THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2008, *112,* 6399–6400
Published on Web 07/01/2008

Does an Ethene/Benzenium Ion Complex Exist? A Discrepancy between B3LYP and MP2 Predictions

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Received: April 01, 2008; Revised Manuscript Received: June 19, 2008

To investigate the possible existence of a complex between the benzenium ion and ethene, computations employing B3LYP and MP2 were carried out. The two methodologies gave conflicting answers; B3LYP confirmed the existence, but according to MP2, the structure found by B3LYP transforms into an ethylbenzenium ion. Computations utilizing the CCSD and QCISD methods showed the B3LYP result to be correct; 21 kJ/mol is needed to separate the two moieties.

Introduction

The possible existence or nonexistence of complexes (the word complex is restricted to mean weak π-type interactions) between benzenium ions and alkenes or benzene and alkenium ions is of interest to mass spectroscopists.[1–9] To bring further information on this subject, we have studied the possible existence of a stable (i.e., a local energy minimum state) complex between ethene and a benzenium ion. In this connection, we have encountered a case where the two commonly applied computation schemes, MP2 and density functional theory (DFT) represented by the B3LYP functional, are at variance.

In cases where possible weakly bound complexes are studied, it is not unusual to compare the computational DFT (in this case B3LYP) results with those obtained from the MP2 method and base the evaluation of the merits of the DFT method on basis of the closeness to the MP2 result. However, in the present case, B3LYP predicted the existence of a stable benzenium ion/ethene complex, whereas MP2 predicted that this complex would transform, without any activation energy barrier, into ethylbenzenium (ethyl-1H-benzene).

To find out which result is correct and resolve the uncertainty caused by this lack of agreement between the two quantum chemical methods, further geometry optimizations on the complex structure predicted by B3LYP were carried out at the CCSD/ and QCISD/6-311++G(d,p) levels.

CCSD and QCISD both found the complex to be a stable structure, albeit with slightly changed positions of the ethene molecule relative to the benzenium ion compared to the result from B3LYP. The calculated structures are all very similar and can be represented by Figure 1, which is the CCSD result. The complex has C_s symmetry, and the symmetry plane is the paper plane. It is clearly seen that the ethene molecule is situated quite far from the benzenium ion, typical for a very weak interaction.

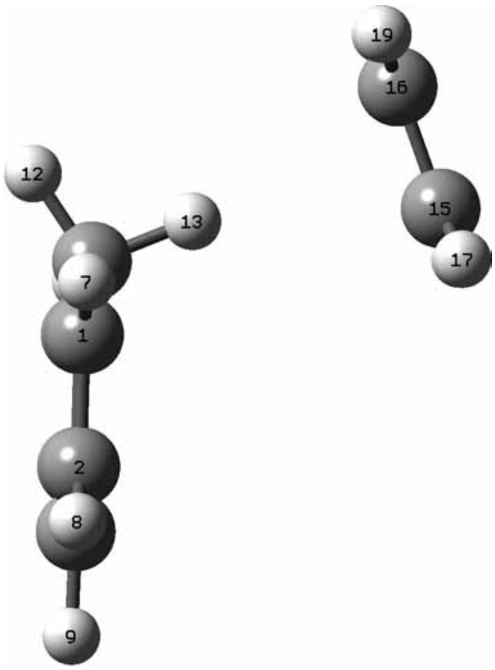

Figure 1. The benzenium ion/ethene complex.

The full structure description is given as Supporting Information, but the more interesting geometric characteristics are given in Table 1 with the same atomic numbering as that used in Figure 1.

Computational Section

All computations that are reported here were carried out by means of the Gaussian 03 program package.[10] It is known that the outcome of quantum chemical computations tends to depend strongly on the quality of the basis set that is being used. We have therefore studied a range of basis sets: 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311++G(d,p), cc-pVTZ, and GTlarge.[10] In addition to the computations on B3LYP and MP2, these basis sets were also utilized for Hartree−Fock calculations.

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10.1021/jp8027879 CCC: \$40.75 © 2008 American Chemical Society

TABLE 1: Important Interatomic Distances (Å) in the Ethene/Benzenium Ion Complex[a]

level of theory	$H^{13}-C^{15}$	$H^{13}-C^{16}$	$C^{6}-H^{13}$
B3LYP/6-311++G(d,p)	2.516	2.520	1.133
QCISD/6-311++G(d,p)	2.583	2.551	1.124
CCSD//6-311++G(d,p)	2.601	2.570	1.124

[a] Atomic numbering as that in Figure 1.

The B3LYP calculations were carried out with the ultrafine integration grid as defined in Gaussian 03, and for all calculations, the convergence criteria were set to tight (opt = tight). The CCSD and QCISD methods' calculations, which were used to settle the issue whether the complex represents a stable state or not were, because of the long computation times, only carried out with the 6-311++G(d,p) basis set. The smaller basis sets were considered uninteresting.

