Long-lived Gas-phase Dianions Containing Tetrahedrally Coordinated Oxygen Atoms: $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$

Andreas Dreuw,* Heike Schweinsberg, and Lorenz S. Cederbaum

Theoretische Chemie, Physikalisch-Chemisches Institut Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

Received: September 4, 2001

Searching for new stable gas-phase dianions, the long-lived dianions $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$ dianions have been discovered computationally, which are the first dianions that contain tetrahedrally coordinated oxygen atoms. In contrast to known hypermetalated systems such as OLi_4 or OAl_4, where the ligand system forms a bound cluster itself, these dianions have repelling ligands and show characteristics of covalently bond molecules.

Introduction

The existence of small multiply charged negative ions in the gas phase is by no means trivial, because such systems have to compensate the strong electrostatic repulsion of the excess negative charges. Indeed, this is the reason most of the small dianions known from condensed phases spontaneously emit an electron when they are brought into the gas phase. The most prominent examples are CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}, which are now well established to be electronically unstable dianions.[1−5] They can only exist in condensed phases due to the stabilizing effects of the surrounding molecules or counterions. Nevertheless, several dianions have already been found experimentally and theoretically to form stable species in the gas-phase, e.g., LiF_3^{2-},[6] BeF_4^{2-},[7,8] C_7^{2-},[9,10] SiC_6^{2-},[11,12] BeC_4^{2-},[13,14] $PtCl_6^{2-}$,[15] etc. For an overview the reader is referred to reviews in this field.[16−19]

In general, a free stable gas-phase dianion possesses two major properties: it has to be stable with respect to electron loss and with respect to fragmentation of the nuclear framework. The first requirement is quantified by the electron detachment energy (EDE), which is calculated as the difference between the potential energy surfaces of the monoanion and the dianion. The stability with respect to fragmentation is examined by calculating the energy difference between the dianion and the fragmentation products. When the sum of the energies of the fragmentation products is higher in energy than the energy of the dianion, it is classified to be thermodynamically stable with respect to fragmentation. Otherwise it can be kinetically stable, if the fragmentation is hindered by a sufficiently high energy barrier.

Searching for new stable gas-phase dianions, we have examined mixed O−BN and O−C_2 dianions with standard quantum-chemical methods. Besides stable chainlike and branched isomers of the $OB_4N_4^{2-}$ and OC_8^{2-} dianions, which will be published elsewhere, we have found two remarkable long-lived isomers $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$, which are to our best knowledge the first molecules that possess a tetrahedrally coordinated oxygen atom in a covalent bonding situation. Of course, the normal valence expectation of oxygen may be exceeded in crystals and glasses, but so far the only known individual molecules that possess a tetra or higher coordinated oxygen atom are hypermetalated species. For instance, hyperlithium complexes such as Li_4O and Li_5O have been discovered computationally[20] and later observed mass spectrometrically,[21] and the existence of a structurally surprising square−planar Al_4O hyperaluminum molecule has been predicted theoretically.[22] The substantial stability of such hypermetalated molecules is due to their high degree of ionic character as well as bonding interactions between the ligand metal atoms. In some sense, hypermetalated species can be regarded as metal clusters bound ionically to a centrally located “impurity” heteroatom.[22] This is contrary to the usual bonding situation in covalent complexes where the only bonding interactions are between the central atom and its attached atoms or ligands, e.g., in methane, where the ligand−ligand interactions are repulsive.

Computational Details

The data at the independent particle level were obtained using the standard self-consistent field (SCF) restricted Hartree−Fock (RHF) method for the closed-shell dianions and the restricted open-shell Hartree−Fock (ROHF) approach for the open-shell monoanions. To include correlation, we have employed the Møller−Plesset perturbation theory of second order (MP2) and the coupled-cluster singles plus doubles (CCSD) method. A detailed basis-set study at the Hartree−Fock (HF) level of theory has shown that it is sufficient to use a standard Dunning double-ζ plus polarization basis-set (DZP),[23] which is further augmented with an additional s-type and a p-type diffuse function, to take account for the diffuse character of the outer valence orbitals of the dianions.[24] It is not necessary to apply larger basis sets, such as triple-ζ basis sets, since this has only negligible effects on the results. The geometries of the examined $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$ dianions have been optimized at the RHF, MP2, and CCSD levels of theory and all presented structures correspond to minima on the potential energy surfaces, i.e., all harmonic frequencies possess real values. The electron detachment energies (EDEs) of the dianions are given by Koopman’s Theorem (KT), which relates the RHF orbital energy of the highest occupied orbital to the EDE and the so-called Δ-methods. The Δ-methods comprise the computation of the difference of the total energies of the monoanion and the dianion. In this work we have employed ΔSCF, ΔMP2, and ΔCCSD.

