

Electron Propagator Theory of Guanine and Its Cations: Tautomerism and Photoelectron Spectra

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

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506–3701

Received May 8, 2000. Revised Manuscript Received September 18, 2000

Abstract: Electron propagator methods are applied to the ionization energies of the five most stable tautomers of guanine. Excellent agreement with gas-phase photoelectron spectra is obtained for the amino-oxo form of 7H-guanine. According to ionization energy assignments, both 9H-guanine and its amino-oxy tautomers also may be present in the gas phase. The presence of amino-oxy 7H-guanine, however, is less certain, due to its higher total energy. In all cases, the lowest ionization occurs from a π level. There are strong correlation effects for higher cationic states. Energy orderings of π and σ hole states are different for each of the isomers.

Introduction

Photoionization and tautomerism of purines and pyrimidines are fundamental processes in radiation damage to genetic material and other in aspects of nucleic acid reactivity.^{1–4} Of the five nucleotide bases, guanine seems to be the most susceptible to tautomerism.⁵ At least three distinctive forms were found in matrix isolation experiments: 9H-guanine in its amino-oxo form and two rotamers of the amino-oxy form.⁶

Photoelectron spectra (PES) may provide useful information on tautomerism in both pyrimidine and purine bases.¹ Guanine PES^{7–9} are difficult to study in the gas phase due to a rather high boiling point and a tendency to decompose at elevated temperature. The spectrum of a freshly vaporized sample¹⁰ reportedly changes with time, but the causes of this evolution were not specified.

PES of guanine consist of three wide regions with five bands. The first band with a maximum at 8.28 eV is well defined and is separated from the next peak by -1.4 eV. This peak was assigned to ionization from the highest molecular orbital (MO) of π type. Three less resolved maxima at 9.9, 10.4, and 11.2 eV occur in a wide band between 9.6 and 12.0 eV that exhibits several shoulders. Each of these has been assigned to n and π MOs, but no resolution between the two types was possible in these experiments.¹⁰ The third spectral region, comprising energies from 13 to 17 eV, is completely undefined. Assignments were based on semiempirical CNDO/S calculations and assumed the amino-oxo (keto) 7H form of guanine. A summary

Table 1. Photoelectron Spectra of Guanine and Derivatives (eV)

	guanine ¹⁰	1-Me ¹⁰	7-Me ¹⁰	9-Me ¹⁰	1,9-DiMe ²	O,9-DiMe ²
π_1	8.28	7.98	8.16	8.02	8.09	7.96
π_2	9.9	9.6	9.7	9.6	9.5	9.2
n_1	9.9	9.6	9.7	9.6	9.5	9.2
π_3	10.4	10.0	10.4	10.3	10.0	10.0
n_2	10.4	10.0	10.4	10.3	10.0	10.0
π_4	11.2	10.8	10.9	10.86	11.0	10.6
n_3	11.2	10.8	10.9	11.32	11.0	11.29
π_5	13.0	12.9	13.10	13.3	12.31	12.3

of these data and assignments for related molecules with one or two methyl substituents appear in Table 1.

Isomers of guanine were thoroughly optimized at the MBPT-(2) level with the 6-31G*¹¹ and 6-31G**^{5,12} basis sets. In the former calculations,¹¹ planarity of all structures was assumed, while NH₂ pyramidalization was established subsequently.⁵ Five structures (four tautomers and one rotamer) were found to be within ~ 4 kcal/mol of each other. Of these, two oxo forms were the lowest and had virtually the same energy. There were some indications that inclusion of higher polarization functions might invert the relative stabilities of oxo and oxy tautomers.⁵ Two transition states between oxo and oxy tautomers were examined as well.⁵ Since the lowest barrier to an intramolecular H-shift was no less than 35 kcal/mol, such a process is prohibited in the gas phase or under the conditions of matrix isolation. Thus, if more than one form was actually observed in the latter type of experiment,⁶ tautomeric equilibria must have been reached prior to isolation. A clear indication of this effect was obtained in a recent work on intramolecular proton transfer in hydrated tautomers of guanine.¹³

Both vertical and adiabatic ionization potentials of 7H- and 9H-guanine were calculated recently as energy differences between neutral and cationic states with the B3LYP density functional and the 6-31G* basis.¹⁴ Deviation of the calculated vertical ionization energy (8.05 eV) from PES values was 0.19–0.23 eV for 7H-guanine. A larger discrepancy with experiment

* Author for correspondence. E-mail: ortiz@ksu.edu.

