Diffuse-Bound and Valence-Bound Anions of Cytosine

O. Dolgounitcheva, V. G. Zakrzewski, and J. V. Ortiz*

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506-3701

Received: March 22, 2001

Diffuse-bound and valence-bound anions of cytosine have been examined with correlated, ab initio calculations employing large basis sets. Five structures of the cytosine anion have been considered for both kinds of anions. Adiabatic electron affinities of neutrals and vertical electron detachment energies were determined with perturbative, coupled-cluster and electron propagator methods. Basis sets with many diffuse, atom-centered functions were used. Among the five tautomeric cytosine structures, only the 1H-amino-oxo isomer is capable of forming both diffuse and valence-bound anions. Two imino-oxo isomers produce valence-bound anions with positive vertical electron detachment energies. The most stable neutrals, the amino-oxy tautomers, have adiabatic electron affinities that are negative with respect to both dipole-bound and valence-bound anionic forms. Valence-bound, amino-oxy anions are not even vertically bound with respect to electron loss. Diffuse-bound anions of the amino-oxy and imino-oxo isomers have negative adiabatic electron detachment energies. Close agreement with the lowest peak in an anion photoelectrum spectrum obtains for the vertical electron detachment energy of the diffuse-bound anion of 1H-amino-oxo cytosine. A peak of higher energy is assigned to the valence-bound anions of 1H-amino-oxo and imino-oxo tautomers.

Introduction

The response of nucleic acids to electron capture, removal or transport influences many important biochemical phenomena.[1] Mechanisms of mutation, radiation damage of genetic material and the possibility of DNA-based electrical conduits are among these related topics. Thymine and cytosine are considered to be the most likely sites for localization of extra electrons in DNA strands.[2] Two types of bound anions can be formed by electron attachment to nucleotide bases. Formation of conventional or valence-bound (VB) anions is expected in condensed media. In the gas phase, molecules with high dipole moments may favor dipole-bound or diffuse-bound (DB) anions. DB anions observed in photodetachment−photoelectron (PDPE) experiments correspond to sharp, intense peaks with low electron binding energies. VB anions are characterized in the same experiments by wider peaks at higher energies which may display vibrational structure.[3,4] Resonant dissociation of bases by sub-ionization electrons is associated with VB anion intermediates.[5] Vertical electron affinities of base neutrals corresponding to resonances in electron transmission experiments are generally assigned to states where the surplus electron occupies a valence, π orbital.[6]

Experiments[3,4,6−10] and calculations[11,12] indicate that uracil forms an adiabatically stable, DB anion. A VB anion is observed when uracil is coordinated to a single water molecule and both kinds of anions are found when uracil is complexed to a Xe atom.[4] Calculations have shown that, in the absence of a coordinated solvent molecule, the VB anion of uracil is adiabatically unstable.[12,13]

Unlike uracil, gas-phase cytosine has a number of close-lying tautomeric forms.[14,15] In recent PDPE spectra of pyrimidinic base anions,[7] two peaks were found in the case of cytosine. One of these peaks, at 85 ± 8 meV, was sharp, while another, at 0.230 eV, was wider and significantly less intense. These peaks were assigned to amino-oxy and amino-oxo DB anions, respectively. The larger dipole moment of the amino-oxo tautomer of cytosine provides a qualitative justification for this conclusion.

Stable anions of cytosine with lifetimes of at least 10 μs were produced in electron scattering experiments.[5] Dissociative electron attachment to cytosine proceeds through formation of a long-lived anion.

Density functional calculations obtain negative or positive values for the adiabatic electron affinity of cytosine, depending on the choice of the functional.[16−18] These calculations consider only VB anions, for diffuse basis functions that are appropriate for DB anions are absent.

Adamowicz and co-workers performed correlated, ab initio calculations on three tautomers of cytosine and corresponding anions.[19] Uncharged and anionic structures were optimized at the MP2/6-31++G** and UMP2/6-31++G** levels, respectively. These authors found a metastable VB anion of the amino-oxo tautomer with a vertical electron detachment energy (VEDE) of 0.084 eV at the MP2/UMP2 level. This value increased to 0.102 eV when single-point, ΔMP4 calculations were performed. The adiabatic electron detachment energy of this anion was negative, however. For amino-oxy tautomers, VB anions had negative VEDEs. DB anions were examined with a basis set that included six diffuse s and p functions at a hydrogen atom nearest to the positive end of the molecular dipole. With this basis set and MP4, the following AEAs were obtained for cytosine tautomers: 0.058 eV (amino-oxo tautomer) and 0.022 and 0.006 eV (amino-oxy tautomers). The authors of ref 19 considered these three results to be qualitatively consistent with the experimental results of ref 7, but they could only speculate on the reasons for the numerical discrepancies.

