Electronic Spectroscopy

Deutsche Ausgabe: DOI: 10.1002/ange.201511230
Internationale Ausgabe: DOI: 10.1002/anie.201511230

Electronic Characterization of Reaction Intermediates: The Fluorenylium, Phenalenylium, and Benz[*f*]indenylium Cations and Their Radicals

*Jan Fulara, Arghya Chakraborty, and John P. Maier**

Abstract: *Three vibrationally resolved absorption systems commencing at 538, 518, and 392 nm were detected in a 6 K neon matrix after mass-selected deposition of* $C_{13}H_9^+$ *ions (*$m/z = 165$*) produced from fluorene in a hot-cathode discharge ion source. The benz[f]indenylium (BfI*$^+$*: 538 nm), fluorenylium (FL9*$^+$*: 518 nm), and phenalenylium (PHL*$^+$*: 392 nm) cations are the absorbing molecules. Two electronic systems corresponding to neutral species are apparent at 490 and 546 nm after irradiation of the matrix with* $\lambda < 260$ *nm photons and were assigned to the FL9 and BfI radicals, respectively. The strongest peak at 518 nm is the origin of the* $2\,{}^1B_2 \leftarrow \tilde{X}\,{}^1A_1$ *absorption of FL9*$^+$*, and the 490 nm band is the* $2\,{}^2A_2 \leftarrow \tilde{X}\,{}^2B_1$ *origin of FL9. The electronic systems commencing at 538 nm and 546 nm were assigned to the* $1\,{}^1A_1 \leftarrow \tilde{X}\,{}^1A_1$ *and* $1\,{}^2A_2 \leftarrow \tilde{X}\,{}^2A_2$ *transitions of BfI*$^+$ *and BfI. The 392 nm band is the* $1\,{}^1E' \leftarrow \tilde{X}\,{}^1A_1'$ *transition of PHL*$^+$*. The electronic spectra of* $C_{13}H_9^+/C_{13}H_9$ *were assigned on the basis of the vertical excitation energies calculated with SAC-CI and MS-CASPT2 methods.*

The challenge in probing reaction intermediates is that they are short-lived and thus difficult to characterize. In the last decades, pulse radiolysis and flash photolysis techniques have been employed for the in situ synthesis and characterization of transient organic species.[1–3] The main impuissance of these techniques is that they are not species-selective. With this concern, the approach involving isolation of mass-selected ions and their neutralization in solid neon serves a pivotal role in the spectroscopic characterization of transient organic intermediates.[4]

The spectroscopic investigation of the fluorenylium cation (FL9$^+$), a textbook example of an antiaromatic carbenium ion, has been a standing goal in physical organic chemistry. Some information has been obtained by the photolysis of 9-hydroxyfluorene (9-OH-FL) in H_2O/CH_3OH solution. A broad transient absorption identified around 515 nm was assigned to FL9$^+$,[5,6] in agreement with previous studies, such as the photolysis of 9-OH-FL within metal zeolites[2] and 9-diazafluorene (9-DAFL) in CH_3OH.[3] Recently, an investigation of the photochemical products of 9-DAFL in amorphous water ice in the infrared and optical domain confirmed that the broad absorption at 515 nm originates from FL9$^+$.[7]

The FL9$^-$ anion was the focus of gas-phase photoelectron studies that provided vibrational frequencies for the ground state and the first excited state of neutral FL9.[8,9] This radical, which was produced by electron bombardment and UV photolysis of fluorene and trapped in solid argon, has also been studied by infrared, Raman, and UV/Vis spectroscopy.[10,11] The bands observed in the vibrational spectra were attributed to specific modes of FL9 on the basis of calculated ground-state frequencies. Electronic absorptions apparent in an argon matrix starting at 494.6 nm were assigned to the $1\,{}^2A_2 \leftarrow \tilde{X}\,{}^2B_2$ system of FL9.[11]

The spectroscopic properties of another reactive intermediate, namely phenalenylium (PHL$^+$), have been hardly explored. A weak absorption observed after γ-radiolysis of 7,7*a*-dihydro-6*bH*-cycloprop[*a*]acenaphthylene in a freon matrix was tentatively assigned to PHL$^+$.[1] NMR studies have established its D_{3h} structure.[12] The corresponding neutral phenalenyl radical (PHL) is a resonance-stabilized species with a doublet ground state. In solution, PHL dimerizes spontaneously, forming σ and π associates. PHL has been characterized in frozen *n*-pentane by an emission feature[13] and in the gas phase by resonant ionization spectroscopy.[14]

