Ionisation potential and electron affinity of free 5’,8-cyclopurine-2’-deoxynucleosides. DFT study in gaseous and aqueous phase

Boleslaw T. Karwowski

Department of Biopharmacy, Medical University of Lodz, 90-151 Lodz, Poland

Received 23 May 2009; Accepted 10 August 2009

Abstract: Oxidatively generated damage to DNA frequently appears in the human genome as an effect of aerobic metabolism or as the result of exposure to exogenous oxidizing agents. Due to these facts it was decided to present, for the first time, the electron affinity, ionization potential of 5’,8-cyclo-2’-deoxyadenosine/guanosine (cdA, cdG) in their 5’R and 5’S diastereomeric forms. For all points of quantum mechanics studies presented, the density functional theory (DFT) with B3LYP parameters on 6-311++G** basis set level was used. The zero-point vibrational corrected adiabatic electron affinity (AEA) and adiabatic ionization potential (AIP) were calculated. Additionally the vertical electron affinity (VEA), vertical detachment energy (VDE) and vertical ionization potential were taken into consideration. AEA in eV (gaseous/aqueous phase) are as follows: 0.3/1.81 (5’R)cdA, 0.13/1.76 (5’S)cdA, 0.17/1.49 (5’R)cdG, 0.14/1.53 (5’S)cdG and AIP followed the order 7.43/5.59(5’S)cdG, 7.49/5.60(5’R)cdG, 7.77/5.97(5’R)cdA, 7.84/5.93(5’S)cdA. The obtained AIPs were found to be lower than that for corresponding natural nucleosides. Therefore, even though the 5’,8-cyclopurine-2’-deoxynucleoside level in a cell was judged as low, they can play an important role in the stability, replication and transcription of genes.

Keywords: DNA damage • cyclopurine-2’-deoxynucleosides • DFT • adiabatic ionization potential • adiabatic electron affinity

1. Introduction

Under ionizing radiation, which interacts with the cells’ environment, damage to genetic information can appear [1]. From another point of view, in DNA structure, modifications of sugar or base units are presented as a product of the free radicals’ actions [2,3]. Therefore, the major goal in nucleic acid biochemistry has been to establish the threshold energies necessary to ionize the canonical nucleosides or their modifications [4]. The majority can be removed during the BER (base excision repair) process [5]. From the point of view of DNA repair processes, 5’,8-cyclopurine-2’-deoxynucleoside (cPN) [6] are substrates for NER (nucleotide excision repair) machinery [7]. Their frequency and level in a living cell is still an open question, even though some data covering this field exists in literature [8]. Cyclopurines disturb the spatial geometry of DNA, weakening the hydrogen bonds between complementary bases in the double helix [9,10]. Moreover, they are more exposed to the influence of free radicals, therefore, their level in DNA can be upset due to forward reactions. Looking at the issue from a different angle, the appearance of different diastereomeric forms of the 5’,8-cyclo-5’-deoxyadenosine (cdA) or 5’,8-cyclo-5’-deoxyguanosine (cdG) [11] (Fig. 1) in the direction of electron migration, in this author’s opinion, is able to block this process and successfully protect some of the remaining DNA against degradation. To support this hypothesis, an attempt was made to determine the adiabatic ionization potential (AIP) and adiabatic electron affinities (AEA) of cyclopurines. Due to the fact that it is difficult to determine experimentally the AIP of cdA and cdG, a theoretical gaseous and aqueous phase calculation was performed.

© Versita Warsaw and Springer-Verlag Berlin Heidelberg.
basis functions per C, N, O atoms and 7 basis functions per H atoms [13]. For characterisation of the stationary point of all the investigated molecules, the harmonic vibration was calculated at the B3LYP/6-311++G** level. Moreover, using this strategy, the contribution of zero-point vibrational correction and thermal contribution to the free energies was considered. For all energy calculations, the scale factor 0.97 for 6-311++G** basis set was used [14]. The solvent effect was described for an aqueous medium, applying Tomasi’s polarized continuum model (PCM) [15], dielectric constant of water $\varepsilon=78.39$.

