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# LCAO-MO CALCULATIONS ON CHEMICAL REACTION PATHWAYS—I

## HYDROGEN BONDING AND CHARGE TRANSFER IN π-COMPLEXES OF ELECTROPHILIC AROMATIC SUBSTITUTION

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**Abstract**—CNDO energy surfaces on the interaction of HF with benzene and pyridine are presented. At the energy minima the HF molecule is situated above one bond of the aromatic ring. At room temperature the HF molecule oscillates rapidly along the ring, since the energy barriers between the individual minima are only small ( ~ 1·2 kcal/mole). Weak interactions between the molecules very similar to ordinary hydrogen bonds are found. There are no energy minima corresponding to Dewar's strong π-complexes. In contrast to the HF/benzene system the π-complex between a proton and benzene ($C_6H_7^+$) is characterized by extended charge transfer. The excess proton is involved in a covalent three-center, two electron bond.

## INTRODUCTION

In the discussion of electrophilic aromatic substitution[1,2] a mechanism had been postulated which involves π-complexes with charge-transfer interaction.[3] The same type of interaction has been proposed for hydrogen bonding[4] and this suggestion has been verified theoretically.[5] In cases where the substrate in aromatic substitution is a proton acid the resemblance of π-complexes and simple hydrogen bonded systems should be a particularly close one.

When benzene is dissolved in anhydrous HF a homogeneous phase results with a 1 : 1 molar composition, which is a bad conductor and does not show any deuterium exchange in the case of deuterated benzene.[6] The interaction is a very weak one, and the species may be described as an association complex. The aromatic system remains nearly undisturbed.[7] Predictions have been made concerning the geometries of such complexes,[7] which could be low-energy intermediates in substitution reactions. In this context they became familiar to organic chemists as π-complexes. However, some trouble arose in the literature due to this nomenclature, and another definition was introduced in which the name "π-complex" was used also for a high-energy complex characterized by extensive charge separation and a strong dative bond to the π-electrons.[8,9] Species of this type are, for instance, postulated as intermediates in some intermolecular rearrangements.[9] For the reasons mentioned above it seemed to be of interest to examine π-complexes in continuing former work done in the field of hydrogen bonding. Previous papers have dealt with semiempirical LCAO-MO calculations of hydrogen-bonded systems. In all structures investigated[10-14] the proton interacted with a lone pair in the acceptor molecule. The CNDO/2 procedure[15-17] was found to be appropriate for a semiquantitative description of hydrogen bonds, nicely reproducing experimental geometries within a limit of accuracy ± 10% as well as with the correct order of relative bond strength. The resulting stabilization energies, however, are to some extent overestimated.[12]

This paper presents calculations on the systems benzene/HF, [benzene/H]$^+$, and pyridine/HF with fixed geometries in the aromatic systems, simulating the postulated $\pi$-complexes. The perturbations in the aromatic ring should only be small, thus justifying our assumption of fixed bond lengths and angles in the arenes. Increased attention is paid to the resulting interaction so as to clarify whether there is any difference between normal hydrogen bonding and $\pi$-bonding or not.

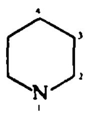
We performed CNDO/2 calculations on all systems, in the case of benzene/HF the influence of one center, two-electron exchange integrals (INDO-method[18]) on the results was examined as well.

## METHOD OF CALCULATION

In performing our calculations we regarded the whole complex as one single entity, and, maintaining fixed values for the arene coordinates, evaluated the total SCF-energy as a function of the six cartesian coordinates of the H and F centers. Of course, the whole six-dimensional energy surface could not be computed, but an approach was made by successive one-dimensional variations.

Proceeding in the point-by-point approach, we started with the calculation of a system with infinitely separated molecules (using geometries shown in Table 1). Any subsequent variations were carried out by treating one distinct coordinate or auxiliary coordinate (cf. following section) as a variable parameter which had to be chosen so as to minimize the energy.

TABLE 1. STARTING GEOMETRIES

| Molecule | Geometry | Origin | Molecule | Geometry | Origin |
|---|---|---|---|---|---|
| HF | $R_{HF} = 1{\cdot}004$ | 1 |  | $R_{CH} = 1{\cdot}08$ | 4 |
| | $R_{HF} = 1{\cdot}006$ | 2 | | $R_{NC_2} = 1{\cdot}34$ | |
| Benzene* | $R_{CC} = 1{\cdot}400$<br>$R_{CH} = 1{\cdot}080$<br>$\sphericalangle$ CCC = 120 | 3 | | $R_{C_2C_3} = 1{\cdot}39$<br>$R_{C_3C_4} = 1{\cdot}40$<br>$\sphericalangle$ CNC = 116 | |
| | $R_{CC} = 1{\cdot}384$<br>$R_{CH} = 1{\cdot}118$ | 1 | | $\sphericalangle$ NCC = 124<br>$\sphericalangle$ $C_2C_3C_4$ = 120 | |

1—CNDO/2 optimized values.
2—INDO optimized values.
3—Standard assumption[21].
4—Experimental[22].

