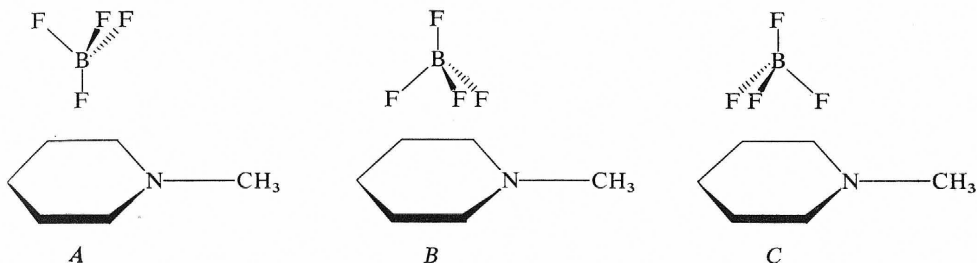


FIG. 5
The Studied Configurations of the Ion-Pair II

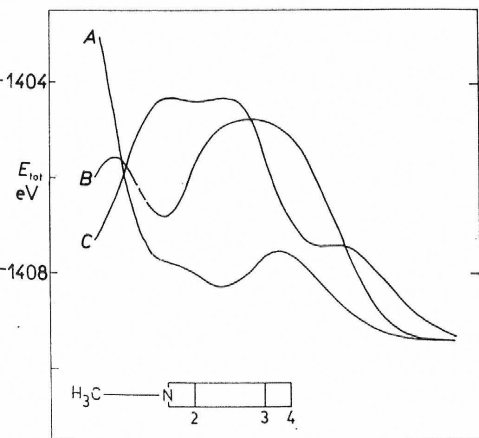


FIG. 6
Dependence of EHT Energy of the Ion-Pairs II in Configurations *A*, *B* and *C* for the Anion BF_4^- in the Plane Perpendicular to the Ring Plane and Crossing it at 1 and 4 Position

Distance of the nearest fluorine atoms from the ring plane is 200 pm.

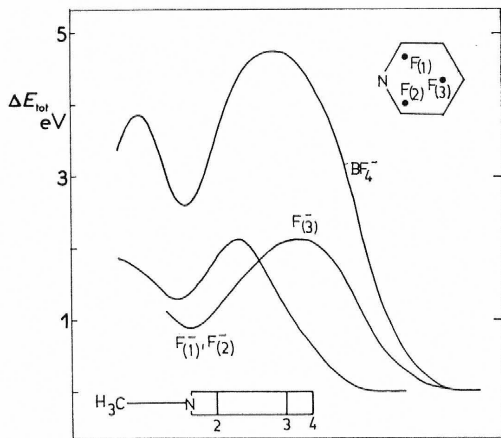


FIG. 7
Comparison of EHT Energies of the Ion-Pairs I and II for the Anions X^- in the Plane Perpendicular to the Ring Plane and Crossing it at 1 and 4 Positions (for $\text{F}_{(3)}^-$ and BF_4^-) and in Coplanar Planes at a Distance 125 pm (for $\text{F}_{(1)}^-$ and $\text{F}_{(2)}^-$)

Position of F^- anions is given in the right-hand upper part.

equivalent orientations of F^- anion gives a curve very close to the calculation result of the whole BF_4^- anion. Hence it can be concluded that EHT calculation of ion-pair $MePy^+ - BF_4^-$ agrees with ionic behaviour of the salt *II* in dilute aqueous solutions.

The authors are indebted to workers of SPS SONP, Kladno for the calculations and to workers of Central Laboratories of their Institute for the measurements of IR spectra.

REFERENCES

1. Kuthan J., Böhm S., Skála V.: This Journal, in press.
2. Karrer P.: *Helv. Chim. Acta* 20, 418 (1937).
3. Rerat C.: *Acta Crystallogr.* 15, 427 (1962).
4. Sharpe A. G.: *Quart. Rev., Chem. Soc.* 11, 49 (1957).
5. Murrell J. N., Kettle S. F. A., Tedder J. M.: *Valence Theory*, p. 332. Wiley, London—New York—Sydney 1965.
6. Sharp D. W. A., in the book: *Advances in Fluorine Chemistry*, Vol. 1 (M. Stancey, J. C. Tatlow, A. G. Sharpe, Eds). Butterworths, London 1960.
7. Copeland R. F., Conner S. H., Meyers E. A.: *J. Phys. Chem.* 70, 1288 (1966).

Translated by J. Panchartek.