(1) Kim, N. S.; Zhu, Q.; LeBreton, P. R. *J. Am. Chem. Soc.* **1999**, *121*, 11516.

(2) LeBreton, P. R.; Yang, X.; Urano, S.; Fetzer, S.; Yu, M.; Leonard, N. J.; Kumar, S. *J. Am. Chem. Soc.* **1990**, *112*, 2138.

(3) Becker, D.; Sevilla, M. D. In *Advances in Radiation Biology*; Lett, J. T., Adler, H., Eds.; Academic Press: New York, 1993; Vol. 17, pp 121–180.

(4) Steenken, S. *Chem. Rev.* **1989**, *89*, 503.

(5) Leszczynski, J. *J. Phys. Chem.* **1998**, *102*, 2357.

(6) Szczepaniak, K.; Szczesniak, M. *J. Mol. Struct.* **1987**, *156*, 29.

(7) Lin, J.; Yu, C.; Peng, S.; Akiyama, I.; Li, K.; Lee, L. K.; LeBreton, P. R. *J. Am. Chem. Soc.* **1980**, *102*, 4627.

(8) Hush, N. S.; Cheung, A. S. *Chem. Phys. Lett.* **1975**, *34*, 11.

(9) Dougherty, D.; McGlynn, S. P. *J. Chem. Phys.* **1977**, *67*, 1289.

(10) Lin, J.; Yu, C.; Peng, S.; Akiyama, I.; Li, K.; Lee, L. K.; LeBreton, P. R. *J. Phys. Chem.* **1980**, *84*, 1006.

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

(12) Stewart, E. L.; Foley, C. K.; Allinger, N. L.; Bowen, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 7282.

(13) Gorb, L.; Leszczynski, J. *J. Am. Chem. Soc.* **1998**, *120*, 5024.

(14) Hutter, M.; Clark, T. *J. Am. Chem. Soc.* **1996**, *118*, 7574.

occurred for the 9H-guanine calculation (7.90 eV). Semiempirical electron propagator calculations on the ionization energies of a number of guanine isomers have been reported as well.¹⁵

Here, we apply *ab initio*, electron propagator theory^{16–19} to the ionization spectra of five isomers of guanine. The recently developed partial third-order approximation (P3)²⁰ is used throughout the paper. P3 and the outer valence Green's function approximations^{18,21} were compared in our recent study on ionization energies of uracil and adenine.²² P3 gave excellent agreement with experimental PES. The accuracy and efficiency of P3 calculations of ionization energies of large organic molecules, including fused heterocycles, have been amply demonstrated.^{23–25}

Methods

All calculations were performed with the GAUSSIAN 98 suite of programs.²⁶ The five most stable isomers of guanine from ref 11 were reoptimized with MBPT(2) and the 6-311G** basis set.²⁷ No symmetry was imposed on any structure; amino nitrogens are allowed to pyramidalize. Optimized structures were used for P3 calculations of ionization energies with the same basis set. The active space for propagator calculations included all valence, occupied MOs, and all virtual MOs.

P3 ionization energies include relaxation and correlation corrections to Hartree–Fock (HF) canonical orbital energies. To each ionization energy, there corresponds a Dyson spin–orbital

$$\phi^{\text{Dyson}}(x_1) = \int \Psi_{\text{neutral}}(x_1, x_2, x_3, \dots, x_N) \Psi_{\text{cation}}(x_2, x_3, x_4, \dots, x_N) dx_2 dx_3 dx_4 \dots dx_N \quad (1)$$

whose normalization integral equals the pole strength, p , where

$$p = \int |\phi^{\text{Dyson}}(x_1)|^2 dx_1$$

(15) Leão, M. B. C.; Longo, R. L.; Pavão, A. C. *J. Mol. Struct.* **1999**, *490*, 145.

(16) Ortiz, J. V. *Adv. Quantum Chem.* **1999**, *35*, 33.

(17) Ortiz, J. V. In *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: Singapore, 1997; Vol. 2, p 1.

(18) Niessen, W. von; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57.

(19) Öhrn Y.; Born, G. In *Advances in Quantum Chemistry*; Löwdin, P. O., Ed.; Academic: New York, 1981; Vol. 13, p 1.

(20) Ortiz, J. V. *J. Chem. Phys.* **1996**, *104*, 7599.

(21) Cederbaum, L. S. *J. Phys. B* **1975**, *8*, 290.

(22) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **2000**, *80*, 831.