Results and Discussion

As is often found, the geometrical structure obtained from B3LYP showed little dependence on the choice of basis set, and a structure like the one in Figure 1 was invariably found.

The computations based on the Hartree−Fock level of theory gave essentially the same structure as the B3LYP scheme. A stable complex was found, irrespective of the basis set quality.

Quite a different situation was encountered when MP2 calculations were carried out. When the basis sets 6-31G(d), 6-31G(d,p), and 6-31+G(d,p) were utilized, a stable complex, essentially the same as that in Figure 1, was found. However, when structure optimizations (always with a starting geometry equal to the B3LYP/6-311++G(d,p) geometry) were carried out with large basis sets, the structure finally converged to an ethylbenzenium ion (ethyl-1H-benzene) and not a complex like that in Figure 1. The calculations were carried out with the basis sets 6-311++G(d,p), cc-pVTZ, and GTlarge. A C−C bond, C^3-C^{15} (C^3 is partially covered by H^8 in Figure 1) was formed. This means that when MP2 calculations with a large basis set are carried out, no stable benzenium ion/ethene is found. The potential energy surface in this case displays a monotonic decrease toward an alkylbenzenium structure. However, calculations at the much higher level of theory, QCISD and CCSD with the basis set 6-311++G(d,p), showed that there is a local potential surface minimum corresponding to a stable benzenium ion/ethene complex. The Hessian matrix calculated in the B3LYP case shows clearly that the ethene molecule can move quite freely relative to the benzenium ion; the lowest vibrational frequency is only 5.4 cm^{-1} (a rotational vibration about an axis nearly coinciding with the C^6-H^{13} axis), and the five lowest vibrations are all below 100 cm^{-1}. A low vibrational frequency obviously implies that movement along that particular mode costs very little energy, and all of these low-frequency vibrations are related to movements of the ethene molecule relative to the benzenium ion. Calculations based on the G3−B3 formalism in Gaussian 03 show that at 0 K, the energy difference between the complex and the separated benzenium ion and ethene is 20.7 kJ/mol. The corresponding energies (no ZPE correction) based on CCSD (at the CCSD geometry) and B3LYP (at the B3LYP geometry) are 20.6 and 18.3 kJ/mol, respectively.

Further details about the ethylbenzenium system will be published elsewhere. We consider the disagreement between B3LYP and MP2 to be important because it emphasizes that when we are interested in unusual molecular structures and molecular properties, the standard methods may fail. In a case like the present, it is doubtful that the weakly bonded complex can be studied directly experimentally; therefore, the main source of information will be theory.

Conclusion

It has been shown that an ethene molecule and a benzenium ion form a complex. The complex is not strongly bonded, but about 21 kJ/mol is needed to dissociate it. This result is in agreement with the B3LYP methodology. The MP2 method fails to recognize the complex as a stable entity and predicts that it will contract to an ethylbenzenium ion. Computations utilizing a higher level of theory, that is, CCSD and QCISD, confirm that the B3LYP result is qualitatively correct.

Supporting Information Available: *XYZ* coordinates for the benzenium/ethene complex in Figure 1 as determined by CCSD/6-311++D(d,p). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Audier, H. E.; Monteiro, C.; Robin, D. *New J. Chem.* **1989**, *13*, 621–624.

(2) Berthomieu, D.; Audier, H. E.; Denhez, J. P.; Monteiro, C.; Mourgues, P. *Org. Mass Spectrom.* **1991**, *26*, 271–275.

(3) Berthomieu, D.; Brenner, V.; Ohanessian, G.; Denhez, J. P.; Millié, P.; Audier, H. E. *J. Am. Chem. Soc.* **1993**, *115*, 2505–2507.

(4) Berthomieu, D.; Brenner, V.; Ohanessian, G.; Denhez, J. P.; Millié, P.; Audier, H. E. *J. Phys. Chem.* **1995**, *99*, 712–720.

(5) Harrison, A. G.; Wang, J. Y. *Int. J. Mass Spectrom.* **1997**, *160*, 157–166.

(6) Holman, R. W.; Gross, M. L. *J. Am. Chem. Soc.* **1998**, *111*, 3560–3565.

(7) Miklis, P. C.; Ditchfield, R.; Spencer, T. *J. Am. Chem. Soc.* **1998**, *120*, 10482–10489.

(8) Heidrich, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3208–3210.

(9) Ishikawa, Y.; Yilmaz, H.; Yanai, T.; Nakajima, T.; Hirao, K. *Chem. Phys. Lett.* **2004**, *396*, 16–20.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2004.

JP8027879