The appropriate adiabatic electron affinities (AEA) were obtained as the difference between the energies of the appropriate neutral form ($E_{\text{neutral}}$) and anion one ($E_{\text{anion}}$) at their optimized geometries $\text{AEA} = E_{\text{anion}}(r_e) - E_{\text{neutral}}(r_e)$ [16]. In this study, the electron affinity is defined as the released energy when the electron is added to a neutral molecule [17].

---

### 2. Experimental Procedures

#### 2.1. Computational Methodology

The molecular geometries of neutral 5′,8-cyclopurine-2′-deoxynucleosides in the gas phase were initially optimized by molecular mechanics using the UFF force fields. All subsequent calculations were performed by the density functional theory (DFT) using the generalized gradient approximation (GGA) exchange-correction functional, in which the B3LYP functional was implemented (Becke’s three-parameter hybrid HF/DFT exchange functional, and the Lee-Yang-Parr correlation functional). For all calculations the 6-311++G** [12] basis set with polarisation and diffuse functions was used - yielding 473 and 495 basis functions per cdA and cdG respectively. The triple-$\zeta$ quality 6-311++G** basis set was represented as a number of atomic orbitals composed of $M_{\text{C,N,O}}/M_{\text{H}}$ (5s4p1d / 4s1p), consisting of 23 basis functions per C, N, O atoms and 7 basis functions per H atoms [13]. For characterisation of the stationary point of all the investigated molecules, the harmonic vibration was calculated at the B3LYP/6-311++G** level. Moreover, using this strategy, the contribution of zero-point vibrational correction and thermal contribution to the free energies was considered. For all energy calculations, the scale factor 0.97 for 6-311++G** basis set was used [14]. The solvent effect was described for an aqueous medium, applying Tomasi’s polarized continuum model (PCM) [15], dielectric constant of water $\varepsilon=78.39$.

The appropriate adiabatic electron affinities (AEA) were obtained as the difference between the energies of the appropriate neutral form ($E_{\text{neutral}}$) and anion one ($E_{\text{anion}}$) at their optimized geometries $\text{AEA} = E_{\text{anion}}(r_e) - E_{\text{neutral}}(r_e)$ [16]. In this study, the electron affinity is defined as the released energy when the electron is added to a neutral molecule [17].
The vertical electron affinities VEA were obtained as the difference between the energies of the appropriate neutral form \( E_{\text{Neutral}} \) and anion one \( E_{\text{Anion}} \) at optimized neutral geometries \( \text{VEA} = E_{\text{Neutral}}(r_e, 0) - E_{\text{Anion}}(r_e, 0) \) [16].

The vertical detachment energy VDE were obtained as the difference between the energies of the appropriate neutral form \( E_{\text{Neutral}} \) and anion one \( E_{\text{Anion}} \) at optimized anion geometries \( \text{VDE} = E_{\text{Neutral}}(r_e, -) - E_{\text{Anion}}(r_e, +) \) [16].

From the definition, the ionisation potential is the amount of energy required to remove an electron from molecule. The suitable adiabatic ionisation potential (AIP) was obtained as the difference between the energies of the appropriate cationic form \( E_{\text{Cation}} \) and neutral one \( E_{\text{Neutral}} \) at their optimized geometries \( \text{AIP} = E_{\text{Cation}}(r_e^+) - E_{\text{Neutral}}(r_e, 0) \) [17].

The vertical ionization potential VIP were obtained as the difference between the energies of the appropriate cationic form \( E_{\text{Cation}} \) and neutral one \( E_{\text{Neutral}} \) at their optimized geometries \( \text{VIP} = E_{\text{Cation}}(r_e^+) - E_{\text{Neutral}}(r_e, 0) \) [17].

The calculations of all the structures were performed with Gaussian 03 Revision D.01 [18].