(23) Ortiz, J. V.; Zakrzewski, V. G.; Dolgounitcheva, O. In *Conceptual Trends in Quantum Chemistry*; Kryachko, E. S., Ed.; Kluwer: Dordrecht, 1997; Vol. 3, p 465.

(24) Zakrzewski, V. G.; Dolgounitcheva, O.; Ortiz, J. V. *J. Chem. Phys.* **1997**, *107*, 7906.

(25) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *J. Phys. Chem. A* **1997**, *101*, 8554.

(26) 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.; Peterson, 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, revision A8; Gaussian, Inc.: Pittsburgh, PA, 1998.

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

Table 2. Total (au) and Relative (kcal/mol) Energies

isomer	MBPT(2)/6-311G(d,p)	ΔE
9H-guanine	−541.24072	0
7H-guanine	−541.24039	0.21
<i>cis</i> -amino-oxy 9H-guanine	−541.23974	0.61
<i>trans</i> -amino-oxy 9H-guanine	−541.23881	1.20
<i>cis</i> -amino-oxy 7H-guanine	−541.23420	4.09

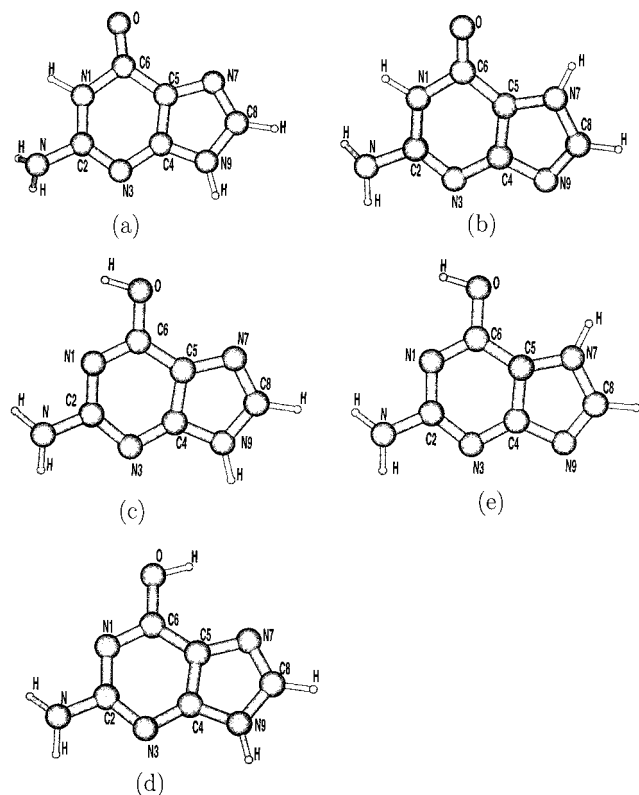


Figure 1. Guanine tautomers: (a) 9H-guanine; (b) 7H-guanine; (c) *cis*-amino-oxy 9H-guanine; (d) *trans*-amino-oxy 9H-guanine; (e) *cis*-amino-oxy 7H-guanine.

In the zeroth-order electron propagator, ionization energies are given by Koopmans's theorem, Dyson orbitals (DOs) equal canonical HF orbitals, and pole strengths equal unity. In the present P3 calculations, however, DOs are proportional to canonical HF orbitals, and pole strengths lie between 1 and 0. Perturbative arguments leading to the P3 approximation remain valid when pole strengths are above 0.8, for in these cases, nondynamical correlation is not qualitatively important. Normalized DOs discussed below are identical to canonical HF orbitals. Since the DOs are subject to a nonlocal, energy-dependent potential defined by the P3 self-energy matrix, relaxation and correlation corrections to ionization energies and pole strengths appear. Derivations of the P3 approximation and its relationships with many-body perturbation theory for ground states and with equation-of-motion, coupled-cluster methods for ionization energies are presented in refs 17 and 20.