* CNDO/2 optimized values were used in calculations on $C_6H_7^+$ only because of consecutive variation of the ring-geometry[20].

The calculations were performed by means of the semi-empirical SCF-LCAO-MO-methods CNDO/2 and INDO introduced by Pople *et al.*[15-18] The original parametrization was used without modifications in order to make the results comparable with former calculations; besides, this parametrization had been chosen in order to attain good agreement with experimental geometries. Since resulting energy changes are differences between large numbers, an extraordinarily high numerical accuracy had to be presupposed and consequently 64 binary digital units were used in all computation steps. The calculations reported were executed utilizing the FORTRAN IV programs CNDO/2 of Segal (QCPE 91) and CNINDO of Dobosh (QCPE 141*), both slightly modified and adapted to the IBM 360/44 computer at the Institut für Statistik. Universität Wien.

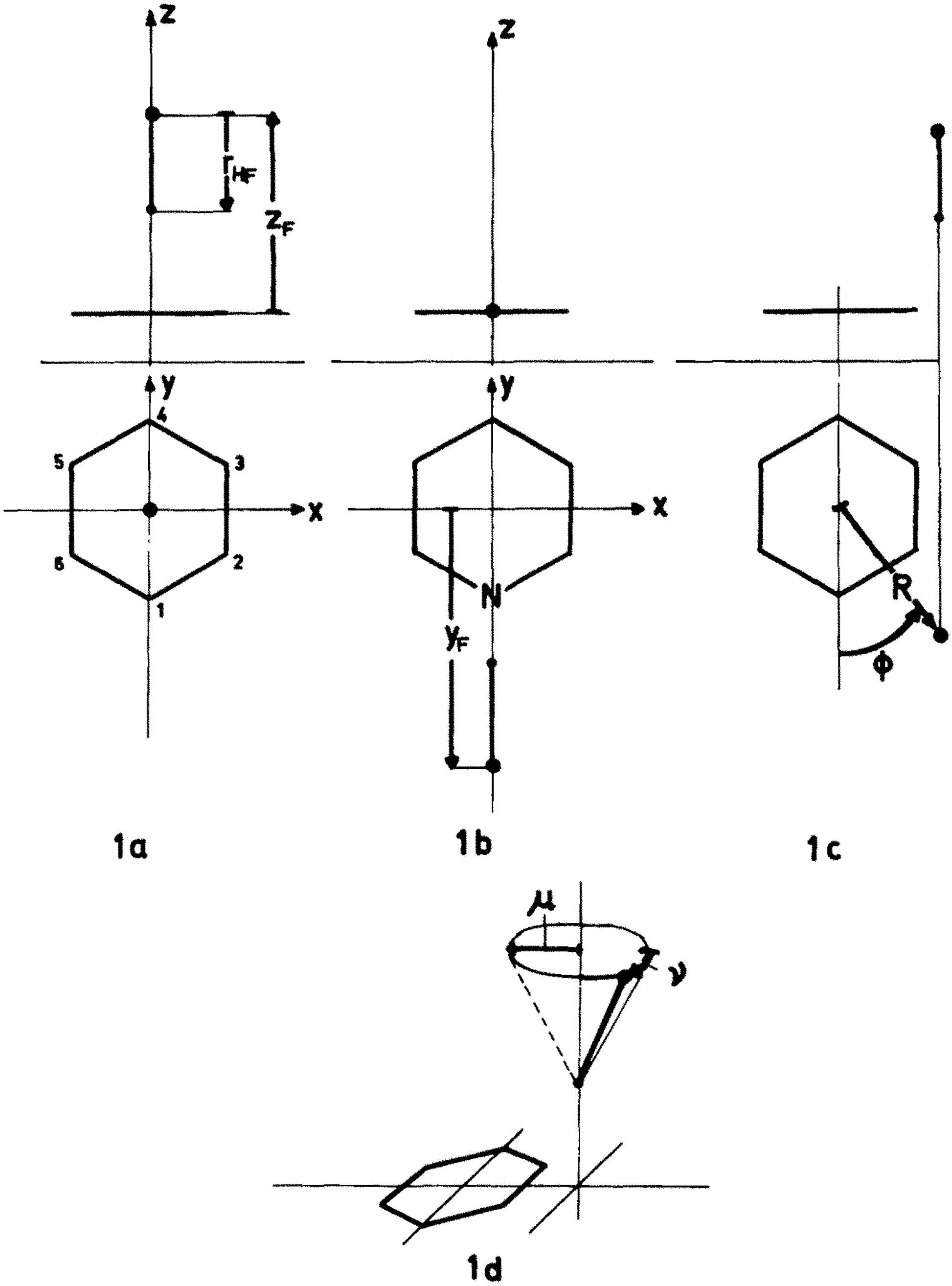


Fig. 1. Choice of coordinate-systems and variation parameters.

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* QCPE = Quantum Chemistry Program Exchange, Bloomington, Indiana.

## ENERGY MINIMIZATION PROCEDURE

In addition to the coordinates of F ($x_F$, $y_F$ and $z_F$) the auxiliary coordinates $r_{HF}$, $R$, $\phi$, $\omega$, $\theta$, $\mu$ and $\nu$ (Figs 1 and 5) were treated as variable parameters. All but one of the independent variables were retained constant in any single variation series. The preceding energy minimum was taken as a starting point for the following variation.

