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Accessory Publication

Pitfalls in the Photoelectron Spectroscopic Investigations of Benzyne.

Photoelectron Spectrum of Cyclopentadienylideneketene.

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Cartesian coordinates for **12** B3LYP/6-311G(d,p)

C	-0.5993935778	-2.4946100834	0.
C	0.8738239628	-2.2783916433	0.
C	1.1249126654	-0.9566961485	0.
C	-1.2201196612	-1.2999408471	0.
C	-0.1797810135	-0.2497747213	0.
C	-0.3904028587	1.0708142386	0.
H	-1.0708578046	-3.4679745101	0.
H	1.6056200158	-3.0749148449	0.
H	2.0803515544	-0.4543738282	0.
H	-2.2793129735	-1.0936465208	0.
C	0.054158939	2.2801649901	0.
O	0.2897681519	3.4260454689	0.

$- E_{tot}$ =	344,3527 au	9370,39 eV
$- E+_{Zp-c}$=	344,268474 au	9368,10 eV
ΔSCF =	0,3207 au	8,73 eV

Cartesian coordinates for **12** MP2/6-311G(d,p)

C	-0.5820363335	-2.5075815232	0.
C	0.8775357695	-2.2323000199	0.
C	1.074787654	-0.8888514447	0.
C	-1.2556229717	-1.3269907688	0.
C	-0.2575737182	-0.2431870322	0.

C	-0.5429926365	1.0802042628	0.
H	-1.0185773195	-3.499981566	0.
H	1.646337934	-2.9969235837	0.
H	2.0118418678	-0.3459603504	0.
H	-2.325292675	-1.1635663506	0.
C	0.1396573247	2.2114284638	0.
O	0.5207025043	3.3204114628	0.

SCF Done: E(RHF) = -342.222163897 hartrees
Sum of electronic and zero-point Energies= -343.274766
Sum of electronic and thermal Energies= -343.268027
Sum of electronic and thermal Enthalpies= -343.267083

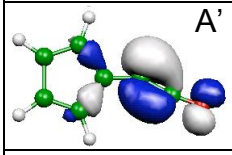
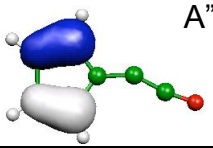
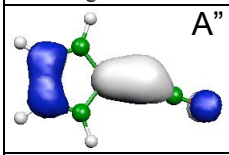
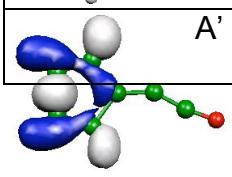
Sum of electronic and thermal Free Energies= -343.306159

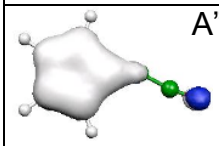
Cartesian coordinates for **12** HF/6-311G(d,p)

C	-0.5820363335	-2.5075815232	0.
C	0.8775357695	-2.2323000199	0.
C	1.074787654	-0.8888514447	0.
C	-1.2556229717	-1.3269907688	0.
C	-0.2575737182	-0.2431870322	0.
C	-0.5429926365	1.0802042628	0.
H	-1.0185773195	-3.499981566	0.
H	1.646337934	-2.9969235837	0.
H	2.0118418678	-0.3459603504	0.
H	-2.325292675	-1.1635663506	0.
C	0.1396573247	2.2114284638	0.
O	0.5207025043	3.3204114628	0.

SCF Done: E(RHF) = -342.222163897 hartrees
Sum of electronic and zero-point Energies= -343.274766
Sum of electronic and thermal Energies= -343.268027
Sum of electronic and thermal Enthalpies= -343.267083
Sum of electronic and thermal Free Energies= -343.306159

Table 1. Calculated [B3LYP/6-311G(d,p); MP2/6-311G(d,p)(ΔSCF)] and experimental ionization energies (IEs) for **12** (all values in eV).

nature of MO	$-\varepsilon^{KS}$	TD-DFT	MP2(ΔSCF)	Exp.
 A’	6.61	8.73[a]	8.72[a]	8.9
 A”	6.73	8.75	8.80	
 A”	7.91	9.98	9.97	10.2
 A’	10.68	12.66		

 A”	10.70	12.75		

[a]ΔSCF value (see computational details below)

Cartesian coordinates for **17** B3LYP/6-311G(d,p)

C	-0.6888965452	-1.2460180007	-1.7673680969
C	-1.1661790461	-0.0054186614	-0.9689804146
C	-0.7212817203	1.26965138	-1.7308818502
C	0.8676247131	-1.2281241131	-1.5722796035
C	1.1049692135	0.0197001687	-0.6837968282
C	0.8352423412	1.2862211063	-1.5358162254
C	-0.1580976992	-0.0089231784	0.1665335925
C	-0.3398427942	-0.0306685488	1.4751521631
C	0.0155355785	-0.0424266058	2.7060069523
O	0.1966731006	-0.0549280479	3.8652353734
H	-0.9848136913	-1.181823984	-2.8171352175
H	-1.1237189033	-2.159713887	-1.3568556625
H	-2.2126398983	-0.023191018	-0.6724808011
H	-1.1793423111	2.1595448314	-1.2941738156
H	-1.0158615248	1.2283510048	-2.7821723466
H	1.4112163152	-1.1523184981	-2.5170448201
H	1.2090257055	-2.1337703879	-1.0665566498
H	2.0451975288	0.0238695975	-0.1361612177
H	1.3802475253	1.2517869073	-2.4821813878
H	1.153434842	2.1853456151	-1.0039983735