Results and Discussion

MBPT(2) total energies and relative energies are presented in Table 2. Optimized structural parameters of five guanine tautomers may be found in Table 3. Tables 4–8 present Koopmans's theorem (KT), P3 and experimental ionization energies. Below each P3 result, the corresponding pole strength (PS) is listed in parentheses. Structures of tautomers and an atomic numbering scheme are given in Figure 1. Figure 2 displays ± 0.05 orbital contours produced with the program

Table 3. Optimized Geometries of Guanine Isomers

isomer ^a	1	2	3	4	5	1	2	3	4	5	
	Bond Lengths (Å)					Angles (deg)					
C ₄ C ₅	1.396	1.396	1.404	1.398	1.407	C ₆ C ₅ C ₄	118.7	123.3	114.1	115.4	117.7
C ₅ C ₆	1.446	1.436	1.407	1.406	1.400	C ₅ C ₄ N ₃	129.7	124.2	127.8	126.9	123.3
C ₅ N ₇	1.376	1.366	1.381	1.380	1.370	N ₁ C ₆ C ₅	108.8	108.1	120.6	120.3	119.8
C ₄ N ₃	1.364	1.374	1.339	1.337	1.348	C ₂ N ₁ C ₆	127.4	126.2	118.6	117.8	117.8
C ₆ N ₁	1.432	1.409	1.324	1.319	1.315	N ₃ C ₂ N ₁	124.2	125.1	127.7	128.6	127.8
C ₂ N ₃	1.308	1.300	1.335	1.340	1.328	C ₂ N ₃ C ₄	111.5	113.5	111.4	111.1	113.5
C ₂ N ₁	1.371	1.384	1.359	1.360	1.368	N ₇ C ₅ C ₄	111.6	105.7	111.9	112.4	105.8
C ₄ N ₉	1.369	1.371	1.372	1.375	1.380	C ₅ C ₄ N ₉	104.7	110.6	104.3	104.0	110.2
C ₈ N ₇	1.323	1.370	1.321	1.323	1.374	C ₈ N ₉ C ₄	106.9	104.3	106.8	107.0	104.2
C ₈ N ₉	1.375	1.325	1.377	1.377	1.319	N ₇ C ₈ N ₉	112.9	113.1	113.7	113.4	113.9
C ₆ O	1.215	1.222	1.339	1.343	1.349	C ₃ N ₇ C ₈	103.8	106.3	103.3	103.2	105.8
C ₂ N ₆	1.386	1.392	1.380	1.378	1.383	N ₁ C ₆ O	120.2	122.7	118.6	117.7	119.9
C ₈ H	1.081	1.081	1.082	1.082	1.082	N ₁ C ₂ N ₆	115.9	114.4	115.1	114.7	114.5
N ₁ H	1.013	1.013				N ₉ C ₈ H	121.8	125.2	121.5	121.6	125.0
N ₉ H	1.010		1.009	1.010		C ₄ N ₉ H	125.3		125.6	125.8	
N ₇ H		1.010			1.009	C ₅ N ₇ H		125.8			126.9
N ₆ H	1.011	1.012	1.008	1.008	1.009	C ₆ N ₁ H	113.6	114.9			
OH			0.967	0.967	0.967	C ₆ OH			104.7	106.0	
						C ₂ N ₆ H	110.6	109.6	113.8	113.9	112.9

^a 1. 9H-Guanine, 2. 7H-Guanine, 3. *cis*-Amino-oxo 9H-guanine, 4. *trans*-Amino-oxo 9H-guanine, 5. *cis*-Amino-oxo 7H-guanine.

Table 4. 7H-Guanine Ionization Energies, eV

MO type	KT	P3 PS	exp. ¹⁰
π_1	8.38	8.27 0.90	8.28
σN_+	11.70	9.91 0.88	~9.9
π_2	10.59	9.94 0.88	~9.9
$\sigma N-\sigma O$	12.26	10.27 0.87	~10.4
π_3	11.95	10.58 0.87	~10.4
σN_-	13.10	11.06 0.87	~11.2
π_4	12.59	11.24 0.88	~11.2
π_5	14.90	13.29 0.85	~13.0
π_6	16.12	14.31 0.87	
σ	16.94	14.77 0.87	
σ	16.58	14.91 0.87	
σ	17.31	15.58 0.88	
π_7	17.72	15.62 0.82	

Table 5. 9H-Guanine Ionization Energies, eV

MO type	KT	P3 PS	exp. ¹⁰
π_1	8.12	8.13 0.89	8.28
$\sigma N-\sigma O$	11.68	9.82 0.88	~9.9
$\sigma N-\sigma O$	12.00	10.02 0.87	~9.9
π_2	11.10	10.20 0.88	~10.4
π_3	11.71	10.40 0.87	~10.4
π_4	12.49	11.12 0.88	~11.2
σN	13.51	11.50 0.88	~11.2
π_5	14.89	13.28 0.84	~13.0
π_6	16.16	14.35 0.85	
σO	16.74	14.50 0.87	
σ	16.32	14.62 0.87	
σ	17.19	15.48 0.87	
π_7	17.79	15.71 0.83	

MOLDEN²⁸ for 7H-guanine. A correlation diagram for ionization energies is given in Figure 3.