---

* Corresponding author. E-mail: andreas.dreuw@tc.pci.uni-heidelberg.de. FAX: +49-6221-545221.

10.1021/jp013377f CCC: $22.00

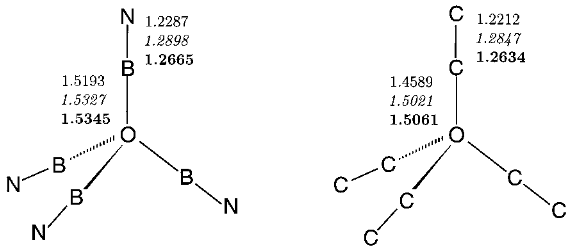

Figure 1. Structures of the dianions $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$. The optimized bond lengths are given in Å at the SCF (plain text), MP2 (italics), and CCSD (bold face) levels of theory.

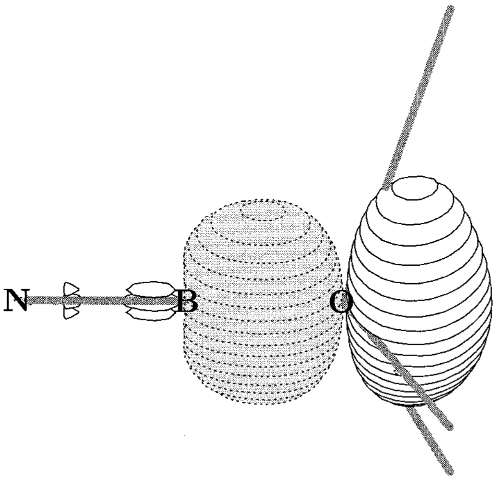

Figure 2. Molecular orbital of $O(BN)_4^{2-}$ describing a σ bond between the central oxygen and a boron atom.

Results and Discussion

In this communication, we present our ab initio data for the dianions $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$. Both molecules are strictly tetrahedral and possess closed-shell $^1A_1$ electronic ground states. Due to the isoelectronic character of the BN and CC ligands, the examined dianions are also isoelectronic. The geometries of both dianions have been optimized at the SCF, MP2, and CCSD levels of theory (Figure 1). Because the CCSD method is known to give reliable geometric parameters, we focus here on the discussion of our results for the CCSD optimized structures. On that level of theory, the O−B bond of the $O(BN)_4^{2-}$ dianion has a length of 1.5345 Å, which corresponds to a slightly prolonged covalent O−B single bond. The B−N bond of this system is 1.2665 Å long and can be seen as a B−N triple bond. In analogy, the O−C bond of the $O(C_2)_4^{2-}$ dianion with a length of 1.5061 Å has also typical single-bond character. Not surprisingly, the C−C bond corresponds to a prolonged C−C triple bond showing a length of 1.2634 Å. The prolongation of the bond lengths in dianions is a common phenomenon and is due to the pronounced electrostatic repulsion of the negatively charged ligands.

The character of the O−B and O−C single bonds can be further corroborated by analyzing the molecular orbitals of the systems and by performing an analysis of the nature of the bonding in the framework of the NBO (natural bond orbitals) formalism.[25] In both systems molecular orbitals are found that possess mainly character of O−B or O−C σ-bonds. As an example, one molecular orbital of that type of the $O(BN)_4^{2-}$ dianion is displayed in Figure 2. Furthermore, the NBO analysis provides clear evidence for the existence of 16 covalent bonds, four lone pairs and nine core pairs in both dianions. The nine core pairs obviously correspond to the atomic 1s orbitals and the lone-pair orbitals have, according to the NBO analysis, sp-hybridized character in both systems. The lone pairs of $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$ dianions are located at the N and the terminal C atoms, respectively, and point along the C_3 axes away from the molecules. The 16 covalent bonds found in both dianions by NBO analysis correspond to four single bonds between the central oxygen atom and the attached ligand atoms and to four triple B−N and C−C bonds in $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$, respectively. Additionally, the NBO analysis reveals that the covalent O−B and O−C bonds are strongly localized at the oxygen atom by about 80%. Performing an NBO analysis for methane for comparison, it shows that about 60% of the C−H bonds are localized at the carbon. In the water molecule about 75% of the O−H bonds are localized at the oxygen and in methanol, the covalent C−O bond is strongly localized at the oxygen atom by about 68% according to an NBO analysis. Comparing the value of about 80% localization at the oxygen for the O−B and O−C bonds with the values for this clearly covalent reference system, it becomes evident that the O−B and O−C single bonds of $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$ correspond to strongly polarized covalent σ-bonds.

