THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2008, *112,* 11017–11020
Published on Web 10/15/2008

Basis Set Superposition Error Effects Cause the Apparent Nonexistence of the Ethene/Benzenium Ion Complex on the MP2 Potential Energy Surface

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Received: August 05, 2008; Revised Manuscript Received: September 29, 2008

In a recent Letter (*J. Phys. Chem. A* 2008, *112*, 6399) Kolboe and Svelle reported that the ethene/benzenium ion complex found by B3LYP transforms into an ethylbenzenium ion when MP2 with a large basis set is used. We find that the failure of MP2 to locate the ethene/benzenium ion complex is due to large basis set superposition errors.

Introduction

In a recent Letter in this journal,[1] Kolboe and Svelle reported a case where B3LYP and MP2 calculations gave conflicting answers: B3LYP predicted the existence of an ethene/benzenium ion complex, whereas the structure transformed into an ethylbenzenium ion when the MP2 method in combination with a large basis set including diffuse functions was employed. According to CCSD and QCISD calculations, the B3LYP result is correct. However, no explanation was given for the apparent failure of MP2.

Over the past few years we have similarly encountered cases, all concerning molecules containing an aromatic ring, where B3LYP and MP2 give discrepant results. For example, for the indole−water complex B3LYP calculations yield two different π-bonded minima with the water molecule bonded to either the pyrrole or the phenol ring,[2] whereas MP2 yield only one minimum with the water molecule interacting with both rings simultaneously.[3,4] The different indole−water structures predicted by MP2 and B3LYP are likely the result of missing dispersion interactions in the B3LYP calculations. More recently, we encountered discrepancies between structures optimized with B3LYP and MP2 while studying the tyrosyl−glycine (Tyr−Gly) dipeptide. In general, MP2 predicts more compact Tyr−Gly structures than B3LYP.[5] More detailed studies on the two conformers that changed most from B3LYP to MP2 geometry optimization showed that neither B3LYP nor MP2, when coupled with the medium-sized basis set 6-31+G(d), is able to predict the correct structures of these conformers.[6,7] B3LYP fails because it cannot describe the dispersion interactions that are important in interactions with aromatic rings, and MP2 fails because the potential energy surface is distorted by large intramolecular basis set superposition error (BSSE) effects (which are known to be large in MP2 but essentially negligible in B3LYP calculations). Similarly, Salvador et al. recently found that intramolecular BSSE effects are responsible for the nonplanarity of benzene and other arenes obtained by correlated ab initio methods.[8]

In the current paper we investigate the cause for the different results obtained by B3LYP and MP2 for the ethene/benzenium ion complex. As ethene/benzenium is a charged complex, it is expected that dispersion is less important than in the neutral systems mentioned above, suggesting that B3LYP may give correct results. Therefore, distortion of the MP2 potential energy surface by BSSE seems the likely reason for the discrepant results observed for the ethene/benzenium ion complex. We show that this is indeed the case, thereby issuing a warning against uncorrected MP2 geometry optimization of molecular systems where BSSE may be significant.

Methodology

Geometry optimizations of the ethene/benzenium ion complex and the ethylbenzenium ion were carried out with B3LYP and MP2, using the 6-31G(d) and 6-311++G(d,p) basis sets. The ethene/benzenium geometry optimizations used the CCSD/6-311++G(d,p) structure provided in ref 1 as the starting geometry. For the ethene/benzenium ion complex, all energies were corrected for BSSE using the counterpoise procedure, taking the benzenium ion and ethene molecules as the fragments. Monomer deformation energies were taken into account. No counterpoise corrections were carried out for the ethylbenzenium ion.

Counterpoise-corrected geometry optimizations of the ethene/benzenium ion complex were carried out at the MP2/6-311++G(d,p) level of theory. Potential energy curves were created by optimizing the C_s-symmetric ethene/benzenium ion at fixed R_{CC} distances between 2.8 and 4.5 Å (see Figure 1 for the definition of R_{CC}). The calculations were carried out with Gaussian 98[9] and Gaussian 03.[10] The B3LYP calculations employed Gaussian's "ultrafine" integration grid.