Geometries and Relative Stabilities. MBPT(2) optimization with the 6-311G** basis set places the 9H form of guanine below all others, but the 7H form is only 0.21 kcal/mol higher. Two amino-oxo forms of 9H-guanine are very close to the major tautomer. The *cis*-amino-oxo tautomer of 7H-guanine is the least stable of the five forms under consideration. All molecules are clearly nonplanar. Significant distortion of the six-membered ring is observed for both oxo forms. The C₅C₆N₁H dihedral angle is the most distorted and its deviation from planarity reaches ~7° in the case of the 7H isomer. Nonplanarity in the amino group is much more pronounced in the oxo forms and may be as large as 25°.

Photoelectron Spectra. MBPT(2) total energies may produce errors in ionization energies that exceed the ΔE values

displayed in Table 2. None of the structures may be eliminated from further consideration. Therefore, in this section, the compatibility of P3 results with PES is examined for each isomer.

7H-Guanine. P3's first prediction, 8.27 eV, is within 0.01 eV of the experimental peak position of ref 10. Two higher ionization energies at 9.91 and 9.94 eV are also in very good agreement with the observed, unresolved feature at ~9.9 eV. Correlation effects are large for the former ionization energy. The next peak in the experimental PES was observed at ~10.4 eV and was assigned to two unresolved ionizations from π_3 and n_2 DOS. P3 calculations give 10.27 and 10.58 eV and place the nonbonding level at a smaller energy value than the π level. Corrections to the KT ionization energy are very large, as was the case with the lower-lying, nonbonding level. A discernible shoulder in the experimental curve occurs at ~10.5–10.6 eV. The next ionization is predicted at 11.06 eV by P3 and corresponds to the experimental feature at ~11.2 eV. About

(28) Schaftenaar, G. MOLDEN 3.4, CAOS/CAMM Center, The Netherlands, 1998.

Table 6. *cis*-Amino-Oxy 9H-Guanine Ionization Energies, eV

MO type	KT	P3 PS	exp. ¹⁰
π_1	8.17	8.18 0.89	8.28
σ_N	11.31	9.63 0.88	~9.9
π_2	10.52	9.71 0.88	~9.9
π_3	11.92	10.57 0.87	~10.4
σ_{N+}	12.52	10.64 0.88	~10.4
π_4	12.04	10.94 0.87	~11.2
σ_N	13.89	11.83 0.88	~11.2
π_5	15.19	13.42 0.85	~13.0
σ_O	15.89	13.94 0.88	
π_6	16.26	14.24 0.88	
σ	16.55	14.96 0.88	
σ	17.24	15.39 0.88	

Table 7. *trans*-Amino-Oxy 9H-Guanine Ionization Energies, eV

MO type	KT	P3 PS	exp. ¹⁰
π_1	8.24	8.22 0.89	8.28
σ_N	11.26	9.57 0.88	~9.9
π_2	10.53	9.72 0.88	~9.9
π_3	11.88	10.52 0.87	~10.4
σ_{N+}	12.65	10.79 0.88	~10.4
π_4	12.22	11.14 0.87	~11.2
σ_N	13.95	11.86 0.87	~11.2
π_5	15.16	13.40 0.85	~13.0
σ_O	15.73	13.74 0.88	
π_6	16.28	14.25 0.86	
σ	16.69	15.11 0.88	
σ	17.39	15.71 0.85	

1.2 eV separates the σ_{N+} and σ_{N-} levels. The following ionization energy at 11.24 eV also coincides with the peak position at ~11.2 eV observed in ref 10.