Despite these studies, structured optical spectra of FL9$^+$ and PHL$^+$ have not been obtained thus far. Herein, we describe the recording of the electronic spectra of PHL$^+$, FL9$^+$, BfI$^+$, and the corresponding radicals by mass-selected $C_{13}H_9^+$ deposition into a 6 K neon matrix.

The electronic absorption spectrum recorded after mass-selected deposition of $m/z = 165$ cations in solid neon is shown in Figure 1 (blue trace). The spectrum obtained after irradiation of the matrix with $\lambda < 260$ nm photons is shown in red. A small amount (0.003 %) of CH_3Cl was added to the solid neon; CH_3Cl reduces the space charge and suppresses neutralization of the cations during matrix growth. All absorptions in the blue trace, except for those at 490 and 546 nm, were reduced in intensity upon exposure to UV photons. This suggests a cationic nature of the carrier(s). The relative decrements of the band intensities establish the presence of three electronic systems with distinct vibrational progressions starting at 537.8, 518.2, and 392.4 nm (see the Supporting Information, Table S4). The strongest absorption

---

[*] Dr. J. Fulara, A. Chakraborty, Prof. Dr. J. P. Maier
Departement Chemie, Universität Basel
Klingelbergstrasse 80, 4056 Basel (Switzerland)
E-mail: j.p.maier@unibas.ch
Homepage: http://www.chemie.unibas.ch/~maier/

Dr. J. Fulara
Institute of Physics, Polish Academy of Sciences
Al. Lotników, 32/46, 02-668 Warsaw (Poland)

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201511230.

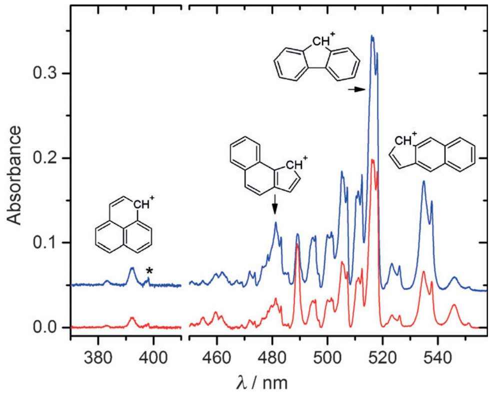


Figure 1. Electronic absorption spectra in a 6 K neon matrix recorded after mass-selected deposition of $C_{13}H_9^+$ cations produced from fluorene (blue trace) and after irradiation with $\lambda < 260$ nm photons (red trace). N_2^+ transition denoted by *.

is at 518.2 nm. These absorption systems are due to three isomers of $C_{13}H_9^+$.

Multiplet bands were observed for the 537.8 and 518.2 nm systems. The 538 nm absorption consists of two doublets, one narrower and the other one broader, that are separated by 101 cm^{-1}. The bands of the 518 nm system are triplets spaced by approximately 50 and 25 cm^{-1}. The features correspond to molecules trapped at energetically different matrix sites.

The $C_{13}H_9^+$ ion was then produced in the source from a mixture of naphthalene and propyne. The spectra obtained after deposition and after irradiation of the matrix ($\lambda <$ 260 nm) are shown in blue and red, respectively, in Figure 2. All of the electronic systems detected previously are evident; however, the relative intensities differ from those in Figure 1. The 392 and 518 nm bands are comparable in intensity when a mixture of naphthalene and propyne is used, but with fluorene as the precursor, the 392 nm band is almost 15 times weaker than that at 518 nm. This finding implies that the 392 nm absorption is due to another isomer of $C_{13}H_9^+$ that is favored by the naphthalene/propyne mixture.