3. Results and Discussion

3.1. Ionization Potential (IP)

As mentioned above, the formed and stabilized radicals of DNA constituents are not uniformly distributed over nucleic acid chains during genome exposure to ionizing radiation. It is well known that the process of radiation-induction can create an excess of electrons and holes [19]. (Electrons and holes can migrate and get trapped at some preferred site of DNA [20]). The experimental determination of ionization potential of nucleic acid components presents some problems, for example: preparation of intact gas-phase nucleosides, nucleotides or nucleic acid bases. Therefore, not so much experimental data exists in literature for the majority of free bases [21]. Due to this limitation, IPs were computed by different quantum methods [22]. Comparison of theoretical and experimental ionization potentials suggests the following order: U>T>C>A>G. Different studies have indicated that pyrimidines possess a significantly higher IP than purines; moreover, guanine has the lowest IP and is the easiest one to oxidize [22]. Furthermore, the cluster of 8-oxo-guanines (one of the most important oxidative lesions [23,24]) is an even more probable unit for trapping holes [25]. In this study, the AIPs of 5’,8-cyclo-2’-deoxyguanosines and 5’,8-cyclo-2’-deoxyadenosines are reported in Table 1. The calculations, with and without ZPE correction, were done in gaseous and aqueous phases for their 5’R and 5’S diastereomeric forms. First of all, at each point of these studies, the guanidine derivative - cdG adopts the lowest AIP value. Additionally, the AIPs of cdAs and cdGs in the gaseous phase are close to the corresponding free base, ranging from 0.25 to 0.35 eV, with the ordering: (5’S)cdG < (5’R)cdG < (5’R)cdA < (5’S)cdA.

The order of AIPs calculated in an aqueous environment was:

(5’S)cdG < (5’R)cdG < (5’S)cdA < (5’R)cdA.

The AIPs and VIPs values of cyclopurines exhibited the same trends for the results obtained in gaseous and aqueous phase. Moreover the difference of energy between diastereomers was neglected, approximately 0.06eV (Table 1). The ionization potential values obtained in water media were significantly lower, around 1.8eV, than that of the gaseous one. Moreover, the AIPs of cyclopurines in water will decrease by another 1.3eV when the solvation energy of electron is considered [26]. Both values of the discussed AIP and VIP obtained in aqueous phase are in the range of the threshold energies required for DNA ionization ~4.9-6.4 eV. Therefore, cyclopurines would be easiest to oxidize and considered as a hole trap during the charge migration through ds-DNA. Additionally, the ionization potential for the 5’S and 5’R diastereomers of cyclopurines exhibited comparable values. Therefore, it can be postulated that the AIP of both diastereomers of cdG and cdA makes them prone to further oxidation under suitable conditions, which can lead to changes of mutagenicity of subsequent derivatives. Studies of 8-oxo-guanosine (the IP of 8-oxoG is lower around 0.3eV than for guanine), and their conversion to cyanuric acid is a good example for the increase of mutagenicity of the second oxidation product of DNA lesion [27].

3.2. Electron Affinity (EA)

The knowledge of the electronic properties of DNA provides information about the trapping site of electrons with simultaneous anion radicals’ formation [19]. These forms are able to participate in different chemical processes which can lead to an alteration of the DNA subunits. The assessment of electron affinities of nucleosides, nucleotides, nucleic acid bases and their products of ionizing radiation was important for the determination of the electron transfer in ds-DNA [30-32]. Moreover, the thermodynamic parameter AEAs discussed in this paragraph governs the ease of reduction of different molecules. Wiley et al. determined the adiabatic electron affinity in eV of nucleobases.
with the following order: Cyt (0.56) < Thy (0.79) < Ura (0.80) < Ade (0.95) < Gua (1.51) [33]. On the other hand, the careful theoretical study of Schaefer (DFT, B3LYP / DZV++ in the gaseous phase) has shown AEAs (in eV) of 2'-deoxynucleosides as follows: dT(0.44) > dC (0.33) > dG (0.09) ≈ dA (0.06) [32]. Historically, the DFT method was used for the first time by Desfrancois [34] to determine the electron affinities of uracil.

The adiabatic electron affinities of cyclopurines calculated in the aqueous and gaseous phases (DFT B3LYP / 6-311++G**), with and without zero-point energy corrections, are reported in Table 1. In each instance, the AEAs were comparable for 5'S or 5'R forms of cdA and cdG in the following order:

- 5',8-Cyclo-2'-deoxyguanosine
  - Gaseous phase
    - AIP = \( E_{\text{cation}}(r_e,+) - E_{\text{neutral}}(r_e,0) \)
    - 5'R: 7.48 (7.49), 5'S: 7.42 (7.43)
    - VIP = \( E_{\text{cation}}(r_e,0) - E_{\text{neutral}}(r_e,0) \)
    - 5'R: 7.88, 5'S: 7.85
  - Aqueous phase
    - AIP = \( E_{\text{cation}}(r_e,+) - E_{\text{neutral}}(r_e,0) \)
    - 5'R: 5.62 (5.60), 5'S: 5.59 (5.54)
    - VIP = \( E_{\text{cation}}(r_e,0) - E_{\text{neutral}}(r_e,0) \)
    - 5'R: 5.90, 5'S: 5.86

- 5',8-Cyclo-2'-deoxyadenosine
  - AIP = \( E_{\text{cation}}(r_e,+) - E_{\text{neutral}}(r_e,0) \)
    - 5'R: 7.76 (7.77), 5'S: 7.83 (7.84)
    - VIP = \( E_{\text{cation}}(r_e,0) - E_{\text{neutral}}(r_e,0) \)
    - 5'R: 6.00 (5.97), 5'S: 5.96 (5.94)

Moreover, the AEA values of all studied cyclopurines are close to zero with ZPE correction in gaseous phase, due to the ±0.12 eV error bracket of the methodology used [35]. Therefore, as in other theoretical studies of AEAs of nucleosides, positive adiabatic electron affinities were found for cyclopurines too.

The attachment of the electron to the cyclopurine system forces deviation from the base planarity in the geometry of exoamino groups (Table 3) [36]. On the other hand, from the works of Adamowicz [37] and Deka [38] it is known that in covalent anions the extra electron enters the LUMO of the molecules. Contrary to that in dipole-bound anions, the electron is bound by dipole fields of the neutral molecules without influencing the structure of molecules [38]. Based on the small geometry fluctuation and on the values of dipole moments of cdGs, which are significantly high in both discussed phases, (aqueous phase: 11.3 (5'R)cdG, 10.0 (5'S)cdG; gaseous phase: 7.8 (5'R)cdG, 6.9 (5'S)cdG) it seems that the excess electron in 5',8-cyclo-2'-deoxyguanosines is bonded through their dipole moment [36]. The above postulate is in good agreement with the data obtained for cdAs. The lower dipole moment was not sufficient to bind the excess charge via dipolar interactions in the gaseous phase (gaseous phase: 4.0 (5'R)cdA, 2.0 (5'S)cdA) [36]. However, the calculation in the aqueous phase exhibited the higher dipole moments (aqueous phase: 6.4 (5'R)cdA, 4.1 (5'S)cdA) in the border value which leads to charge binding via dipolar interactions. Therefore, distortions in structures of 5',8-cyclo-2'-deoxyadenosines anions are clearly observed [36]. The vertical electron affinities are presented in Table 2. The VEAs give a good insight into explaining the geometry distortion for the anion stabilization and into simply analyzing their nature. VEA for (5'S)cdA in the gaseous phase adopted a negative value which indicated an unbound anion character. In the remaining cases, obtained in the gaseous phase, VEA values are close to zero. Therefore the nature (bound/ unbound) of transient anions are unclear. However, the fact that all VEAs are lower than AEAs at each point of calculation indicated the relaxation of electron density simultaneously with changes in spatial geometry of the

Table 1. Adiabatic Ionization Potential and Vertical Ionization Potential in eV of 5',8-cyclo-2'-deoxynucleoside calculated by DFT B3LYP/6-311++G**, values with ZPE are given in parenthesis.

| 5',8-Cyclo-2'-deoxyguanosine | Aqueous phase | Gaseous phase |
|------------------------------|--------------|--------------|
| 5'R                          | 5.62 (5.60)  | 7.48 (7.49)  |
| 5'S                          | 5.59 (5.54)  | 7.42 (7.43)  |

| 5',8-Cyclo-2'-deoxyadenosine | Aqueous phase | Gaseous phase |
|------------------------------|--------------|--------------|
| 5'R                          | 5.96 (5.94)  | 7.76 (7.77)  |
| 5'S                          | 5.86 (5.85)  | 7.83 (7.84)  |
molecules in question. Following the definition “The vertical energy detachment comparison with AEA can tell us how important is the geometry relaxation of fixed nuclei in the transition to the neutral from anion” [16]. The VDEs of cyclopurines are relatively small in the range 0.12-0.31 eV, due to that these anions should not be observed during the experiments (Table 2). Additionally even the positive values of VDE have been found for all discussed molecules, their anions may be less stable due to the small AEs. However, the nature of (5’R)cdA remains uncertain due to the moderate values of VDE, AEA and due to the dipole moment. The close VDE values between 5’R/5’S diastereomers of cdA and cdG reflect the fact that the spatial geometry of the neutral molecule and anion species are quite similar. This phenomenon appears as a result of the rigid geometry of 5’,8-cyclopurine-2’-deoxyribonucleoside.