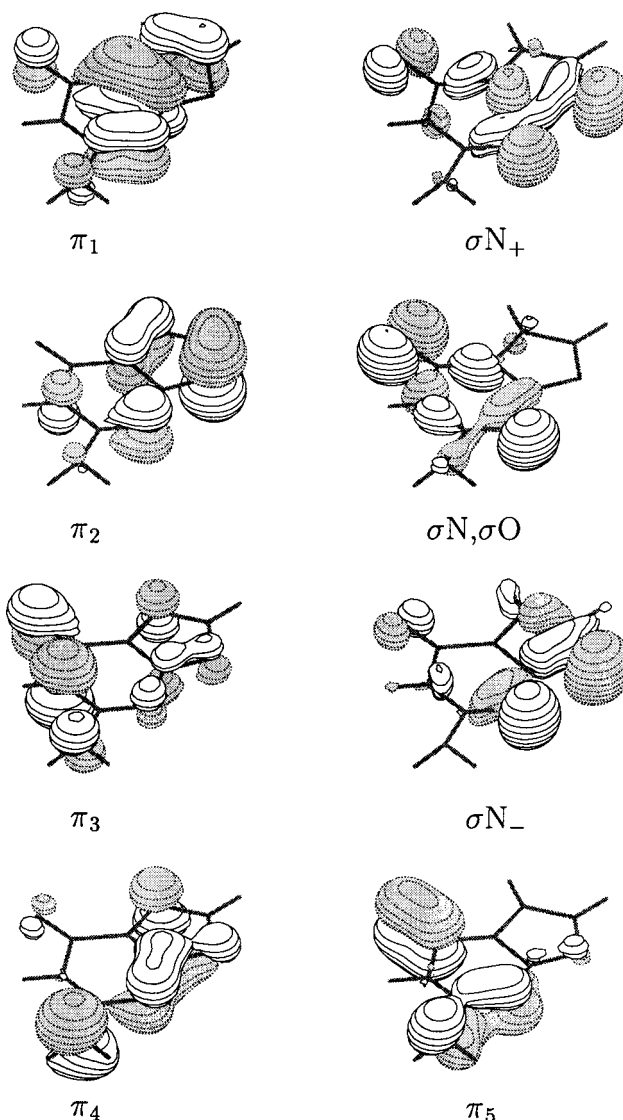
To this point, pole strengths (listed within parentheses under each P3 result in Tables 4–8) are rather large (that is, close to unity) indicating the chiefly one-electron character of the ionizations. Somewhat lower values pertain to the higher π ionization energies.

Ionization from the π_5 level was tentatively placed at 13.0 eV in ref 10. The experimental band is wide and structured. Our P3 calculations give 13.29 eV for this ionization.

Ionization energies above 13.5 eV have not been assigned before. There are three well-defined peaks at ~14.3, ~14.7, and ~15 eV.¹⁰ Corresponding P3 calculated peak positions are at 14.31, 14.77, and 14.91 eV. The ionization energy at 14.77 eV marks the onset of σ levels distributed over the molecular core.

Table 8. *cis*-Amino-Oxy 7H-Guanine Ionization Energies, eV

MO type	KT	P3 PS	exp. ¹⁰
π_1	8.35	8.18 0.89	8.28
σ_N	11.18	9.50 0.88	~9.9
π_2	10.12	9.57 0.86	~9.9
π_3	11.85	10.49 0.87	~10.4
σ_{N+}	12.42	10.52 0.88	~10.4
π_4	12.24	11.10 0.87	~11.2
σ_N	13.57	11.53 0.87	~11.2
π_5	15.18	13.41 0.85	~13.0

**Figure 2.** 7H-Guanine DO plots.

For this isomer of guanine, excellent agreement was found between P3 predictions and the observed spectrum. Comparisons with related molecules with one or two methyl substituents may aid the present assignments (see Table 1). Addition of a single methyl group reduces the first few ionization energies by 0.1–0.3 eV, and somewhat larger shifts occur for dimethyl substitu-