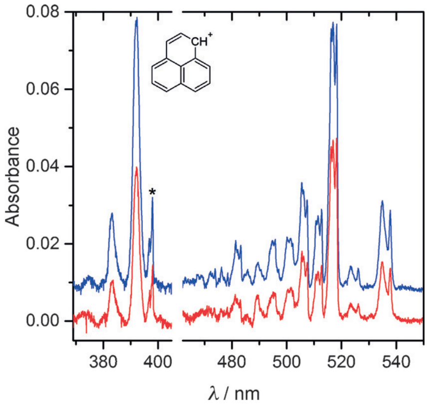
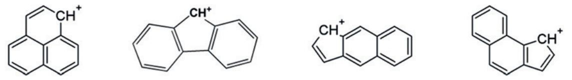


Figure 2. Electronic absorption spectra in a 6 K neon matrix recorded after mass-selected deposition of $C_{13}H_9^+$ cations produced from a mixture of naphthalene and propyne (blue trace) and after irradiation with $\lambda < 260$ nm photons (red trace). N_2^+ absorption denoted by *.

A broad feature at 515 nm, which was observed after photolysis of 9-diazafluorene in amorphous water ice, was previously assigned to the absorption of FL9$^+$,[7] and is close to the 518 nm band detected in the present studies. The 518 nm system is the most intense absorption observed after deposition of $C_{13}H_9^+$ ions produced from fluorene, and hence FL9$^+$ is proposed to be the carrier of the 518 nm system. However, there are two other cationic origins at 538 and 392 nm, and for a complete structural assignment, theoretical calculations on the plausible isomers of $C_{13}H_9^+$ were carried out.

The five isomers FL1$^+$–FL4$^+$ and FL9$^+$, which are produced by removal of a hydrogen atom from different peripheral carbon atoms of fluorene (Chart S1), PHL$^+$, two benzindenyl cations (BeI$^+$ and BfI$^+$), and a biphenyl-like structure with one phenyl and one cycloheptatriene PHT$^+$ were considered for the ground-state optimization. Calculations were performed with the DFT method using the M06-2X functional[15] and the cc-pVTZ basis set.[16] Our calculations revealed that PHL$^+$ is the global minimum, and that FL9$^+$ is 114 kJ mol^{-1} higher in energy. BeI$^+$ and BfI$^+$ are less stable than PHL$^+$ by 130 and 181 kJ mol^{-1}, respectively (Figure 3). PHT$^+$ and FL1$^+$–FL4$^+$ are higher-energy structures (by ca. 250 and 300 kJ mol^{-1}) and unlikely to be formed in the source.



Phenalenylium	Fluorenylium	Benz[*f*]indenylium	Benz[*e*]indenylium
PHL 0.0 *0.0*	**FL9** 113.9 *58.0*	**BfI** 129.5 *81.3*	**BeI** 181.3 *92.6*

Figure 3. Relative ground-state energies (in kJ mol^{-1}, including the ZPE correction) of $C_{13}H_9^+$ isomers (acronyms in bold) and their neutral analogues (values in italics) calculated by DFT using the M06-2X functional and the cc-pVTZ basis set.

The vertical electronic excitation energies of the five lowest-energy $C_{13}H_9^+$ isomers were calculated by time-dependent (TD) DFT, symmetry-adapted cluster configuration interaction (SAC-CI),[17,18] and multistate multi-configurational second-order perturbation (MS-CASPT2) methods[19] using the equilibrium coordinates obtained during the DFT optimization. The results are presented in Table S1. Furthermore, TD-DFT calculations were carried out on FL1$^+$–FL4$^+$ (Table S1). Among the nine considered $C_{13}H_9^+$ isomers, only three, namely FL9$^+$, BeI$^+$, and BfI$^+$, possess strong electronic transitions (Table 1) in the visible region close to the 518 and 538 nm systems. Based on these calculations, the 518 nm system was assigned to the $2\,^1B_2 \leftarrow \tilde{X}\,^1A_1$ transition of FL9$^+$. The main configuration of the ground state is b_1: 2 2 2 0 0 0, a_2: 2 2 2 0 0 0 with a reference weight (r.w.) of 0.775. The $2\,^1B_2$ system results from the $4b_1 \leftarrow 3a_2$ (r.w. = 0.149) and $4b_1 \leftarrow 2a_2$ (r.w. = 0.537) excitations (see Figure S1). Several vibrational features are apparent in the spectra (Table S4) and were assigned with reference to the ground-state frequencies calculated by DFT (Table S2). A comparison between the experimental spectrum and the calculated vibrational frequencies is shown in Figure S4. The