Results and Discussion

Two dissimilar C_s-symmetric ethene/benzenium ion complexes were found, labeled complex **1** and **2**, which differ in the orientation of the ethene molecule with respect to the benzenium ion (see Figure 1). Both are true minima (with no imaginary frequencies) on the B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) potential energy surfaces, with very similar energies (see Table 1). However, complex **1** is a transition state

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10.1021/jp806986t CCC: $40.75

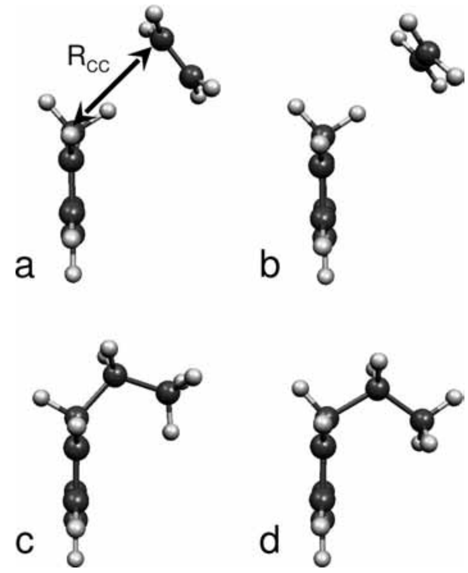

Figure 1. Ethene/benzenium ion complex and the ethylbenzenium ion optimized with B3LYP/6-311++G(d,p): (a) ethene/benzenium ion complex **1**; (b) ethene/benzenium ion complex **2**; (c) eclipsed ethylbenzenium ion; (d) staggered ethylbenzenium ion.

on the MP2/6-31G(d) surface (with a small imaginary frequency of 4 cm^{-1}). When the C_s symmetry was relaxed this structure converged to complex **2**, which is a true minimum at this level of theory. Complex **1** converged to a C_s-symmetric ethylbenzenium ion when the MP2/6-311++G(d,p) method was employed. However, counterpoise-corrected geometry optimization at this level of theory did yield an ethene/benzenium ion complex. This suggests that the apparent nonexistence of the ethene/benzenium ion complex on the MP2/6-311++G(d,p) potential energy surface is due to large BSSE effects at this theory level. We explore this in more detail below.

As compared to the other geometries, the CP-corrected MP2/6-311++G(d,p) geometry exhibits a shorter distance between the benzenium ion and ethene fragments (R_{CX} in Table 1), and a more parallel arrangement of these (τ_{plane} in Table 1). These structural features are consistent with the large interaction energy predicted by MP2. To investigate this further, we performed CCSD(T)/6-311++G(d,p) calculations at the CP-corrected MP2/6-311++G(d,p) geometry. The counterpoise-corrected CCSD(T)/6-311++G(d,p) interaction energy (computed using the MP2/6-311++G(d,p) deformation energies) is −17.32 kJ/mol, i.e., 6 kJ/mol less than the corresponding MP2 result. This indicates that MP2 overestimates the ethene/benzenium ion interaction, though the different interaction energies could also be partially due to differences in the MP2 and CCSD(T) minimum-energy geometries. A counterpoise-corrected CCSD(T) geometry optimization would be required to unequivocally resolve this issue.

Complex **2** is a transition state on the uncorrected MP2/6−311++G(d,p) potential energy surface (imaginary frequency: 24 cm^{-1}) and transformed into an ethylbenzenium ion (with a staggered orientation of the ethyl fragment) when the symmetry was relaxed. Counterpoise-corrected geometry optimization of the C_s-symmetric structure of complex **2** yielded a complex with an interaction energy similar to that of the structure obtained by standard geometry optimization, but with a larger distance between the benzenium ion and ethene fragments, and a slightly less parallel arrangement of the benzenium and ethene fragments. These structural differences are consistent with an overestimated interaction (caused by BSSE) in the uncorrected structure. When the symmetry was relaxed, counterpoise-corrected geometry optimization led to complex **1**, confirming that complex **2** is not a true minimum on the counterpoise-corrected MP2/6-311++G(d,p) surface.

Table 1 shows that the BSSE is larger in the MP2/6-311++G(d,p) calculations than in the MP2/6-31G(d) calculations. Naturally, the BSSE must vanish at the complete basis set limit, and must therefore at one point decrease with increasing basis set quality. However, before that point is reached it is possible that the BSSE increases with increasing basis set size, as larger basis sets allow more opportunity for the "basis-function stealing" process that underlies BSSE. This is particularly the case when diffuse functions are included in the basis set, as these are more easily accessible to the other fragment. In contrast, the BSSE is smaller in the B3LYP/6-31++G(d,p) calculations than in the B3LYP/6-31G(d) calculations. This reflects the smaller basis set dependence of density functional theory, which implies that 6-311++G(d,p) is already close to the B3LYP complete basis set limit.