In the above-mentioned calculation, the solvent effect was taken into consideration as a part of the preliminary study results. Data obtained in the aqueous phase exhibited an increase in the value of the discussed parameters. However, the energetic difference in the case of diastereomers of cdA and cdG was relatively small (Tables 1, 2). Due to this, future study with microsolvation effect will be necessary.

Finally, it should be pointed out that in the cell environment the natural and modified nucleosides are solvated molecules, therefore, the discussed parameters, in the aqueous phase should be taken into future consideration with a comprehensive microsolvation study.

4. Conclusion

Tandem base modification can occur in DNA as the result of ionizing radiation or oxidative stress. In this study the electronic properties (adiabatic/vertical ionisation potential and adiabatic/vertical electron affinities, vertical detachment energy) of 5’R and 5’S diastereomers of 5’,8-cyclo-2’-deoxyadenosine / guanosine in their cationic, neutral and anionic forms were studied by density functional theory (DFT B3LYP/6-311++G**) in gaseous and aqueous phases. The zero-point vibrationally corrected adiabatic electron affinity (AEA) and adiabatic ionization potential (AIP) were calculated. Additionally the vertical electron affinity (VEA), vertical

---

Table 2. Adiabatic Electron Affinities, Vertical Electron Affinities and Vertical Detachment Energy in eV of 5’,8-Cyclo-2’-deoxyribonucleoside calculated by B3LYP/6-311++G**, values with ZPE are given in parenthesis.

| 5’,8-Cyclo-2’-deoxyribonucleoside | Gaseous phase | Aqueous phase |
|----------------------------------|--------------|--------------|
|                                   | 5’R          | 5’S          | 5’R          | 5’S          |
|                                   | AEA= $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,-)$ | $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,-)$ |
|                                   | 0.11 (0.17) | 0.08 (0.14)  | 1.40 (1.49)  | 1.45 (1.53)  |
|                                   | VEA= $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,0)$ | $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,0)$ |
|                                   | 0.08         | 0.03         | 1.14         | 1.11         |
|                                   | VED= $E_{\text{neutral}}(r_e,-) - E_{\text{anion}}(r_e,-)$ | $E_{\text{neutral}}(r_e,-) - E_{\text{anion}}(r_e,-)$ |
|                                   | 0.12         | 0.12         | 1.88         | 2.02         |
|                                   | AEA= $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,-)$ | $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,-)$ |
|                                   | 0.19 (0.27) | 0.05 (0.13)  | 1.68 (1.81)  | 1.69 (1.76)  |
|                                   | VEA= $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,0)$ | $E_{\text{neutral}}(r_e,0) - E_{\text{anion}}(r_e,0)$ |
|                                   | -0.01        | -0.19        | 1.40         | 1.35         |
|                                   | VED= $E_{\text{neutral}}(r_e,-) - E_{\text{anion}}(r_e,-)$ | $E_{\text{neutral}}(r_e,-) - E_{\text{anion}}(r_e,-)$ |
|                                   | 0.31         | 0.27         | 2.02         | 2.18         |

---

Adiabatic Electron Affinity in gaseous phase

| Free nucleobase           | Free 2’-deoxyribonucleoside [32] |
|---------------------------|----------------------------------|
| Guanine -0.04 [22] (0.96 [33]) | Guanosine 0.09                  |
| Adenine -0.26 [22]         | Adenosine 0.06                   |
| (0.012[34], 1.51 [33])     |                                  |