The algorithm used was different for the two types of hydrogen bonds considered. In the case of $\pi$-bonds a variation of $z_F$ (and consequently $z_H$) was carried out in step 1, thus causing an approach of HF to the center of the ring with the HF axis perpendicular to the ring plane (Fig 1a).

Step 2 involved a minimization of the energy of the complex with respect to a variation of $r_{HF}$ (Fig 1a). The subsequent steps 3 and 4 included variations of $x_F$ and $y_F$- or, accordingly, the polar coordinates $R_F$ and $\phi_F$-(Fig 1c). In these steps the two dimensional energy-surfaces described were obtained (Fig 3 and Fig 4).

Continuing with the geometry given by the minimum of this energy surface, variations of $z_F$ and $r_{HF}$ were performed once more in steps 6 and 7, and afterwards the HF axis was tilted, this motion being characterized by the angles $\mu$ and $\nu$ (Fig 1d). Further variations of $x_F$, $y_F$ and $z_F$ (steps 8–10) finished the procedure.

When the nitrogen–lone pair participated in the hydrogen-bond, the approach of the HF molecule was realised initially in the plane of the ring (equivalent to a variation of $y_F$, Fig 1b). In the next step we optimized $r_{HF}$. Finally, the variation of $\omega$ and $\theta$ resulted in a two dimensional energy surface (Fig 5).

## RESULTS

In general, the approach of the molecules leads to "Morse-type" potential functions

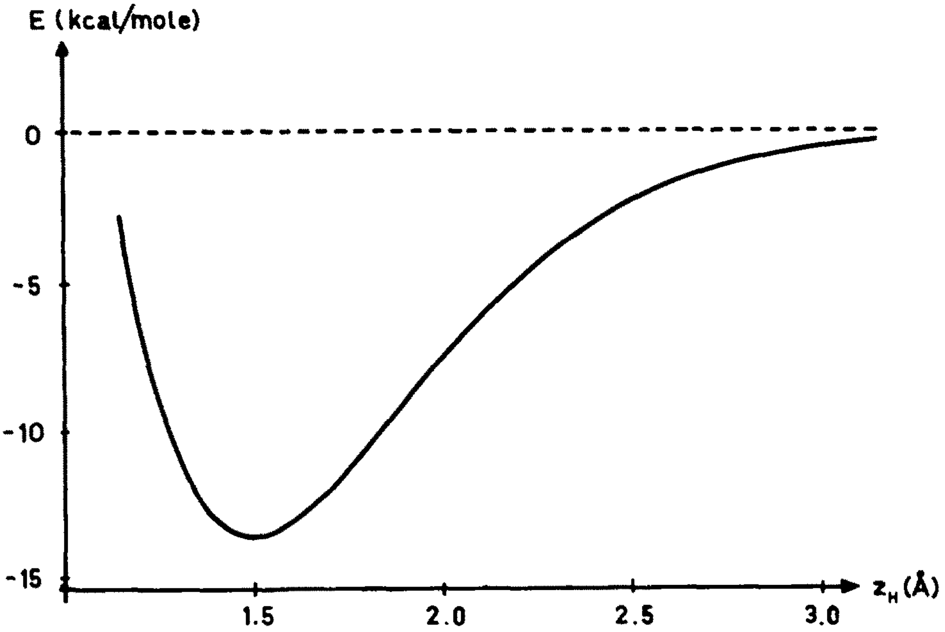


FIG. 2. "Morse-type" energy curve for the approach of HF towards the ring center (congruent for benzene and pyridine)

which on separation reach continuously the correct energies of the isolated molecules (Fig 2). Hence the one-determinantal approximation of the simple CNDO method is able to describe complex formation. It is to be noted, that no activation energy can be detected at all for the formation of $\pi$-complexes.