TABLE 1: Energetic and Structural Parameters of the Ethene/Benzenium Ion Complexes 1 and 2 Computed at Different Levels of Theory

method/basis set	energy (E_h)[a]	ZPE (E_h)[b]	minimum?[c]	R_{CX} (Å)[d]	τ_{plane} (deg)[e]	ΔE^{noCP} (kJ/mol)[f]	ΔE^{CP} (kJ/mol)[g]	BSSE (kJ/mol)	ΔZPE (kJ/mol)[h]
				Ethene/Benzenium Ion Complex **1**					
B3LYP/6-31G(d)	−311.151982	0.163095	yes	2.37	142.0	−24.89	−21.60	−3.28	2.29
B3LYP/6-311++G(d,p)	−311.233494	0.161610	yes	2.43	142.0	−18.26	−17.41	−0.85	1.99
MP2/6-31G(d)	−310.043148	0.164841	TS	2.31	153.7	−26.99	−20.50	−6.49	2.36
MP2/6-311++G(d,p)	converged to an ethylbenzenium ion complex								
MP2/6-311++G(d,p)/CP	−310.226768		yes	2.25	170.9	−31.72	−23.37	−8.35	
CCSD/6-311++G(d,p)[i]	−310.296701			2.50	158.5	−20.62	−15.00	−5.62	
				Ethene/Benzenium Ion Complex **2**					
B3LYP/6-31G(d)	−311.151949	0.163112	yes	2.37	138.8	−24.89	−21.52	−3.37	2.33
B3LYP/6-311++G(d,p)	−311.233464	0.161632	yes	2.44	137.9	−18.19	−17.33	−0.86	2.05
MP2/6-31G(d)	−310.043178	0.164898	yes	2.32	149.1	−27.20	−20.58	−6.63	2.50
MP2/6-311++G(d,p)	−310.226246	0.162106	TS	2.16	168.3	−30.66	−21.99	−8.67	4.54
MP2/6-311++G(d,p)/CP	−310.226528		TS	2.30	162.5	−30.03	−22.73	−7.29	

[a] Counterpoise-corrected total energy. [b] Zero-point energy of the ethene/benzenium ion complex. [c] TS: structure is a first-order transition-state structure. [d] X is the midpoint of the C=C bond of the ethene molecule. [e] Angle between the planes of the benzenium and ethene molecules. [f] Uncorrected ethene−benzenium interaction energy. [g] Counterpoise-corrected ethene−benzenium interaction energy. [h] Zero-point vibrational correction to the interaction energy (computed using harmonic vibrational frequencies). [i] CCSD structure taken from ref 1.

TABLE 2: Energetic Parameters of the Staggered and Eclipsed Ethylbenzenium Ion Complexes Computed at Different Levels of Theory

method/basis set	energy (E_h)	ZPE (E_h)[a]	minimum?[b]	ΔE (kJ/mol)[c]
		Eclipsed Ethylbenzenium Ion		
B3LYP/6-31G(d)	−311.183668	0.168117	TS	11.95
B3LYP/6-311++G(d,p)	−311.259807	0.166488	TS	11.91
MP2/6-311++G(d,p)	−310.268477	0.168496	TS	9.78
		Staggered Ethylbenzenium Ion		
B3LYP/6-31G(d)	−311.188219	0.168287	yes	0.00
B3LYP/6-311++G(d,p)	−311.264345	0.166750	yes	0.00
MP2/6-311++G(d,p)	−310.272200	0.168355	yes	0.00

[a] Zero-point energy of the ethylbenzenium ion complex. [b] TS: structure is a first-order transition-state structure. [c] Energy relative to the staggered ethylbenzenium ion.