---
detachment energy (VDE) and vertical ionization potential were taken into consideration. AEA in eV (gaseous/aqueous phase) are as follows: 0.3/1.81 (5’R) cdA, 0.13/1.76 (5’S)cdA, 0.17/1.49 (5’R)cdG, 0.14/1.53 (5’S)cdG and AIP followed the order 7.43/5.59(5’S)cdG, 7.49/5.60(5’R)cdG, 7.77/5.97(5’R)cdA, 7.84/5.93(5’S) cdA. The close VDE values between diastereomers of cdA and cdG reflect the fact that the spatial geometry of the neutral molecule and anion species are quite similar. This phenomenon appears as a result of the fixed rigid geometry of 5’,8-cyclopurine-2’-deoxynucleoside. The obtained AIPs were found to be lower than that of the corresponding natural nucleosides. Therefore, even though the 5’,8-cyclopurine-2’-deoxynucleoside level in a cell was judged as low they can play an important role in the stability, replication and transcription of genes.

Acknowledgements

The author would like to thank the Medical University of Lodz (502-13-704) for support.

References

[1] J. Cadet, P. Vigny, In: H. Morrison (Ed.), Bioorganic Photochemistry (Wiley, New York, 1990)
[2] J. Cadet, T. Douki, J.-L. Ravanat, In: J. Fuchs, M. Podda, L. Packer (Eds.), Redox-genome interactions in health and disease (Marcel Dekker Inc, New York, 2003)
[3] (a) J. Cadet, T. Douki, D. Gasparutto, J.-L. Ravanat, Mutat. Res. 5, 531 (2003); (b) M.S. Cooke, M.D. Evans, M. Dizdaroglu, J. Lunec, FASEB J. 17, 1195 (2003)
[4] M.K. Shukla, J. Leszczynski, J. Biomol. Struct. Dynam. 25, 93 (2007)
[5] A. Sancar, L.A. Lindsey-Boltz, K. Ünsal-Kaçmaz, S. Linn, Annu. Rev. Biochem. 73, 39 (2004)
[6] (a) P.J. Brooks, DNA Repair 7, 1168 (2008); (b) P. Jaruga, M. Dizdaroglu, DNA Repair 7, 1413 (2008)
[7] A. Sancar, J.T. Reardon, In: W. Yang (Ed.), Advances in Protein Chemistry (Elsevier Academic Press, New York, 2004) 69
[8] K. Renderath, G-D. Zhou, R.L. Somers, J.H. Robbins, P.J. Brooks, J. Biol. Chem. 276, 36051 (2001) and references therein
[9] K. Miaskiewicz, J.H. Miller, A.F. Fuciarelli, Nucleic Acids Res. 23, 515 (1995)
[10] P. Hobza, J. Šponer, Chem. Rev. 99, 3247 (1999)
[11] (a) K. Keck, Z. Naturforsch B 23, 1034 (1968); (b) H.P.C. Hogenkamp, J.Biol. Chem. 238, 477 (1962); (c) J. Cadet, T. Douki, D. Gasparutto, J.-L. Ravanat, Rad. Phys. Chem. 72, 293 (2005); (d) P. Jaruga, M. Birincioglu, H. Rodriguez, M. Dizdaroglu, Biochemistry 41, 3703 (2002); (e) M. Dizdaroglu, P. Jaruga, H. Rodriguez, Free Radical Biol. Med. 30, 774 (2001); (f) E.E. Schroder, J.C. Budzinski, J.D. Wallace, J.D. Zimbrick, H.C. Box, Int. J. Radiat. Biol. 68, 509 (1995); (g) M.-L. Dirksen, W.F. Brakely, E. Holwitt, M. Dizdaroglu, Int. J. Radiat. Biol. 54, 195 (1988); (h) B.J. Brooks,
A
Ionisation potential and electron affinity
of free 5',8-cyclopurine-2'-deoxynucleosides.
DFT study in gaseous and aqueous phase

[12] W.J. Hehre, L. Radom, P. Schleyer, R.J.A. Pople, Ab Initio Molecular Orbital Theory (Wiley, New York, 1986)

[13] R. Krishnan, H.B. Schlegel, J.A. Pople, J.Chem. Phys. 72, 4654 (1980)

[14] L.T. Nguyen, T.N. Le, M.T. Nguyen, J. Chem. Soc., Faraday Trans. 94, 3541 (1998)

[15] S. Miertus, J. Tomasi, Chem. Phys. 65, 239 (1982)