### *Benzene/HF*

The optimized highly symmetric $\pi$-complex ($C_{6v}$) with the HF molecule on the sixfold symmetry axis of the benzene ring shows a stabilization energy of approximately 14 kcal/mole. As in hydrogen-bonding to lone pairs the INDO procedure leads to a still higher value (16 kcal/mole).

Further optimization of the geometry produces additional stabilization of about 5·5 kcal/mole. At the energy minimum the HF molecule has a bond length of 1·030 Å (1·004 Å in free HF) and is placed in the plane of symmetry bisecting two carbon–carbon bonds. The hydrogen lies 1·53 Å above the plane of the ring and the HF axis is tilted through an angle of 8°. Results of INDO calculations are very similar (Table 2).

TABLE 2. MINIMUM ENERGY GEOMETRIES

| System | Method | $r_{HF}$ | $R_H$ | $\phi_H$ | $z_H$ | $z_F$ | $\nu$ | $\mu$ | $\omega$ | $\theta$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Benzene/HF | INDO | 1·044 | 1·310 | 30,90 or 150 | 1·486 | 2·526 | $\nu = \phi$<br>30, 90 or 150 | 5 | — | — |
| Benzene/HF | CNDO | 1·030 | 1·340 | 30, 90 or 150 | 1·530 | 2·547 | $\nu = \phi$<br>30,90 or 150 |  | — | — |
| Pyridine/HF; $\pi$ | CNDO | 1·027 | 1·339 | 27 | 1·496 | 2·520 | 27 | 4 | — | — |
| Pyridine/HF, l.p. | CNDO | 1·030 | 2·830 | 0 | 0·0 | 0·0 | — | — | 0 | 0 |
| $[\text{Benzene/H}]^{+*}$ | CNDO | — | 1·250 | 30, 90 or 150 | 1·070 | — | — | — | — | — |

* Using CNDO/2 minimized benzene-geometries.

The full two dimensional energy surface obtained by variation of $x_F$ and $y_F$ shows a similar shape for both SCF methods too: an energy groove is found along the carbon–carbon bonds with six minima outside the carbon-skeleton (Fig 3).

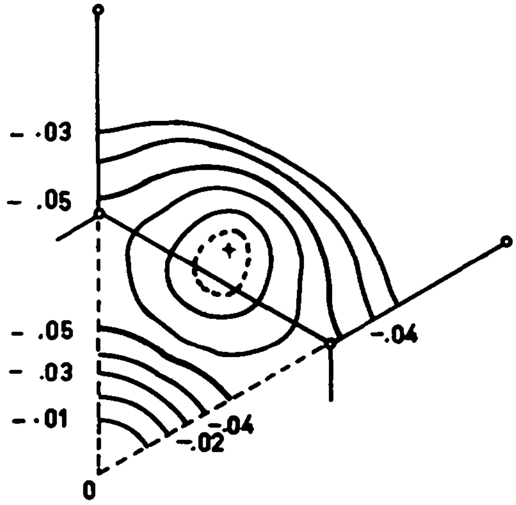


FIG. 3. Energy surface of benzene/HF [$E = E(R,\phi)$]

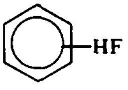
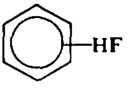
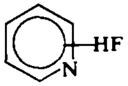
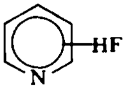
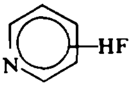
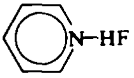
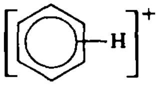
The maximum change of bond orders in benzene is 0·05. In particular, C—H bond orders remain unchanged to a good approximation. This result now justifies our premise of π-complexes with unaltered arene geometries. The HF bond is weakened a little, and bond orders of 0·218 are found for the bonds formed between the proton and the nearest ring carbons.

A charge transfer of 0·077 units from benzene to HF is found. Additional polarization is induced in HF. $\sigma_{HF}$* increases from 0·452 in free HF to 0·587 in the π-complex. Besides, induced polarization arises in the benzene with the positive end of the dipole opposite to HF, just as expected.