TABLE 1: Vertical Electron Detachment Energies of the Dianions $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$ Calculated at the SCF, MP2, and CCSD Optimized Geometries

	$O(BN)_4^{2-}$			$O(C_2)_4^{2-}$		
EDE/eV	SCF	MP2	CCSD	SCF	MP2	CCSD
theoretical method						
KT	2.86	2.70	2.77	2.76	2.47	2.63
ΔSCF	2.38	2.24	2.07	2.08	1.83	1.66
ΔMP2	2.00	2.06	2.14	1.83	2.24	2.33
ΔCCSD		2.00	2.03		2.03	2.06

The calculation of the vertical EDEs of $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$ has clearly shown that both tetrahedral systems are stable with respect to vertical electron loss. At the CCSD optimized geometry, the vertical EDE of the $O(BN)_4^{2-}$ dianion has values of 2.77 eV at the level of KT, 2.07 eV at the level of ΔSCF, 2.12 eV at the ΔMP2 level and 2.03 eV at the CCSD level of theory (Table 1). The overestimation of the EDE by KT is well understood and is due to the lack of relaxation and correlation within this approximate approach. Surprisingly, the influence of correlation on the EDE is only very small for this molecule. Analogously, the vertical EDE of $O(C_2)_4^{2-}$ possesses values of the same magnitude: 2.63, 1.66, 2.33, and 2.06 eV at the theoretical levels of KT, ΔSCF, ΔMP2, and ΔCCSD, respectively (Table 1). These values indicate that the dianions $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$ are very stable with respect to vertical electron emission. We would like to mention that, according to our calculations, no structurally related monoanion exists.

The examination of the stability of the systems with respect to several possible fragmentation channels revealed that the most important fragmentation channel is the energetically strongly favored dissociation of the dianion $O(BN)_4^{2-}$ into two monoanionic fragments $O(BN)_3^-$ and BN^- and, analogously, for the $O(C_2)_4^{2-}$ dissociation into $O(C_2)_3^-$ and C_2^-. These channels are energetically favored due to the strong electrostatic repulsion between the dissociation products. Both dianions have been found to be thermodynamically unstable with respect to these fragmentation channels, since the sums of the total energies of the fragmentation products are lower than the total energies of the dianions by 1.3 and 2.8 eV for $O(BN)_4^{2-}$ and $O(C_2)_4^{2-}$, respectively. Therefore, we have estimated the barrier heights connected with these dissociation pathways at the SCF and MP2 levels of theory, which both give barrier heights of about 1.3

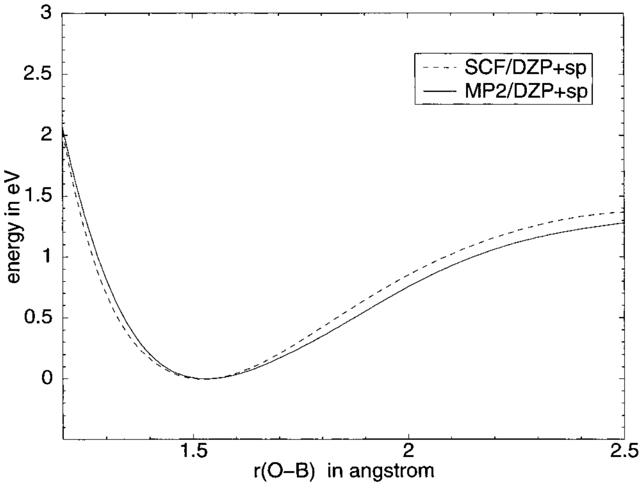

Figure 3. Calculated dissociation pathway of $O(BN)_4^{2-}$ into $O(BN)_3^-$ and BN^- at the SCF and MP2 levels of theory. All geometrical parameters are allowed to relax during the dissociation process.

eV for the $O(BN)_4^{2-}$ dianion (Figure 3). Due to the electrostatic repulsion between the monoanionic fragments, the asymptotic behavior of the barrier is known to be of the form $1/r$ and for this reason very broad. Due to the broadness of the barrier, the corresponding tunneling process is very unlikely and, therefore, the dissociation of $O(BN)_4^{2-}$ can be assumed to be extremely slow. Note that a similar dissociation behavior has been prognosticated previously for the BeF_4^{2-} dianion.[7] Although this system is thermodynamically unstable by 3 eV and has a barrier height of only 0.6 eV, BeF_4^{2-} has recently been detected experimentally in a mass spectrometer.[8] For this reason, the estimated barrier height for $O(BN)_4^{2-}$ coincides with a very long lifetime of the dissociation process and is no relevant decay channel. Analogous results have been found for the dissociation of the $O(C_2)_4^{2-}$ system. We mention that the energy of the monoanion is higher than the energy of the dianion along the above minimum energy path to dissociation.