In this work, we perform ab initio geometry optimizations for several tautomers of cytosine and for the corresponding DB and VB anions. Relative energies are determined with basis sets designed for calculations on both kinds of anions.

* To whom correspondence should be addressed. E-mail: ortiz@ksu.edu.

10.1021/jp0110760 CCC: $20.00
Published on Web 08/30/2001

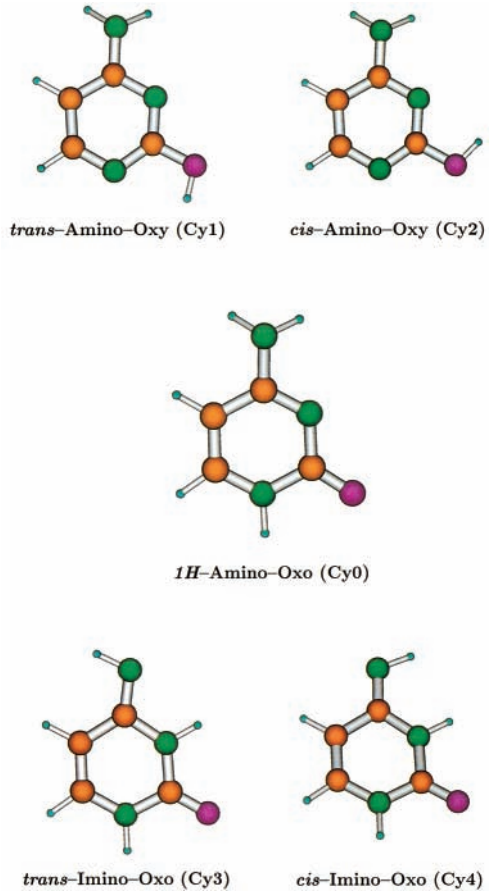

Figure 1. The lowest lying isomers of cytosine.

TABLE 1: MP2/6-311++G Structures of Cytosine**

isomer	E_{tot} (au)	ΔE (kcal/mol)	μ (D)
Cy0	−393.97695	2.34	7.35
Cy1	−393.98068	0.	3.56
Cy2	−393.97948	0.75	4.67
Cy3	−393.97451	3.87	5.56
Cy4	−393.97179	5.58	2.91

Results and Discussion

Calculations. All calculations were performed with the GAUSSIAN-98 suite of programs.[20] Figures were generated with the MOLDEN package.[21]

The five lowest tautomers of cytosine[14,15] are the 1H-amino-oxo (Cy0), *trans*-amino-oxy (Cy1), *cis*-amino-oxy (Cy2), *trans*-imino-oxo (Cy3), and *cis*-imino-oxo (Cy4) forms shown in Figure 1. These structures were optimized at the MBPT(2) (also known as MP2)[22] level with the 6-311++G** basis[23] Total energies, relative energies, and dipole moments are given in Table 1. At this level of optimization, Cy1 was the lowest form, but Cy2 was only 0.75 kcal/mol higher. The amino-oxo form, Cy0, is 2.34 kcal/mol above Cy1.

Corresponding DB anions were obtained in UMP2 optimizations with the same basis set. Each anion's structure differed little from that of the corresponding neutral isomer. Spin contaminations were negligible. At this point, no binding of the additional electron was indicated, but calculation of positive electron affinities generally requires a basis set with many diffuse and polarization functions.

The nearly saturated, diffuse basis set described in our work on uracil[12] was used subsequently. This basis, known as B2, contains additional diffuse s and p functions on each atom. One set of diffuse functions is employed for C, N and O atoms and two sets were used for hydrogen. The corresponding exponents are 0.0146 for C, 0.0213 for N, 0.0282 for O, and 0.012 and 0.001 for H. To obtain VEDEs, neutral total energies at optimized geometries of anions were calculated. Table 2 contains these total energies, adiabatic electron affinities (AEAs) of cytosine isomers and VEDEs of the respective DB anions. AEAs were calculated as differences between a neutral MP2 energy and an anion's UMP2 energy. VEDEs are the differences of a neutral MP2 energy at an anion geometry and an optimized anion UMP2 energy.