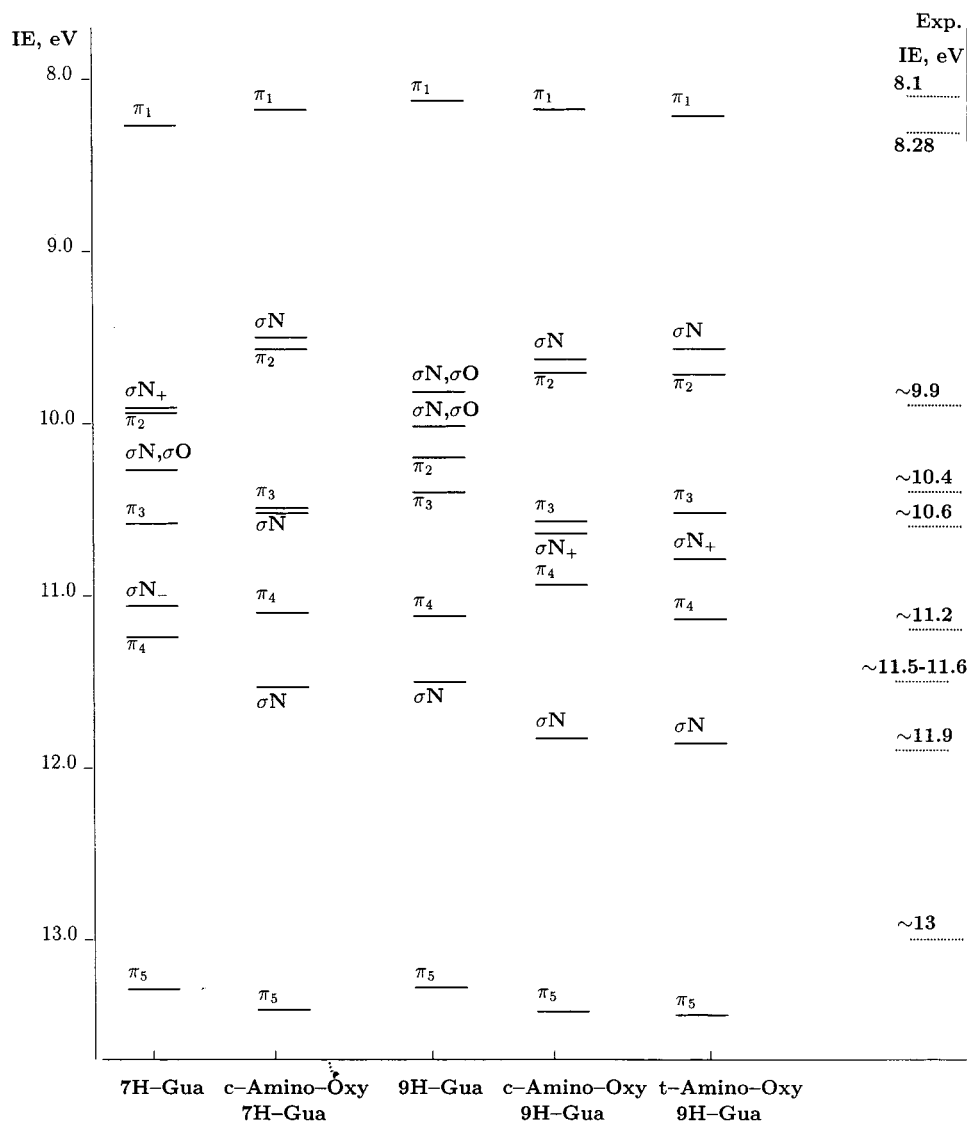


Figure 3. Correlation diagram for ionization energies of guanine tautomers.

tion. Peaks for 7Me-guanine are in good agreement with P3 values after applying a 0.2 eV shift.

9H-Guanine. Corrections to *KT* nearly vanish for the first ionization energy, which occurs at 8.13 eV in our P3 calculations. The next experimental peak at ~9.9 eV is not resolved and was assigned to ionizations from π_2 and n_1 orbitals. P3 calculations place two final states at 9.82 and 10.02 eV, and these are assigned to ionizations from σ DOs. Koopmans defects are large (about 2 eV) in both cases. P3 places the following π state at 10.20 eV. The next π state, which corresponds to ionization from the highly delocalized π_3 DO, is located at 10.40 eV.

As was the case with 7H-guanine, the Koopmans defects are very large for delocalized, σ -type orbitals. However, the net effect of correlation leads to a different ordering of these higher DOs. Whereas in 7H-guanine the order is $\pi_1, n_1, \pi_2, n_2, \pi_3$, this is no longer the case with 9H-guanine where the order of levels is $\pi_1, n_1, n_2, \pi_2, \pi_3$. Such an abundance of ionized states in a very narrow energy range provides for the unusually wide peak at ~10.4 eV.

The following ionized state has π character as well, and its calculated position, 11.12 eV, corresponds rather well with the experimental value of ~11.2 eV. An experimental peak at ~11.2 eV has two unassigned shoulders to the right of its maximum.

One of these shoulders corresponds rather closely to the P3 value of 11.50 eV. A value of 13.28 eV is obtained for ionization from the π_5 DO. The pole strength is slightly lower here. Three ionizations are predicted at 14.35, 14.50, and 14.62 eV. The lowest of these pertains to ionization from a π_6 DO, while the second in the group corresponds to ionization from an oxygen lone-pair function partially delocalized over the molecular core. At the last energy (14.62 eV), σ bonding levels first appear. Another σ level is predicted at 15.48 eV.