*[Benzene/H′]*$^+$.

The π-complexes between benzene and $H^+$ or HF have similar geometries, but the free proton is shifted more towards the ring (Table 2 and Fig 6).

TABLE 3. STABILIZATION ENERGY, CHARGE TRANSFER AND INDUCED POLARIZATION IN AROMATIC π-COMPLEXES

| System | Method | $E_{tot}$[aeu] | $\Delta E$[kcal/mole]* | $\Delta q$† | $\Delta\sigma_{HF}$‡ |
|---|---|---|---|---|---|
|  | INDO | −72·7376 | 23·85 | 0·101 | 0·139 |
|  | CNDO | −75·5652 | 19·44 | 0·077 | 0·135 |
|  | CNDO | −79·3397 | 18·81 | 0·073 | 0·135 |
|  | CNDO | −79·3395 | 18·68 | 0·082 | |
|  | CNDO | −79·3390 | 18·25 | 0·081 | |
|  | CNDO | −79·3406 | 19·37 | 0·093 | 0·147 |
|  | CNDO | −47·6039 | 308·00 | 0·714 | — |

* Stabilization energy with respect to infinitely separated molecules.
† Amount of charge transfer from arene to electrophile.
‡ $\Delta\sigma_{HF} = \sigma_{HF} - \sigma^{\circ}_{HF}$, for definition see footnote on p. 6.

A large amount of the positive charge is delocalized over the arene (Table 3). It is carried essentially by the carbons adjacent to and opposite the proton, and by all hydrogens. Bond orders indicate much stronger bonding than in the benzene/HF case. However, the value ($P_{HC}$ = 0·645) is significantly lower than for ordinary covalent C—H bonds ($P_{HC}$ = 0·95).

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*$\sigma_{HF} = (q_F - 8) - (q_H - 1)$

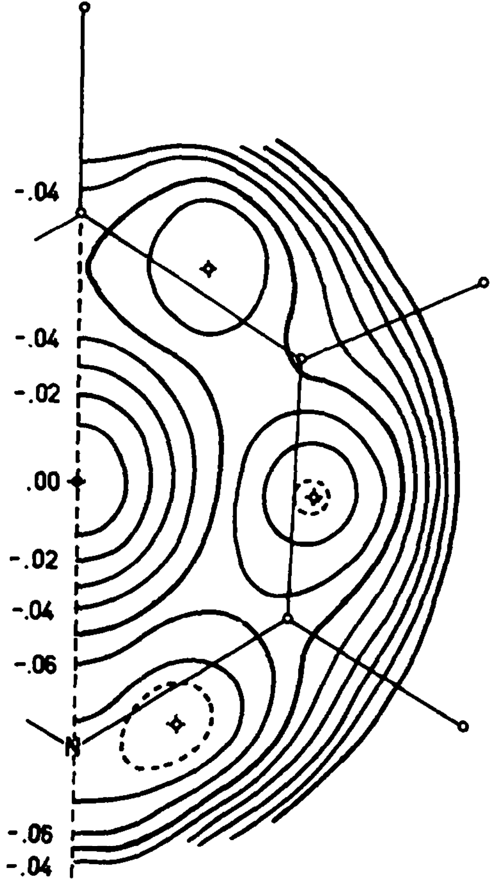


FIG. 4. Energy surface of pyridine/HF [π-complex, $E(R, \phi)$]