TABLE 2: B2 Basis Results on Cytosine and Its DB Anions

procedure		geometry		E_{tot} (au)	AEA (eV)	VEDE (eV)
Cy0	MBPT(2)	Cy0	MBPT(2)	−393.97894		
$Cy0^-$	UMBPT(2)	$Cy0^-$	UMBPT(2)	−393.98063	0.046	
Cy0	MBPT(2)	$Cy0^-$	UMBPT(2)	−393.97850		0.058
Cy1	MBPT(2)	Cy1	MBPT(2)	−393.98258		
$Cy1^-$	UMBPT(2)	$Cy1^-$	UMBPT(2)	−393.98199	−0.016	
Cy1	MBPT(2)	$Cy1^-$	UMBPT(2)	−393.98167		0.009
Cy2	MBPT(2)	Cy2	MBPT(2)	−393.98140		
$Cy2^-$	UMBPT(2)	$Cy2^-$	UMBPT(2)	−393.98124	−0.004	
Cy2	MBPT(2)	$Cy2^-$	UMBPT(2)	−393.98036		0.024
Cy3	MBPT(2)	Cy3	MBPT(2)	−393.97635		
$Cy3^-$	UMBPT(2)	$Cy3^-$	UMBPT(2)	−393.97417	−0.008	
Cy3	MBPT(2)	$Cy3^-$	UMBPT(2)	−393.97564		−0.040
Cy4	MBPT(2)	Cy4	MBPT(2)	−393.97366		
$Cy4^-$	UMBPT(2)	$Cy4^-$	UMBPT(2)	−393.96682	−0.081	
Cy4	MBPT(2)	$Cy4^-$	UMBPT(2)	−393.97259		−0.157

The diffuse nature of all these anions is illustrated by plots of the highest occupied molecular spin−orbital. This spin−orbital is henceforth known as the singly occupied molecular orbital (SOMO), for the remaining occupied spin−orbitals comprise pairs of α and β spin−orbitals with nearly identical spatial functions. In each case shown in Figure 2, the SOMO consists chiefly of a highly diffuse lobe. The $Cy1^-$ and $Cy2^-$ SOMOs are nearly identical.

VB anions were located as minima in preliminary optimizations at the UHF/6-31G**[24] level. These structures were reoptimized with the UMP2/6-311G** and UMP2/6-311++G** procedures. Anions thus obtained differed significantly from parent neutrals in their geometries. For each tautomeric anion of this type, prominent distortions of the pyrimidinic ring were found. Figure 3 shows the optimized, nonplanar structures of the VB anions. All VB anions had some spin contamination, but $\langle S^2 \rangle$ values never exceeded 0.80. π SOMOs of VB anions are shown in Figure 4. With the 6-311++G(2df,2p) basis,[25] MP2 energies of the neutrals, UMP2 energies of valence-type anions and MP2 energies of the neutrals at the anions' geometries were obtained (Table 3). AEAs and VEDEs were calculated in the same manner used for DB anions. Electron propagator methods[26] were used to calculate the vertical electron affinities of the neutral at the anion's geometry (that is, the VEDEs) in those cases where ΔMP2 gave positive values.

Diffuse-Bound Anions. Of the five isomeric cytosine molecules, only the amino-oxo form (Cy0) produces an adiabatically stable, DB anion. An AEA of 0.046 eV obtains with the B2 basis. The VEDE is 0.058 eV when obtained as a UMP2/MP2 difference and is 0.055 eV when obtained directly by OVGF[27] electron propagator calculations. These values differ little from the AEA result. There are two other anions with positive, though small, VEDEs. (These values are in close agreement with the values of ref 19.) These are anions produced by the two lowest neutrals, Cy1 and Cy2. The amino-oxo tautomer has the largest dipole moment (see Table 1). There is no direct correlation, however, between the values of dipole moments

