EFFECT OF CORRELATION ENERGY ON THE STABILITY OF CLASSICAL AND NONCLASSICAL STRUCTURES OF PROTONATED BENZENE

Dietmar HEIDRICH[a], Pavel HOBZA[b], Petr ČÁRSKY[c] and Rudolf ZAHRADNÍK[c]

[a] *Sektion Chemie, Karl-Marx-Universität, Leipzig, DDR*
[b] *Institute of Hygiene and Epidemiology,*
*Centre of Industrial Hygiene and Occupational Diseases, 100 42 Prague 10 and*
[c] *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*
Czechoslovak Academy of Sciences, 121 38 Prague 2

Use is made of the semiempirical EPCE-F2σ method to establish differences in correlation energy between the characteristic structures of protonated benzene. Calculated correlation energies are combined with available *ab initio* SCF data for which the basis set effect is estimated. The energies so obtained are compared with the results of preselected semiempirical methods. The two approaches are in remarkable agreement in predicting the energy barrier for the H-shift in protonated benzene. The difference in correlation energy between the σ-complex and the face-protonated structure is estimated to be over 90 kJ/mol.

Relative energies of classical and nonclassical structures of protonated benzene $(I-III)$ are of considerable chemical interest and their determination has been attempted by various theoretical methods. *Ab initio* calculations on systems of this

I *II* *III*
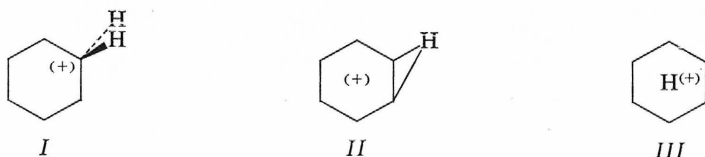
size are of course feasible only with a limited basis set (*e.g.* with the $4-31$G basis set[1]). This implies that the energy predictions must be viewed with some caution since both the basis set and correlation effects may be here important. If semiempirical methods are used, some portion of the correlation energy is implicitly included but a higher reliability is hardly to be expected because of the approximations inherently involved in semiempirical methods. This is particularly true for the predicted energy differences between systems of different structural types. More confidence may be placed in energy predictions for a large system, if the particular

semiempirical method reproduces well the known energy differences for a smaller system of a similar structure. For our purposes, the suitable model systems are the classical (IV) and nonclassical (V) structures of protonated ethylene, for which reliable *ab initio* data, including the correlation energy, are available[2]. We previously[3]

IV   *V*

used these model systems for guidance in the selection of semiempirical methods suitable for the application to structures $I - III$. Among several methods we selected CNDO/2-FK and MINDO/2 which appeared to be the most successful in test calculations on structures IV and V. In this paper, devoted to the estimation of correlation energy in structures $I - III$, we proceed in a similar way. Since the computational method is semiempirical, we test it first on structures IV and V and then we apply it to structures $I - III$.

CALCULATIONS

Correlation energies were calculated by the semiempirical EPCE—F2σ method[4,5] of Pamuk and Sinanoğlu (effective pair correlation energy method with the F2σ approximation). CNDO/2 wave functions and the modified[6] parameter set C were used. For structure $I - V$ we assumed the geometries obtained by complete geometry optimization by means of the CNDO/2-FK method.

RESULTS AND DISCUSSION

The calculated correlation energies are presented in Table I, which also contains the results of reported *ab initio* and semiempirical calculations on structures $I - V$. It is seen that EPCE$-$F2σ reproduces well the difference in correlation energy predicted by CEPA for the two structures of the protonated ethylene. Since the CEPA results may be taken as a reliable standard, the application of EPCE$-$F2σ to the structures of protonated benzene appears to be justifiable. Hence it is possible to draw from entries of Table I the following conclusions: *1*) Correlation energy is higher in bridged forms II and V than it is in classical structures I and IV. The respective difference (stabilization effect) is somewhat larger with protonated benzene. *2*) For the H-shift in protonated benzene, the semiempirical methods predict an energy barrier of about $15 - 30$ kJ/mol. One arrives at the same energy range if the *ab initio* SCF data are corrected for correlation energies. It is, however, assumed that extending the basis set from $4 - 31$G to $6 - 31$G** would be associated with the same effect

of about 35 kJ/mol as is the case for the ethyl cation. *3*) The EPCE$-$F2σ calculations indicate a barrier height toward the lower limit of the estimated range (≈ 15 kJ/mol). Inclusion of a correction for zero-point energies would most likely tend to diminish the barrier height owing to the missing "dissociative" vibrational mode in the saddle point for *II*. It is therefore to be expected that proton migration over the bonds and atoms of the benzene ring is associated with no large energy differences. A different situation is encountered with benzene derivatives for which theoretical studies[3,8,9] predict a higher stability of the σ-complex. *4*) Compared with the σ-complex, the correlation energy stabilizes the π-complex *III* by approximately 95 kJ/mol. This difference may be overestimated. Nevertheless, it demonstrates again the importance of estimating the correlation energy, when *ab initio* SCF calculations are applied to structures of different types. However even the high value of the correlation correction does not alter our prediction concerning the highly unfavourable face-protonation of benzene.

TABLE I

Relative Stabilities[a] of Nonclassical Structures of Prononated Benzene and Ethylene (in kJ/mol)

Method and kind of prediction	Protonated benzene		Protonated ethylene
	bridged form *II*	face-protonated structure *III*	bridged form *V*
Nature of the stationary point[b]	saddle point	maximum	minimum
Ab initio SCF			
4$-$31G	86[c]	highly unfavourable[c]	30·5[d]
6$-$31G**	$\sim 50^{e}$		$-$ 4[d]
Correlation energy			
EPCE$-$F2σ	-35	-94	-20
CEPA[f]			$-23\cdot5$
Semiempirical[g]			
CNDO/2$-$FK	28	290	$-39\cdot5$
MINDO/2	16		$-38\cdot5$

[a] With respect to classical structures *I* and *IV*; [b] refs[1-3]; [c] ref.[1]; [d] ref.[7], with the smaller 4$-$31G basis set structure *V* is a saddle point; [e] estimated on the basis of corresponding calculations on the ethyl cation; [f] ref.[2]; [g] ref.[3].

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