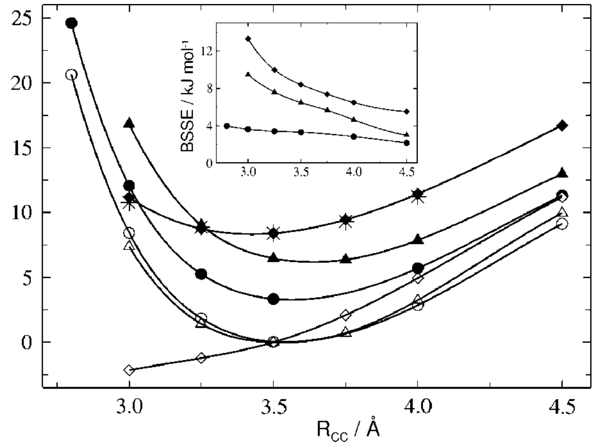

Figure 2. Potential energy profiles for R_{CC} variation. Circles: B3LYP/6-31G(d) profiles. Triangles: MP2/6-31G(d) profiles. Diamonds: MP2/6-311++G(d,p) profiles. Solid symbols: counterpoise-corrected results. Open symbols: uncorrected results. The uncorrected energies at $R_{\mathrm{CC}} = 3.5$ Å were taken as the reference for the relative energies. Stars: counterpoise-corrected MP2/6-311++G(d,p) profile computed using benzene, H^+ and ethene as the fragments in the counterpoise calculation. For more facile comparison with the corresponding profile that used the benzenium ion and ethene molecules as the fragments, the two profiles have been made to coincide at $R_{\mathrm{CC}} = 3.5$ Å. The inset shows the BSSE as a function of R_{CC}.

At all levels of theory the ethylbenzenium ion is more stable than the ethene/benzenium ion complex (by 80−120 kJ/mol, using the total energies listed in Tables 1 and 2). Also for this ion two different C_s-symmetric structures were found, with either an eclipsed or a staggered orientation of the ethyl fragment (see Figure 1). The eclipsed structure is a saddle point with all methods employed (imaginary frequency 212−230 cm^{-1}).

The potential energy profiles for R_{CC} variation in the ethene/benzenium ion complex **1** are shown in Figure 2. The uncorrected and counterpoise-corrected B3LYP curves are almost identical and show a clear minimum at ∼3.5 Å. The uncorrected MP2/6-31G(d) curve also displays a minimum around 3.5 Å, which shifted to a slightly larger value after counterpoise correction. However, the uncorrected MP2/6-311++G(d,p) curve just drops off with decreasing R_{CC}, in agreement with the observation that geometry optimization at this level of theory yields the ethylbenzenium ion. After counterpoise correction a minimum appeared in the MP/6-311++G(d,p) curve. The MP2/6-311++G(d,p) BSSE steeply increases with decreasing R_{CC} (see the inset), thereby pulling down the curve at shorter distances to such an extent that the minimum disappears. The inset also shows that the BSSE is much smaller in the B3LYP calculations, particularly when the 6-311++G(d,p) basis set is used. The BSSE is by no means negligible in the MP2/6-31G(d) calculations, but apparently not sufficiently large to distort the potential energy curve such that the minimum is hidden. Note that also CCSD/6-311++G(d,p) produces a sizable BSSE, and also at this level counterpoise-corrected geometry optimization may be necessary to obtain a reliable structure of the ethene/benzenium ion complex.

Also shown in Figure 2 is the MP2/6-311++G(d,p) profile obtained using benzene, H^+ and ethene as the fragments in the counterpoise calculation. These fragments would be the better choice if one were interested in computing the profile for transition to the ethylbenzenium ion, as this transition would involve elongation, and eventually disruption, of the protonated benzenium C−H bond. It is clear that the choice of fragments does not noticeably affect the profile within the R_{CC} range considered.

Conclusion

Both the ethylbenzenium ion and the ethene/benzenium ion complex exist on the B3LYP and MP2 potential energy surfaces. However, when employing a large basis set with diffuse functions in the MP2 calculations, the ethene/benzenium minimum is missing on the uncorrected surface due to large basis set superposition errors, and uncorrected geometry optimization yields an ethylbenzenium ion structure. This shows that care has to be taken when employing MP2 geometry optimization of molecular systems where BSSE is expected to be large (such as molecules containing aromatic rings). If feasible, counterpoise-corrected geometry optimization should be used.

Acknowledgment. T.v.M. gratefully acknowledges the Royal Society for their support under the University Research Fellowship scheme, and EaStCHEM for computational support via the EaStCHEM Research Computing Facility.

Supporting Information Available: Cartesian coordinates of the ethene/benzenium ion complex and the ethylbenzenium ion optimized at different levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP806986T