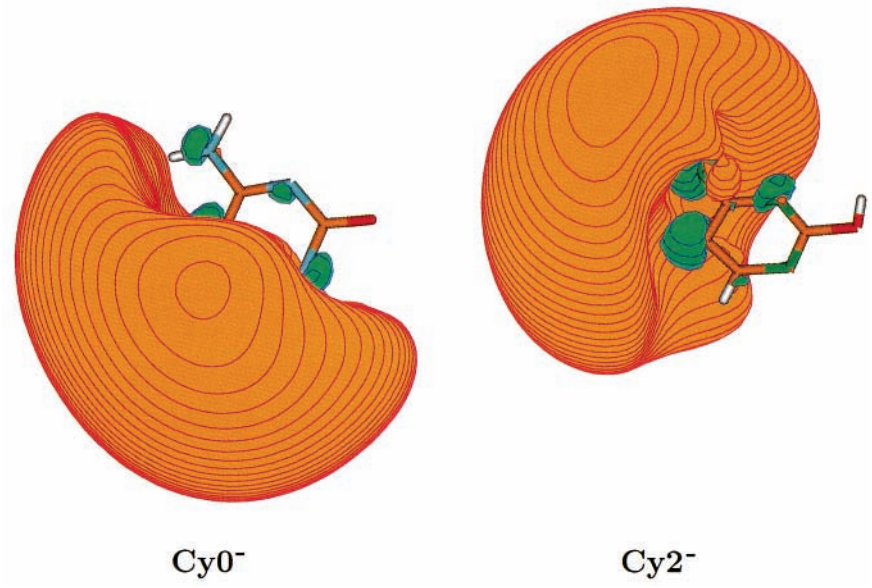

Figure 2. Diffuse-bound, singly occupied molecular orbitals of cytosine tautomers.

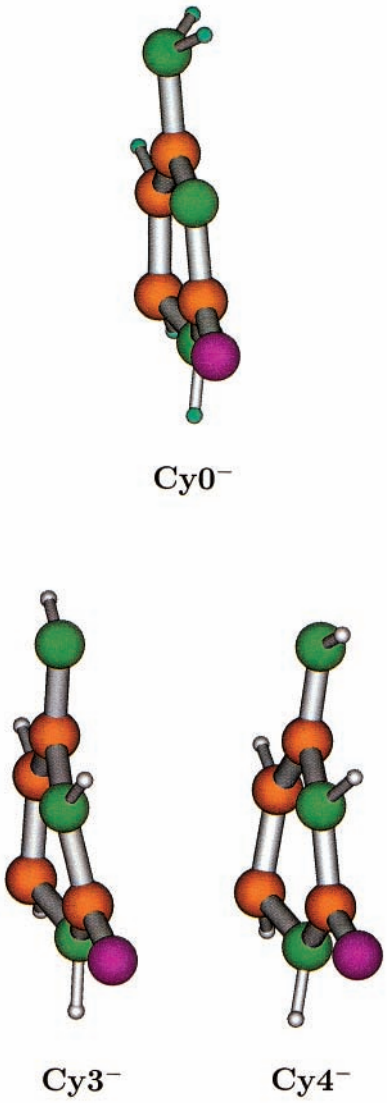

Figure 3. Valence-bound tautomeric cytosine anions stable to vertical electron detachment.

and either AEAs or VEDEs for the other isomers. Both the AEA of Cy0 and the VEDE of its DB anion are in good agreement

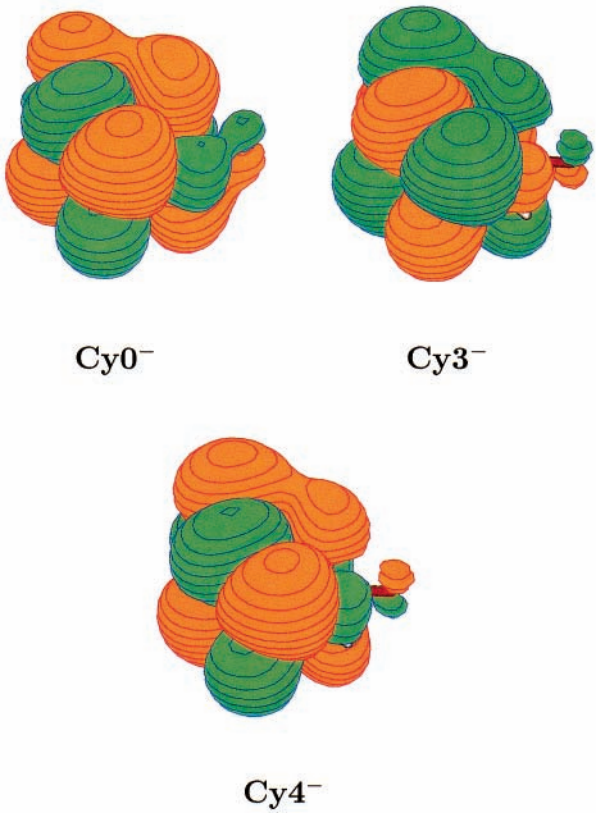

Figure 4. Valence-bound, singly occupied molecular orbitals of cytosine tautomers.

with the experimentally observed feature at 0.085 ± 0.008 eV in ref 7.