Table 1: Vertical excitation energies (in eV) of the strongest transitions (f = oscillator strength) of cationic and neutral $C_{13}H_9$ isomers calculated with the SAC-CI and MS-CASPT2 methods using coordinates obtained from the DFT/M06-2X/cc-pVTZ calculations.[a]

Species	Transition	SAC-CI		CASPT2		Exp.
		[eV]	f	[eV]	f	[eV]
$FL9^+$	$2\,^1B_2\leftarrow\tilde{X}\,^1A_1$	2.34	*0.27*	2.50	*0.31*	2.39
BfI^+	$1\,^1A_1\leftarrow\tilde{X}\,^1A_1$	2.35	*0.26*	2.59	*0.28*	2.31
BeI^+	$2\,^1A'\leftarrow\tilde{X}\,^1A'$	2.01	*0.12*	2.65	*0.15*	2.58
PHL^+	$1\,^1E'\leftarrow\tilde{X}\,^1A_1'$	3.17	*0.26*	3.49	*0.23*	3.16
FL9	$2\,^2A_2\leftarrow\tilde{X}\,^2B_1$	3.27	*0.14*	2.82	*0.01*	2.53
BfI	$1\,^2A_2\leftarrow\tilde{X}\,^2A_2$	2.92	*0.16*	2.52	*0.04*	2.27
BeI	$2\,^2A''\leftarrow\tilde{X}\,^2A''$	2.96	*0.07*	2.67	*0.01*	n.o.
	$3\,^2A''\leftarrow\tilde{X}\,^2A''$	3.77	*0.05*	3.19	*0.01*	n.o.

[a] n.o. = not observed.

vibrational frequencies of $FL9^+$ derived from the spectrum are close to the ones observed for the ground state of FL9 in the photoelectron spectrum of the anion.[9]

Excitation energy calculations (Table 1) show that both BeI^+ and BfI^+ are candidates for the 538 nm absorption system. As BeI^+ is approximately 50 kJ mol^{-1} less stable than BfI^+, the 538 nm system was assigned to the $1\,^1A_1\leftarrow\tilde{X}\,^1A_1$ electronic transition of BfI^+. A weak and broad band is seen around 481 nm (Figure 1, blue trace). The 1389 and 1592 cm^{-1} vibrational progressions of $FL9^+$ overlap in this region, but they are not responsible for the broadness of the 481 nm band. This system is an electronic transition of another isomer of $C_{13}H_9^+$. BeI^+ could be the carrier as calculations predict the most intense ($f = 0.15$) absorption to be around 465 nm (Table 1).

The calculated vertical excitation energies (Table 1) establish that the strong absorption at 392 nm observed for the naphthalene/propyne mixture is due to the phenalenyl cation PHL^+ (Figure 2). SAC-CI and CASPT2 methods predict a strong $1\,^1E'\leftarrow\tilde{X}\,^1A_1'$ electronic transition at 3.17 and 3.49 eV, respectively, which is in agreement with the observed band at 3.16 eV (392 nm). In the $\tilde{X}\,^1A_1'$ state, all π orbitals are filled and correspond to the b_1: 2 2 2 2 0 0 0, a_2: 2 2 0 0 0 configuration with r.w. = 0.802 (see Figure S2). The PHL^+ spectrum consists of one weak vibrational band at 598 cm^{-1} that is blue-shifted with respect to the origin, that is, the excitation of the ν_5 totally symmetric vibration in the $1\,^1E'$ state. The peak detected at 400 nm in haloalkane glass,[1] which was tentatively assigned to PHL^+, is close to that observed in the present study (392 nm).

Although the gas-phase investigation of PHL reported an electronic absorption at approximately 510 nm,[14] no neutral bands were observed around this wavelength in the present study. This implies that the oscillator strength of the visible transition of PHL is much weaker than that of the $1\,^1E'\leftarrow\tilde{X}\,^1A_1'$ transition of PHL^+.