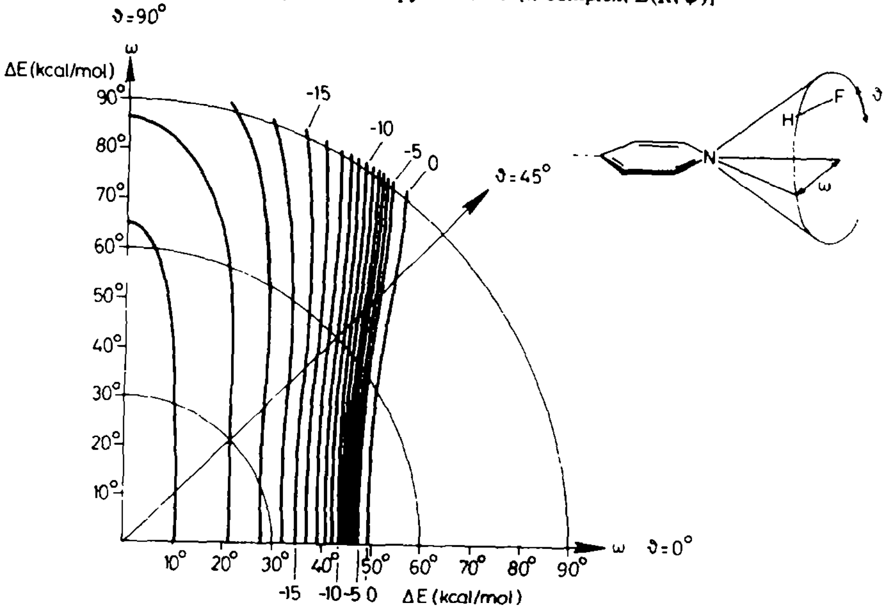


FIG. 5. Energy surface of pyridine/HF [lone pair interaction, $E = E(\omega, \vartheta)$]

### *Pyridine/HF (π-electron interaction)*

All data evaluated resemble the corresponding magnitudes of benzene/HF complexes. The asymmetric charge distribution in pyridine effects the formation of three different and asymmetric minima, the deepest of which is nearest to the nitrogen. Values are collected in Tables 2 and 3 as well as in Fig 4 and 7.

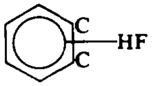
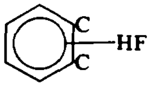
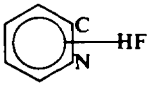
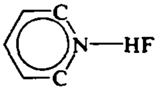
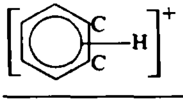
### *Pyridine/HF (lone pair interaction)*

A minimum is found for the HF axis coinciding with the twofold axis of symmetry for pyridine. Distances $r_{HF} = 1{\cdot}03$Å and $r_{NH} = 1{\cdot}43$Å are obtained. The stabilization energy is evaluated as 0·0309 a.e.u. (Tables 2 and 3).

No significant change in energies arises when HF is tilted in a plane perpendicular to the aromatic ring. (This motion is characterized by $\theta = 90°$. Fig 5). On the other hand a rapid loss of stabilization results from motions out of this plane ($\theta = 0°$ in Fig 5).

The N—H bond formed is stronger here than in the comparable π-complex where HF is situated above the nitrogen. The H—F bond is loosened a little more, but all bonds in pyridine remain nearly undisturbed. Furthermore, both charge transfer and induced polarization have higher values than in the case of π-electron interaction (c. f. Tables 2–4).

TABLE 4. SELECTED BOND-ORDERS $P_{AB}^*$ IN AROMATIC π-COMPLEXES

| System | Method | $P_{HF}$ | $P_{HC}$ | $P_{HN}$ |
|---|---|---|---|---|
| HF | INDO | 0·964 | — | — |
| HF | CNDO | 0·973 | — | — |
|  | INDO | 0·883 | 0·247 | — |
|  | CNDO | 0·906 | 0·218 | — |
|  | CNDO | 0·911 | 0·205 | 0·214 |
|  | CNDO | 0·901 | 0·017 | 0·347 |
|  | CNDO | — | 0·647 | — |

* $P_{AB} = \{\sum_{i \in A} \sum_{j \in B} p_{ij}^2\}^{1/2}$.

## DISCUSSION

Several authors have proposed structures for π-complexes between arenes and electrophilic particles.[1,3,7] Our calculations on benzene/HF and pyridine/HF confirm the ideas of H. C. Brown.[7] The interaction in the π-complex is only weak. In the most stable arrangement the electrophilic center is situated above or below one edge of the aromatic molecule, where the π-electron density has its maximum. The electronegative fluorine is tilted away from the $\pi$-electrons. In pyridine the electron cloud is polarized towards the nitrogen and hence the HF-molecule prefers a position above the line between nitrogen and carbon 2. Looking at the energy surface as a whole we find a distinct groove following the hexagon of the aromatic nucleus (Fig 3). The energy barriers between the minima are only small (1·0–1·5 kcal/mole). Accordingly we have to expect the electrophilic particle to jump rapidly from one bond to the other.

Comparison of the energy values in Table 3 indicates that benzene forms stronger $\pi$-complexes than pyridine; this is in agreement with experimental data.