While agreement between experimental peaks with P3 results is not as close for 9H-guanine as for 7H-guanine, it is not possible to determine that the former isomer makes no contribution to guanine PES. Comparisons with methylated species are useful here as well. Peaks for 9Me-guanine listed in Table 1 are in reasonable agreement with the present P3 values.

cis-Amino-Oxy 9H-Guanine. This tautomer of 9H-guanine is only 0.61 kcal/mol higher in energy than 9H-guanine. The first ionized state is predicted by P3 at 8.18 eV, which is very close to the observed peak at 8.28 eV. Two subsequent ionizations are only 0.08 eV apart from one another. The lower state of this pair, predicted at 9.63 eV, pertains to a σN DO. The following ionization that is predicted at 10.57 eV occurs from a π_3 DO. The next σ state is predicted at 10.64 eV and corresponds to a σN_+ , in-phase combination of nonbonding

functions at N_1 and N_7 . Ionization from the π_4 DO is predicted at 10.94 eV. A σN level is predicted at 11.83 eV. As was the case with both oxo tautomers, ionization from the π_5 level has a somewhat lower pole strength. The position of a σO level is predicted at 13.94 eV. The next π state is predicted at 14.24 eV. The onset of $\sigma C-C$, $C-H$ bonding DOs obtains at 14.96 eV.

trans-Amino-Oxy 9H-Guanine. This rotamer is only 0.6 kcal/mol higher in energy than *cis*-amino-oxy 9H-guanine. DO orderings are the same. We conclude that all three isomers of 9H-guanine may be observed in the gas-phase PES.

cis-Amino-Oxy 7H-Guanine. This tautomeric form of 7H-guanine is about 4 kcal/mol higher in energy than amino-oxo 7H-guanine. Its first ionization energy at 8.18 eV is in good agreement with the experimental feature. Two ionizations are predicted around 9.5–9.6 eV. The next two levels are only 0.03 eV apart. Ionization from a π_4 level is placed at 11.10 eV. The next ionized state placed at 11.53 eV by P3 is attributed to a σN DO. The last state under discussion here is predicted at 13.41 eV. Here, the lowest pole strength for a π hole is found.

Dyson Orbitals. Energy shifts displayed in Figure 3 may be accompanied by changes in the DOs shown in Figure 2 for 7H-guanine. For the π_1 DO, however, the redistributions that accompany shifts in proton positions are minor.

Lone-pair lobes on N_3 and N_9 have the same phase in the σN_+ DO. In 9H-guanine, the N_9 lobe disappears in favor of a lobe on N_7 , and the O contribution expands. Shifting a proton from N_1 to O causes the N_1 contribution to this DO to grow and the O contribution to shrink.

π_2 DOs are approximately the same in the 7H and 9H structures, but in the amino-oxy forms, the N_1 and N_3 contributions are accentuated.

In the $\sigma N\sigma O$ DO, N_3 and O contributions are largest in the 7H form. A lone-pair lobe at N_7 becomes prominent in the 9H

form. O lobes disappear in favor of N_1 lobes in the amino-oxy forms.

Minor distortions take place in the π_3 DOs. The most prominent change is enlarged N_{amino} lobes in the amino-oxy structures.

Nonbonding lobes with opposite phases on N_3 and N_9 are the most prominent features in the σN_- DO of 7H-guanine. Replacement of the N_9 lobe with an N_7 lobe occurs in 9H-guanine. In the amino-oxy structures, N_1 lobes are prominent as well.

π_4 DOs in the 9H, amino-oxy structures have smaller N_{amino} contributions than in the 9H keto form.

N_1 contributions to the π_5 DOs are larger in the amino-oxy structures.

Conclusions

Electron propagator calculations in the partial third order approximation were performed on the five lowest isomers of guanine. Ionization energies obtained for 9H-guanine, its amino-oxy tautomers and 7H-guanine are in good agreement with experimental PES, but agreement with prominent peaks is best in the 7H-guanine calculations. The presence of other isomers cannot be excluded, although *cis*-amino-oxy 7H-guanine is the least stable form in MBPT(2) calculations. Koopmans defects are especially large for nonbonding, σN levels. Different orderings of energy levels obtain for tautomers of guanine. Proton shifts induce significant rearrangements in DO amplitudes, especially where N-centered, nonbonding lobes are present.

Acknowledgment. This work was supported by the National Science Foundation under grant CHE-9873897.

JA0015747