$C_{13}H_9^+$ ions produced from fluorene were also deposited in a pure neon matrix. The spectra recorded after deposition and after UV irradiation of the matrix are shown in Figure 4 (in blue and red, respectively). Two absorption systems of neutral $C_{13}H_9$ commencing at 546 and 490 nm dominate the spectrum. The absence of scavenger in the matrix enhances cation neutralization, and hence the signals of the neutral species dominate. It can be assumed that the strongest absorption in Figure 4, with an onset at 490 nm, originates from FL9, because $FL9^+$ is predominately produced from the fluorene precursor. The wavelength of the origin peak of FL9 in neon matrix is close to the 494.6 nm band that was observed after UV photolysis of fluorene in an argon matrix.[10,11] The SAC-CI and CASPT2 calculations predict an intense $2\,^2A_2\leftarrow\tilde{X}\,^2B_1$ electronic transition at 3.27 and 2.87 eV, respectively (Tables 1, S3), which can be compared with the 2.53 eV (489.5 nm) band in Figure 4. FL9 is an open-shell electronic system with one unpaired electron residing in the $4b_1$ π orbital (Figure S3) with the following π electron configuration: b_1: 222u000, a_2: 222000 (r.w. = 0.733). The electron spin is mainly localized on the π_x orbital of C9 (Table S5). The $2\,^2A_2$ state arises from the $4b_1\leftarrow 3a_2$ (r.w. = 0.481) and $4a_2\leftarrow 4b_1$ (r.w. = 0.108) excitations. In the $2\,^2A_2$ state, the electron spin is distributed over the π_x orbitals of C4, C5 and C1, C8 (Table S6). The peaks observed for this system are the result of the excitation of vibrational modes in the $2\,^2A_2$ state (Table S4).

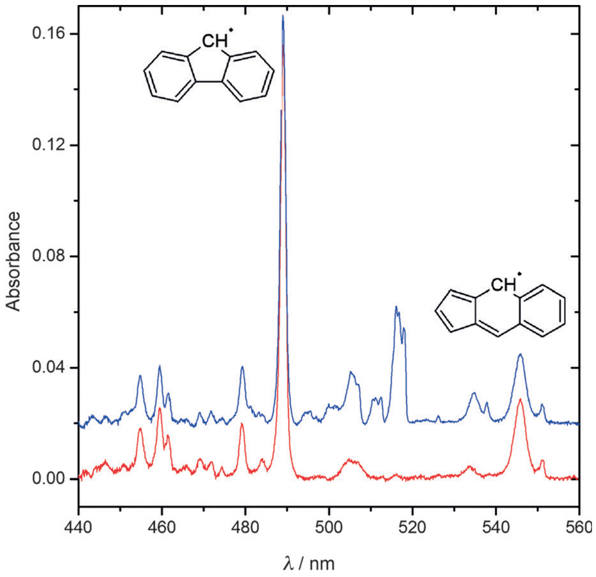


Figure 4. Electronic absorption spectra recorded after mass-selected deposition of $C_{13}H_9^+$ ions from fluorene in pure neon at 6 K (blue) and after irradiation of the matrix with $\lambda < 260$ nm photons (red).

The weaker 546 nm electronic system was assigned to the radical BfI; the corresponding cation is the second most stable structure after $FL9^+$ according to the DFT calculations. The SAC-CI and CASPT2 methods overestimate the $1\,^2A_2\leftarrow\tilde{X}\,^2A_2$ excitation energy of BfI by 0.65 and 0.25 eV, respectively (Table 1).

In conclusion, mass selection in combination with quantum-chemical calculations has enabled the unambiguous characterization of $C_{13}H_9/C_{13}H_9^+$ species. The in situ detection of intermediates helps to understand the pathway of chemical reactions, and with this concern in mind, the presented data may enable the identification of transient $C_{13}H_9/C_{13}H_9^+$

organic species by their electronic spectra. Such a characterization in 6 K neon matrices is the starting point for gas-phase spectroscopy.