Neutral:
SCF Done: E(RB+HF-LYP) = -424.235034688

Zero-point correction= 0.167624 (Hartree/Particle)
Thermal correction to Energy= 0.176110
Thermal correction to Enthalpy= 0.177054
Thermal correction to Gibbs Free Energy= 0.133364
Sum of electronic and zero-point Energies= -424.067411
Sum of electronic and thermal Energies= -424.058925
Sum of electronic and thermal Enthalpies= -424.057981
Sum of electronic and thermal Free Energies= -424.101671

Cation:
SCF Done: E(UB+HF-LYP) = -423.936996948

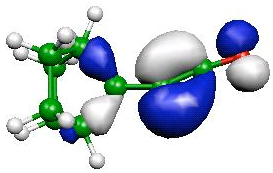
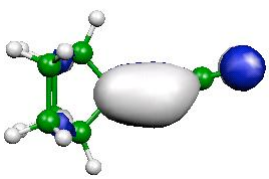
ΔSCF = 0.2980377 au = 8.11 eV

Cartesian coordinates for **17** HF/6-311G(d,p)

C	-0.6890030911	-1.2374343506	-1.7881956119
C	-1.2022165431	-0.0043518728	-1.0129754931
C	-0.7183013778	1.2620690282	-1.7526030045
C	0.8531243507	-1.2227082251	-1.5180103938
C	1.0485946645	0.0164688904	-0.6185015328
C	0.8236704694	1.2765142528	-1.4814209831
C	-0.2523614046	-0.009898495	0.1624171295
C	-0.5231565198	-0.0310385602	1.4726488142
C	0.15013882	-0.0372909768	2.60385125
O	0.5332661396	-0.0447203245	3.7139248577
H	-0.931857124	-1.1653667693	-2.8533655284
H	-1.1422909726	-2.1531876792	-1.3967082164
H	-2.2644189976	-0.0203436949	-0.7645069859
H	-1.1934890858	2.1553775205	-1.3360628056
H	-0.9589505707	1.2141356153	-2.8196343791
H	1.4419977646	-1.1409905323	-2.4375112692
H	1.1642421261	-2.1319476708	-0.9945374906
H	1.9623217908	0.0185248504	-0.0205235207
H	1.4146501078	1.236232883	-2.4023162891
H	1.1125321836	2.1771017908	-0.9309237772

SCF Done: E(RHF) = -421.507163263 hartrees
Zero-point correction= 0.169270 (Hartree/Particle)
Thermal correction to Energy= 0.177744
Thermal correction to Enthalpy= 0.178688
Thermal correction to Gibbs Free Energy= 0.135098
Sum of electronic and zero-point Energies= -422.813872
Sum of electronic and thermal Energies= -422.805399
Sum of electronic and thermal Enthalpies= -422.804454
Sum of electronic and thermal Free Energies= -422.848045

Table 2. Calculated [B3LYP/6-311G(d,p); MP2/6-311G(d,p)(ΔSCF)] and experimental ionization energies (IEs) for **17** (all values in eV).

nature of MO	$-\varepsilon^{KS}$	TD-DFT	MP2(ΔSCF)	Exp.
	5.98	8.11[a]	8.34[a]	8.35
	7.76	9.11		

[a]ΔSCF value (see computational details below)

All calculations were performed using the Gaussian 03program package.[32] The 6-311G(d,p) basis set was used, and geometry optimizations were carried out at the HF as well as the DFT[33] level of theory with the B3LYP[34] functional and confirmed as true minima via frequency analysis, which was also used to calculate zero-point energies (ZPEs) without scaling. Ionization energies were calculated with ΔSCF-DFT, which means that separate SCF calculations were performed to optimize the orbitals of the ground state and the appropriate excited state determinants ($IE=E_{cation}-E_{neut.mol.}$). The TDDFT[35] approach provides a first principles method for the calculation of excitation energies within a density functional context, taking into account the low lying ion calculated by the ΔSCF method. The advantages of this widely employed method of calculation of the first ionization energies (ΔSCF-DFT calculations) have been thoroughly demonstrated.[36]

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36 (a) Joantéguy, S. ; Pfister-Guillouzo, G. ; Chermette, H. *J. Phys. Chem.* **1999**, *103*, 3505- 3511 ; (b) Chrostowska, A. ; Miqueu, K. ; Pfister-Guillouzo, G. ; Briard, E. ; Levillain, J. ; Ripoll, J.-L. *J. Mol. Spectrosc.* **2001**, *205*, 323-330 ; (c) Bartnik, R. ; Baylère, P. ; Chrostowska, A. ; Galindo, A. ; Lesniak, S. ; Pfister-Guillouzo, G. *Eur. J. Org. Chem.* **2003**, 2475-2479 ; (d) Lemierre, V. ; Chrostowska, A. ; Dargelos, A. ; Chermette, H. *J. Phys. Chem. A*, **2005**, *109*, 8348-8355.