Summary and Conclusions

Using standard high-level ab initio quantum chemical methods, we have thoroughly examined two remarkable isomers of the $OB_4N_4^{2-}$ and OC_8^{2-} dianions, which possess a tetrahedrally coordinated central oxygen atom. The $O(BN)_4^{2-}$ and the $O(C_2)_4^{2-}$ dianions turned out to be electronically very stable and to be long-lived with respect to fragmentation into monoanionic fragments. For this reason, we predict the existence of these remarkable molecules in the gas phase, which are, to our best knowledge, the first molecules containing a tetrahedrally coordinated oxygen atom in a covalent bonding situation, where the ligands repel each other.

The dianions $OB_4N_4^{2-}$ and OC_8^{2-} can of course adopt a great variety of different structures, and indeed there exist stable chainlike isomers, $(NBNBOBNBN)^{2-}$, or, analogously, $C_4OC_4^{2-}$, which are lower in energy than the tetrahedral isomers. But nonetheless, the here-described tetrahedral dianions represent long-lived local minima on the potential energy surface and should thus be experimentally observable in addition to the other isomers.

Analysis of the charge distribution of the tetrahedral dianions $O(BN)_4^{2-}$ and the $O(C_2)_4^{2-}$ in the framework of the NBO approach reveals that the central oxygen atom is clearly negatively charged. In the case of the $O(BN)_4^{2-}$ system, the oxygen has a partial charge of -0.99, the boron of $+0.8$, and the nitrogen of -1.1. This strong polarization is due to the differences of the electronegativities of the elements. Even if these numbers overestimate the real charge distribution, the trend is clear, and it is a sequence of alternating negative and positive charges, which strongly stabilizes the excess negative charges of the dianion. The situation is different for the $O(C_2)_4^{2-}$ dianion. Here, the oxygen atom possesses a partial charge of -0.43, the inner carbon atoms of -0.16 and the outer ones of -0.25. Since the inner oxygen atom is already negatively charged by -0.43, only -1.57 charges need to be distributed equally over four C_2 units, which are not polarized due to their homonuclearity. This reduces the electrostatic repulsion of the excess negative charges drastically.

References and Notes

(1) Janoschek, R. *Z. Anorg. Allg. Chem.* **1992** *616*, 101.
(2) Scheller, M. K.; Cederbaum, L. S. *J. Phys. B* **1992** *25*, 2257.
(3) Boldyrev, A. I.; Simons, J. *J. Phys. Chem.* **1994**, *98*, 2298.
(4) Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1994**, *116*, 10761.
(5) Sommerfeld, T. *J. Phys. Chem. A* **2000** *104*, 8806.
(6) Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1993** *99*, 441.
(7) Weikert, H. G.; Cederbaum, L. S.; Tarantelli, F.; Boldyrev, A. I. *Z. Phys. D: Atoms, Molecules and Clusters* **1991** *18*, 229.
(8) Middleton, R.; Klein, J. *Phys. Rev. A* **1999** *60*, 3515.
(9) Schauer, S. N.; Williams, P.; Compton, R. N. *Phys. Rev. Lett.* **1990** *65*, 625.
(10) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *Chem. Phys. Lett.* **1993** *209*, 216.
(11) Dreuw, A.; Sommerfeld, T.; Cederbaum, L. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1889.
(12) Gnaser, H. *Phys. Rev. A* **1999** *60*, R2645.
(13) Klein, J.; Middleton, R. *Nucl. Instrum. Methods Phys. Res. B* **1999** *159*(*1*−*2*), 8−21.
(14) Dreuw, A.; Cederbaum, L. S. *J. Chem. Phys.* **2000** *112*, 7400.
(15) Wang, X.-B.; Wang, L.-S. *J. Chem. Phys.* **1999** *111*, 4497.
(16) Kalcher, J.; Sax, A. F. *Chem. Rev.* **1994**, *94*, 2291.
(17) Scheller, M. K.; Compton, R. N.; Cederbaum, L. S. *Science* **1995** *270*, 1160.
(18) Freeman, G. R.; March, N. H. *J. Phys. Chem.* **1996**, *100*, 4331.
(19) Wang, L.-S.; Wang, X.-B. *J. Phys. Chem. A* **2000** *104*, 1978.
(20) Schleyer, P. v. R.; Wurthwein, E.-U.; Pople, J. A. *J. Am. Chem. Soc.* **1982** *104*, 5839.
(21) Wu, C. H. *Chem. Phys. Lett.* **1987** *139*, 357.
(22) Boldyrev, A. I.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1991**, *113*, 9045.
(23) Dunning, T. H., Jr. *J. Chem. Phys.* **1970** *53*, 2823.
(24) Schweinsberg, H. Diploma Thesis, University of Heidelberg, 2000.
(25) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.