[16] F.A. Evangelista, A. Paul, H.F.Schaefer III, J. Phys. Chem. A 108, 3566 (2004)

[17] J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Method, 2nd edition (Gaussian, Inc. Pittsburgh, PA, 1996)

[18] M.J. Frischet et al., Gaussian 03W, Revision D.01 (Gaussian, Inc., Wallingford CT, USA, 2004)

[19] (a) B. Giese, A. Biland, Chem. Commun. 667 (2002); (b) B. Armitage, Chem. Rev. 98, 1171 (1998); (c) C.J. Burrows, J.G. Muller, Chem. Rev. 98, 1109 (1998)

[20] A.K. Ghosh, G.B. Schuster, J. Am. Chem. Soc. 128, 4172 (2006)

[21] M.K. Shukla, J. Leszczynski, In: J. Sponer, F. Lankas (Eds.), Computational Studies of RNA and DNA (Springer, New York, 2006)

[22] N. Russo, M. Toscano, A. Grand, J. Comput. Chem. 21, 1243 (2000)

[23] (a) S.D. Wetmore, R.J. Boyd, L.A. Eriksson, Chem. Phys. Lett. 322, 129 (2000); (b) X. Yang, X-B. Wang, E.R. Vorpagel, L-S. Wang, Proc. Natl. Acad. Sci. USA. 101, 17588 (2004)

[24] J. Cadet et al., Nuc. Instr. Meth. Phys. Res B. 151, 1 (1999)

[25] V. Gomzi, J.N. Herak, J. Mol. Struct. (Theochem) 683, 155 (2004)

[26] J. Bernas, D. Grand, E. Amouyal, J. Phys. Chem. 84, 1259 (1980)

[27] C. Dherin, D. Gasparutto, T.R. O’Connor, J. Cadet, S. Bpitex, Int. J. Radiat. Biol. 80, 21 (2004)

[28] M.V. Orlov, A.N. Smirnov, Y.M. Varshavsky, Tetrahedron. Lett. 48, 4377 (1976)

[29] A.O. Alyoubi, R.H. Hila, Biophys. Chem. 55, 231 (1995)

[30] (a) A. Ghosh, A. Joy, G.B. Shuster, T. Douki, J. Cadet, Org. Biomol. Chem. 6, 916 (2008); (b) R.N. Barnett, C.L. Cleveland, U. Landman, E. Boone, S. Kanvah, G.B. Schuster, J. Phys. Chem. A 107, 3525 (2003); (c) T. Takada, K. Kawai, M. Fujitsuka, T. Majima, Proc. Natl. Acad. Sci. USA. 101, 14002 (2004); (d) K. Kawai, T. Takada, S. Tojo, T. Majima, J. Am. Chem. Soc. 125, 6842 (2003); (e) K. Kawai, T. Takada, S. Tojo, T. Majima, J. Am. Chem. Soc. 126, 1125 (2004); (f) T. Takada, K. Kawai, M. Fujitsuka, T. Majima, J. Am. Chem. Soc. 128, 11012 (2006)

[31] (a) B. Giese, Curr. Opin.Chem. Biol. 6, 612 (2002); (b) B. Giese, Acc. Chem. Res. 33, 631 (2000)

[32] A.N. Richardson, J. Gu, S. Wang, Y. Xie, H.F. Schaefer III, J. Am. Chem. Soc. 126, 4404 (2004)

[33] J.R. Wiley, J.M. Robinson, S. Ehdai, E.C.M. Chen, E.S.D. Chen, W.E. Wentworth, Biochem. Biophys. Res. Comm. 180, 841 (1991)

[34] C. Desfrancosi, H. Abdoul-Carime, J.P. Scherman, J. Chem. Phys. 104, 7792 (1996)

[35] J.C. Rienstra-Kiracofe, G.S. Tschumper, H.F. Schaefer III, S. Nandi, G.B. Ellison, Chem. Rev. 102, 231 (2002)

[36] B. Karwowski, J. Mol. Struct. – Theochem (in press)

[37] N.A. Oyler, L. Adamowicz, J. Phys. Chem. 97, 11122 (1993)

[38] P. Sarmah, R.C. Deka, Mol. Simulat. 34, 879 (2008)