Valence-Bound Anions. As was the case with uracil,[12] none of cytosine tautomers produces an adiabatically stable VB anion. Furthermore, only VB anions of oxo-forms (Cy0, Cy3, and Cy4) display positive VEDEs at the ΔUMP2 level (Table 3). These VEDE values (0.142−0.271 eV) are within the peak observed in the spectrum of ref 7, where this feature covers a range of 0.2−0.3 eV. An attempt to assess VEDEs of Cy0, Cy3, and Cy4 with OVGF resulted in negative VEDE values: −0.350 eV for Cy0, −0.371 eV for Cy3, and −0.405 for Cy4. The

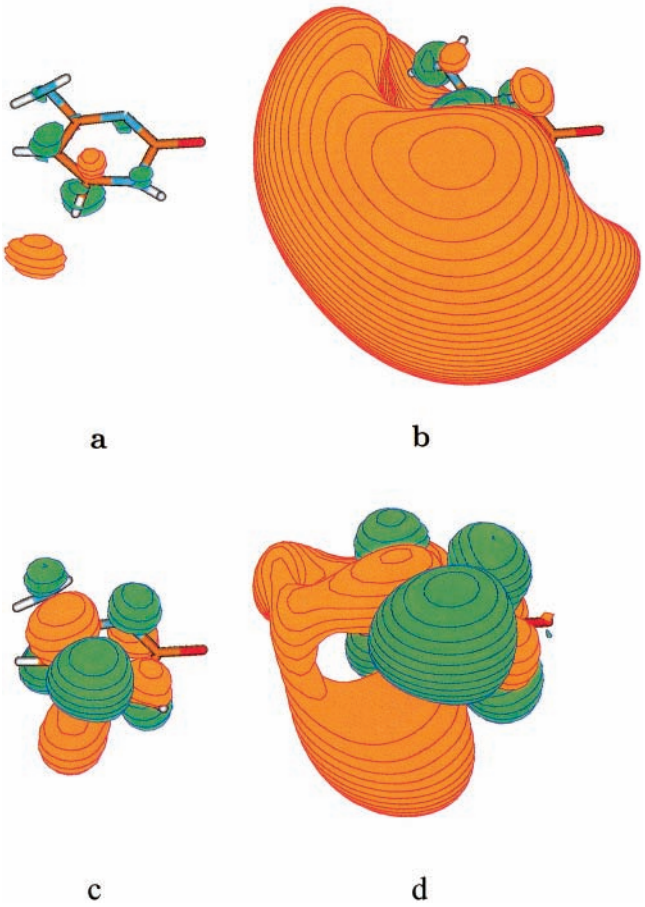

Figure 5. Lowest unoccupied molecular orbitals of 1-H-amino-oxo cytosine at the geometry of its valence-bound anion. (a) LUMO with a contour of 0.03. (b) LUMO with a contour of 0.01. (c) LUMO+1 with a contour of 0.03. (d) LUMO+1 with a contour of 0.01.