Experimental Section

Fluorene and a mixture of naphthalene and propyne seeded in helium were used as precursors of $C_{13}H_9^+$. Ions produced in a hot-cathode discharge source were extracted and guided through an electrostatic bender to a quadrupole mass filter where $m/z = 165$ ions were selected with a mass resolution better than 1 amu. A 2–3 nA beam of $C_{13}H_9^+$ ions was co-deposited with pure neon, or with neon contaminated with a trace of CH_3Cl as an electron scavenger, onto a rhodium-coated sapphire substrate held at 6 K to form an approximately 150 μm thick matrix. The $C_{13}H_9^+$ ions accumulated a charge of 10–20 μC during the 3–4 h of matrix growth. The matrix was probed with broad-band light from halogen and xenon lamps. The light passing through the solid neon matrix parallel to the substrate surface was wavelength-dispersed with a 0.3 m spectrograph and recorded with a CCD camera. The electronic absorption spectra were acquired in several 60–70 nm wide overlapping sections covering 250–1100 nm with a resolution of 0.1 nm.

Acknowledgements

This work was supported by the Swiss National Science Foundation (200020-124349/1). Calculations were performed at the sciCORE facility of the University of Basel (http://scicore.unibas.ch/).

Keywords: density functional calculations · electronic spectroscopy · fluorenylium · phenalenylium · reactive intermediates

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 3424–3427
Angew. Chem. **2016**, *128*, 3485–3488

---

[1] T. Bally, Z. Zhu, J. Wirz, M. Fülscher, J.-Y. Hasegawa, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2311–2318.
[2] M. A. O'Neill, F. L. Cozens, N. P. Schepp, *Tetrahedron* **2000**, *56*, 6969–6977.
[3] a) J. Wang, J. Kubicki, E. F. Hilinski, S. L. Mecklenburg, T. L. Gustafson, M. S. Platz, *J. Am. Chem. Soc.* **2007**, *129*, 13683–13690; b) P. Costa, W. Sander, *J. Phys. Org. Chem.* **2015**, *28*, 71–74.
[4] A. Chakraborty, J. Fulara, J. P. Maier, *Angew. Chem. Int. Ed.* **2015**, *55*, 228–231; *Angew. Chem.* **2016**, *128*, 236–239.
[5] S. L. Mecklenburg, E. F. Hilinski, *J. Am. Chem. Soc.* **1989**, *111*, 5471–5472.
[6] R. A. McClelland, N. Mathivanan, S. Steenken, *J. Am. Chem. Soc.* **1990**, *112*, 4857–4861.
[7] P. Costa, I. Trosien, M. Fernandez-Oliva, E. Sanchez-Garcia, W. Sander, *Angew. Chem. Int. Ed.* **2015**, *54*, 2656–2660; *Angew. Chem.* **2015**, *127*, 2694–2698.
[8] B. Römer, G. A. Janaway, J. I. Brauman, *J. Am. Chem. Soc.* **1997**, *119*, 2249–2254.
[9] J. B. Kim, M. L. Weichman, T. I. Yacovitch, C. Shih, D. M. Neumark, *J. Chem. Phys.* **2013**, *139*, 104301.
[10] J. Szczepanski, J. Banisaukas, M. Vala, S. Hirata, R. J. Bartlett, M. Head-Gordon, *J. Phys. Chem. A* **2002**, *106*, 63–73.
[11] J. Szczepanski, J. Banisaukas, M. Vala, S. Hirata, W. R. Wiley, *J. Phys. Chem. A* **2002**, *106*, 6935–6940.
[12] D. Small, S. V. Rosokha, J. K. Kochi, M. Head-Gordon, *J. Phys. Chem. A* **2005**, *109*, 11261–11267.
[13] W. P. Cofino, S. M. van Dam, D. A. Kamminga, G. P. Hoornweg, C. Gooijer, C. MacLean, N. H. Velthorst, *Mol. Phys.* **1984**, *51*, 537–550.
[14] G. D. O'Connor, T. P. Troy, D. A. Roberts, N. Chalyavi, B. Fückel, M. J. Crossley, K. Nauta, J. F. Stanton, T. W. Schmidt, *J. Am. Chem. Soc.* **2011**, *133*, 14554–14557.
[15] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.
[16] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007–1023.
[17] H. Nakatsuji, K. Hirao, *J. Chem. Phys.* **1978**, *68*, 2053–2065.
[18] H. Nakatsuji, *Chem. Phys. Lett.* **1979**, *67*, 329–333.
[19] J. Finley, P. Malmqvist, B. O. Roos, L. Serrano-Andrés, *Chem. Phys. Lett.* **1998**, *288*, 299–306.

Received: December 3, 2015