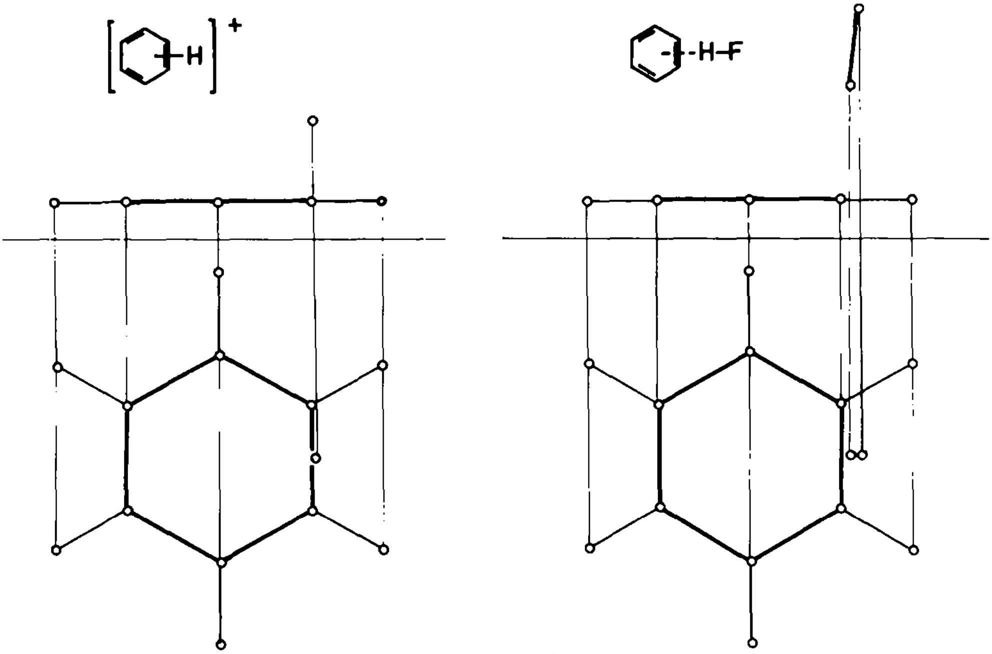


FIG. 6. Minimum energy geometries for benzene/HF and [benzene/H]$^+$ -$\pi$-complexes.

In general, the energy surface for benzene/HF obtained by INDO calculations does not differ greatly from the CNDO-results. Therefore some confidence seems to be justified in these semi-empirical calculations. Energies of interaction between hydrogen bonded molecules calculated by the CNDO method are too large.[12, 19] INDO results are still higher. Hence inclusion of one-center exchange integrals does not bring about any improvement in the discussion of hydrogen bonds to $\pi$-electron systems.

Disregarding solvent effects, the weak $\pi$-complexes represent the first energy minima along the reaction coordinate of aromatic substitution. In our cases the strong $\pi$-complexes proposed by Dewar could evidently be formed by a proton jump from HF to benzene similar to a proton transfer along hydrogen-bonds. In the CNDO energy hypersurface no minimum corresponding to such a structure is found. This result seems reasonable, for in the vapour phase the "ion-pair" **B** has much higher energy than the complex without charge separation **A** and the second energy minimum disappears in the