TABLE 3: 6-311++G(2df,2p) Results on Cytosine and Its VB Anions

procedure		geometry		E_{tot} (au)	AEA (eV)	VEDE (eV)
Cy0	MBPT(2)	Cy0	MBPT(2)	−394.19276		
Cy0$^-$	UMBPT(2)	Cy0$^-$	UMBPT(2)	−394.17343	−0.382	
Cy0	MBPT(2)	Cy0$^-$	UMBPT(2)	−394.16347		0.271
Cy1	MBPT(2)	Cy1	MBPT(2)	−394.19519		
Cy1$^-$	UMBPT(2)	Cy1$^-$	UMBPT(2)	−394.15832	−0.853	
Cy1	MBPT(2)	Cy1$^-$	UMBPT(2)	−394.17081		−0.340
Cy2	MBPT(2)	Cy2	MBPT(2)	−394.19402		
Cy2$^-$	UMBPT(2)	Cy2$^-$	UMBPT(2)	−394.15741	−0.549	
Cy2	MBPT(2)	Cy2$^-$	UMBPT(2)	−394.17038		−0.353
Cy3	MBPT(2)	Cy3	MBPT(2)	−394.19038		
Cy3$^-$	UMBPT(2)	Cy3$^-$	UMBPT(2)	−394.16989	−0.450	
Cy3	MBPT(2)	Cy3$^-$	UMBPT(2)	−394.16239		0.204
Cy4	MBPT(2)	Cy4	MBPT(2)	−394.18759		
Cy4$^-$	UMBPT(2)	Cy4$^-$	UMBPT(2)	−394.16438	−0.522	
Cy4	MBPT(2)	Cy4$^-$	UMBPT(2)	−394.15916		0.142

discrepancies between OVGF and ΔUMP2 results are a consequence of orbital relaxation between anions and neutrals. SOMOs of VB Cy0$^-$ and Cy3$^-$ and LUMOs of corresponding neutrals at the anion geometries closely resemble each other. The neutral LUMOs shown in Figure 5 suggest DB anions, even at the structure of the VB anion. Orbital relaxation in the attachment of an electron to form a VB anion therefore is very strong. The next highest unoccupied molecular orbitals of the neutrals (also shown in Figure 5), however, resemble VB anion SOMOs. Some care must be exercised in the choice of initial guess orbitals when searching for VB anions. If neutral LUMOs are used for this purpose, Hartree−Fock calculations converge to DB states.

TABLE 4: 6-311+G Results on VB Cy0$^-$**

method	Cy0$^-$	Cy0 at Cy0$^-$ Geometry	VEDE (eV)
MBPT(2)	−393.95569	−393.95051	0.141
ADC(3)			0.143
CCSD(T)	−394.04560	−394.03472	0.296

A final set of calculations considers the effects of higher order electron correlation. Table 4 shows total energies and VEDEs pertaining to Cy0 and Cy0$^-$ that were obtained with optimized geometries from previous tables. When the 6-311+G** basis is used, the VEDE of Cy0$^-$ obtained at the UMP2/MP2 level is 0.141 eV. A more exact electron propagator method, the third-order adiabatic construction approximation (or ADC(3)),[28,29] was applied to the VEDE of VB Cy0$^-$. A value of 0.143 eV was obtained by calculating the electron affinity of the neutral at the anion's geometry. CCSD(T) results are even higher: 0.296 eV. Larger VEDE values may be expected from all three methods with use of a larger basis. These calculations indicate that the broader, higher energy feature of ref 7 at 0.230 ± 0.008 eV may be attributed to VB Cy0$^-$. Cy3$^-$ or even Cy4$^-$ also may contribute to this experimental feature.

Future work should consider whether the relatively greater breadth of the peak at 0.230 eV is compatible with calculated vibrational frequencies and Franck−Condon factors associated with electron detachment from VB anions. Calculation of photodetachment cross sections may also assist in making assignments.

Conclusions

Calculations on electron attachment to cytosine isomers indicate that the two peaks observed in the PDPE spectrum of cytosine[7] may be produced by electron detachment from VB and DB anions of the 1H-amino-oxo isomer (Cy0) and perhaps by VB anions of the *trans*-imino-oxo (Cy3) and *cis*-imino-oxo (Cy4) forms. DB Cy0$^-$ is responsible for the lower peak at 0.085 ± 0.008 eV. VB Cy0$^-$ is responsible for the peak at 0.230 eV, but Cy3$^-$ and Cy4$^-$may be present also. The most stable, amino-oxy tautomers of cytosine are not capable of forming DB or VB anions. We conclude that electron binding by two pyrimidinic bases, uracil[12] and cytosine, is essentially the same. Both produce weakly bound, DB anions. Oxo-forms are capable of forming short-lived, VB species that are significantly distorted with respect to neutral structures.

Acknowledgment. We thank Dr. Rainer Weinkauf for insightful comments. This work was supported by the National Science Foundation under grant CHE-9873897.

References and Notes

(1) Colson, A. O.; Sevilla, M. D. *Int. J. Radiat. Biol.* **1995**, *67*, 627 and references therein.