A B

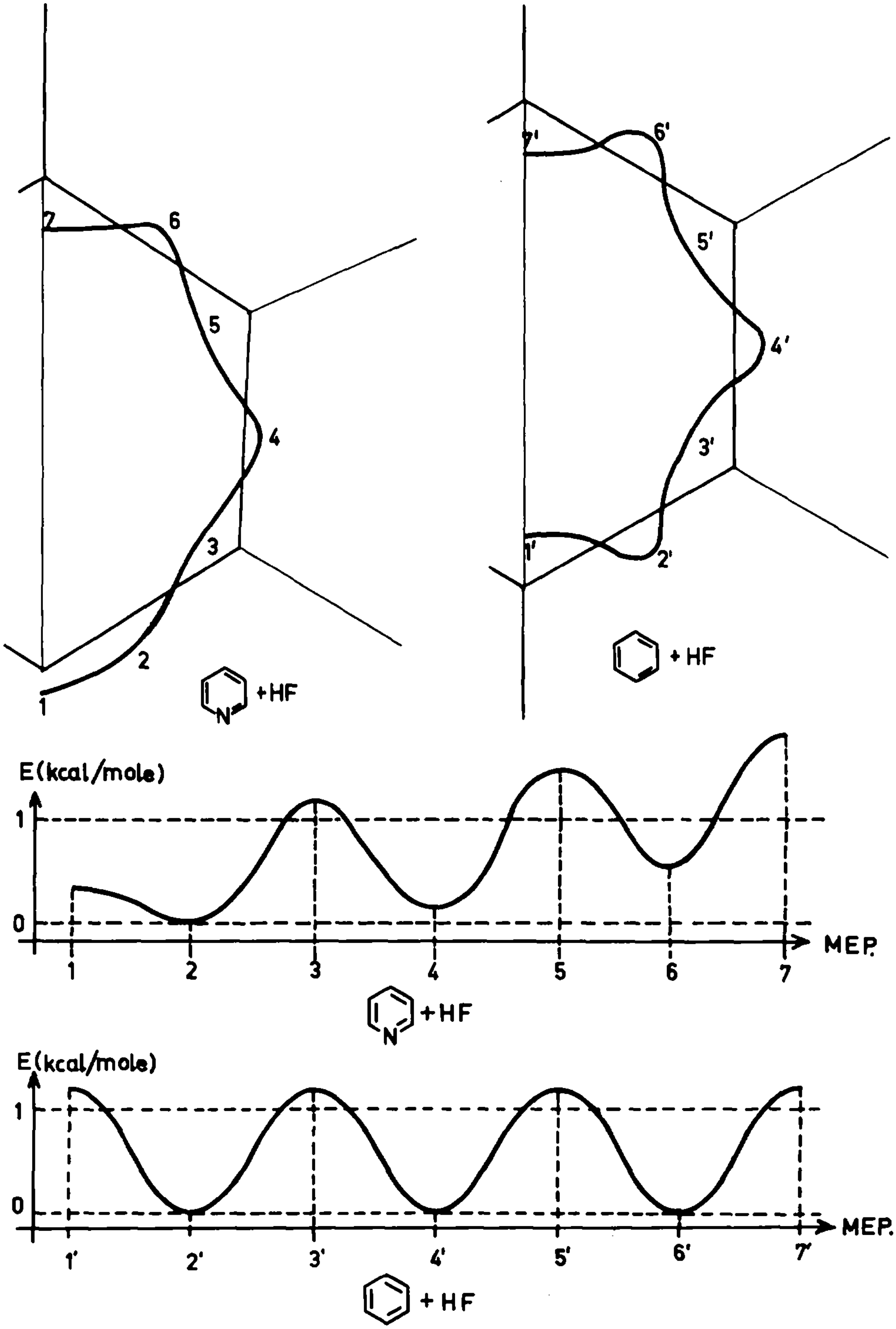
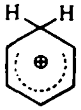


FIG. 7. Minimum energy paths (MEP) and corresponding energy curves in benzene/HF and pyridine/HF π-complexes.

steep slope of the potential curve for the H–F stretching vibration. On the other hand, one has to keep in mind the fact that the CNDO-method does not reproduce the energy of ions correctly. Structures with weak hydrogen bonds to lone pairs have energy for proton transfer calculated too large[19] and an error is introduced in the potential curves. In any case polar solvents would stabilize structure **B** and then the appearance of a second minimum would be more likely.

In contrast to benzene/HF and pyridine/HF the calculations on [benzene/H]$^+$ indicate strong interaction between the proton and the $\pi$-electrons. Thus $C_6H_7^+$ is really a $\pi$-complex according to Dewar's definition. The minimum energy geometry and the bond orders (Tables 2 and 4) show that a covalent three-center bond is formed. The energy of interaction ($\Delta E = 308$ kcal/mole) is certainly too large. This is to be expected, for in general CNDO-calculations overemphasize stabilities of cations.

Preliminary calculations concerning the further reaction path of aromatic substitution indicate that the $\sigma$-complex (**C**) has somewhat higher energy than the $\pi$-complex.



C

However, there are many degrees of freedom in variations of geometry of $C_6H_7^+$ and a lot of structural parameters have to be optimized before one can be certain of knowing the true minimum energy geometries. Further variations might, for instance, lead to additional stabilization of the $\pi$-complex as well, where to a first approximation all C—C bond lengths were taken equal and the benzene ring was assumed planar.[20]

It is interesting to compare hydrogen bonds to lone pairs and to $\pi$-electrons. The striking similarity in elongation of $r_{HF}$ (Table 2), interaction energy ($\Delta E$) and charge-transfer ($\Delta q$) in the different complexes of pyridine/HF (Table 3) indicates that there is no difference in the nature of the binding forces between weak $\pi$-complexes and ordinary hydrogen bonds. Now we can understand easily that no significant loss of stabilization occurs when the HF-molecule is moved from the lone pair to the $\pi$-electron system. The effects of both pure $\pi$-complex and pure hydrogen bond, which are similar in magnitude, are superimposed. However, a rotation of the HF molecule in the plane of pyridine does not allow interaction with $\pi$-electrons at all and the energy increases rapidly outside the direction of the lone pair (Fig 5).

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