(2) Sevilla, M. D.; Becker, D.; Yan, M.; Summerfield, S. *J. Phys. Chem.* **1991**, *95*, 3409. Yan, M.; Becker, D.; Summerfield, S.; Renke, P.; Sevilla, M. D. *J. Phys. Chem.* **1992**, *96*, 1983.

(3) Hendricks, J. H.; Lyapustina, S. A.; de Clercq, H. L.; Snodgrass, J. T.; Bowen, K. H. *J. Chem. Phys.* **1996**, *104*, 7788.

(4) Hendricks, J. H,; Lyapustina, S. A.; de Clercq, H. L.; Bowen, K. H. *J. Chem. Phys.* **1998**, *108*, 8.

(5) Huels, M. A.; Hahndorf, I.; Illenberger, E.; Sanche, L. *J. Chem. Phys.* **1998**, *108*, 1309.

(6) Aflatooni, K.; Gallup, G. A.; Burrow, P. D. *J. Phys. Chem. A* **1998**, *102*, 6205.

(7) Schiedt, J.; Weinkauf, R.; Neumark, D. M.; Schlag, E. W. *Chem. Phys.* **1998**, *239*, 511.

(8) Desfrançois, C.; Abdoul-Carime, H.; Schulz, J. P.; Schermann, J. P. *Science* **1995**, *269*, 1707.

(9) Desfrançois, C.; Abdoul-Carime, H.; Schermann, J. P. *J. Chem. Phys.* **1996**, *104*, 7792.

(10) Desfrançois, C.; Periquet, V.; Bouteiller, Y.; Schermann, J. P. *J. Chem. Phys. A* **1998**, *102*, 1274.

(11) Oyler, N. A.; Adamowicz, L. *J. Phys. Chem.* **1993**, *97*, 11122.

(12) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *Chem. Phys. Lett.* **1999**, *307*, 220.

(13) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *J. Chem. Phys. A* **1999**, *103*, 7912.

(14) Kwiatkowski, J. S.; Leszczynski, J. *J. Phys. Chem.* **1996**, *100*, 941.

(15) Colominas, C.; Luque, F. J.; Orosco, M. *J. Am. Chem. Soc.* **1996**, *118*, 6811.

(16) Russo, N.; Toscano, M.; Grand, A. *Int. J. Quantum Chem.* ***2000***, *21*, 14.

(17) Wetmore, S. D.; Boyd, R. J.; Eriksson, L. A. *Chem. Phys. Lett.* ***2000***, *322*, 129.

(18) Wesolowski, S. S.; Leininger, M. L.; Pentchev, P. N.; Schaefer, H. F. *J. Am. Chem. Soc.* **2001**, *123*, 4023.

(19) Smith, D. M. A.; Jalbout, A. F.; Smets, J.; Adamowicz, L. *Chem. Phys.* **2000**, *260*, 45.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A2; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) Schaftenaar, G. *MOLDEN*, version 3.4; CAOS/CAMM Center: The Netherlands, 1998.

(22) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359 and references therein.

(23) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193. Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. von R. *J. Comput. Chem.* **1983**, *4*, 294.

(24) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(25) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(26) (a) Ortiz, J. V. In *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: Singapore, 1977; Vol. 2, p 1. (b) Ortiz, J. V.; Zakrzewski, V. G.; Dolgounitcheva, O. In *Conceptual Perspectives In Quantum Chemistry*; Calais, J.-L., Kryachko, E., Eds.; Kluwer: Dordrecht, 1997; Vol. 3, p 465. (c) Ortiz, J. V. *Adv. Quantum Chem.* **1999**, *35*, 33 and references therein.

(27) (a) von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57. (b) Zakrzewski, V. G.; von Niessen, W. *J. Comput. Chem.* **1993**, *14*, 13. (c) Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **1995**, *53*, 583.

(28) (a) Schirmer, J.; Cederbaum, L. S.; Walter, O. *Phys. Rev. A.* **1983**, *28*, 1237. (b) von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57. (c) Schirmer, J.; Angonoa, G. *J. Chem. Phys.* **1989**, *91*, 1754.

(29) Zakrzewski, V. G.; Dolgounitcheva, O.; Ortiz, J. V. *Int. J. Quantum Chem.* **1999**, *75*, 607. This work describes the ADC(3) algorithm implemented in the newest version of GAUSSIAN.