

# A search for an inexpensive calculational method for the reliable prediction of the first adiabatic and vertical ionization potentials of carbenes. Photoelectron spectra of two stable carbenes

Heidi M. Muchall, Nick H. Werstiuk, and Biswajit Choudhury

**Abstract:** Photoelectron (PE) spectra of two stable carbenes **7** and **8** have been recorded and the spectra have been interpreted with the aid of eigenvalues and eigenvectors taken from Becke3LYP calculations. For the carbene series **6–8**, the lone pair on the carbene carbon atom is the HOMO. The first adiabatic ionization potential (IP) of eight electronically quite different carbenes has been calculated using semiempirical PM3 and ab initio HF, Becke3LYP, and Becke3PW91 methods (3-21G(\*) and 6-31+G\* basis sets) as well as the CBS-4 model. For the first vertical IP, the HAM/3, Becke3LYP, and Becke3PW91 methods have been employed. CBS-4 and DFT calculations show excellent agreement with experimental values. Considering both accuracy and speed, the method of choice for the prediction of first ionization potentials of carbenes seems to be Becke3LYP/6-31+G\*\*/Becke3LYP/3-21G(\*)

*Key words:* carbenes, electronic structure, first ionization potential, photoelectron spectroscopy, quantum chemical calculations.

**Résumé :** On a déterminé les spectres photoélectroniques (PE) des deux carbènes stables **7** et **8** et on en a fait l'interprétation à l'aide des valeurs et des vecteurs propres obtenus à partir de calculs Becke3LYP. Pour les séries de carbènes **6–8**, la paire d'électron non partagée qui se trouve sur l'atome de carbone du carbène est la HOMO. En utilisant des calculs semi-empiriques PM3 et ab initio HF, les méthodes Becke3LYP et Becke3PW91 (ensembles de base 3-21G(\*) et 6-31+G\*) ainsi le modèle CBS-4, on a calculé le premier potentiel d'ionisation adiabatique (PI) de huit carbènes assez différents d'un point de vue électronique. Pour le premier PI vertical, on a utilisé les méthodes HAM/3, Becke3LYP et Becke3PW91. Les résultats des calculs CBS-4 et DFT présentent un excellent accord avec les valeurs expérimentales. Considérant l'exactitude et la vitesse, la méthode de choix pour prédire les premiers potentiels d'ionisation de carbène semble être la méthode Becke3LYP/6-31+G\*\*/Becke3LYP/3-21G(\*)

*Mots clés :* carbènes, structure électronique, premier potentiel d'ionisation, spectroscopie photoélectronique, calculs de chimie quantique.

[Traduit par la rédaction]

## Introduction

Photoelectron (PE) spectroscopy gives information on electronic structure and binding that can be obtained by no other technique. For PE spectroscopic studies, carbenes have been generated in the gas phase from suitable precursors by techniques such as pyrolysis (1, 2) and microwave discharge (3).<sup>2</sup> Usually, carbenes are more or less short-lived reactive intermediates. To be detected, they must be sufficiently long lived to be ionized. Both the precursor and the lifetime of a carbene can present difficulties to a PE spectroscopic study. First, if the

conversion of the precursor is not complete, ionization bands of the starting compound will still be present in the PE spectrum and possibly overlap with those of the carbene in crucial regions. And, as the carbene is not the only product formed from the starting compound, possible overlap with bands from the other primary products must be taken into account. Second, even if the carbene is generated close to the ionization beam of the spectrometer, rearrangement, fragmentation, and dimerization of the carbene can lead to secondary products whose bands can further complicate the PE spectrum.

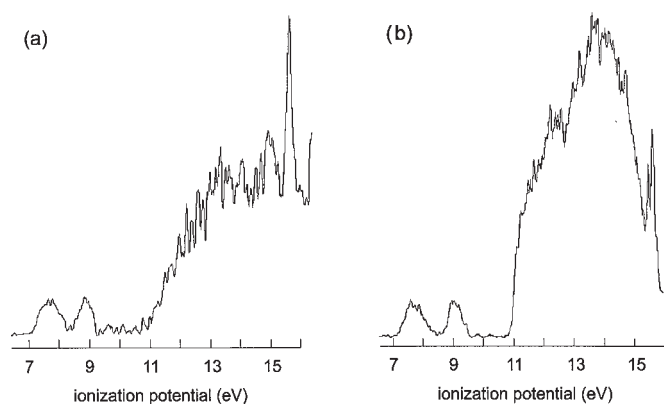
When a carbene is to be generated explicitly, at least problems arising from the precursor can be overcome by simply choosing the most suitable one. When, on the other hand, the carbene is one possible product in a pyrolysis study, all of the items mentioned above are likely to produce a complex PE spectrum. In this case, and especially when the PE spectrum of the carbene is unknown, it is imperative to have a procedure that allows easy, accurate prediction of the first ionization of the carbene, as this is the most likely not to be covered by other ionizations.

Received Aug 25, 1997.

H.M. Muchall,<sup>1</sup> N.H. Werstiuk,<sup>1</sup> and B. Choudhury.  
Department of Chemistry, McMaster University, Hamilton,  
ON L8S 4M1, Canada.

<sup>1</sup> Authors to whom correspondence may be addressed.  
Telephone: (905) 525-9140. Fax: (905) 522-2509. E-mail:  
muchall@mcmaster.ca, werstiuk@mcmaster.ca

<sup>2</sup> An overview of methods for generating reactive intermediates in PE spectroscopic studies was recently given by Chen (4).

**Fig. 1.** UV photoelectron spectra of carbenes (a) **7** and (b) **8**.

Interpretation of the PE spectrum of a molecule is usually achieved via Koopmans' theorem (5), which equates the ionization potential (IP) in question with the negative orbital energy of the respective molecular orbital taken from quantum chemical calculations. While this method often works well when several ionizations can be attributed to one molecule and relative energy differences can be taken as additional information, absolute orbital energies are usually systematically off, sometimes by as much as several electron volts, depending on the calculational method used. This approach is therefore not particularly suited for the prediction of the first ionization.

Yet the first ionization potential is easily accessible by computing the energy difference between the neutral molecule ( $N$  electrons) and its radical cation ( $N-1$  electrons). The geometry of the radical cation can be quite different from that of the neutral, which leads to an energetic separation between the adiabatic and vertical IPs. While the energy difference based on a full geometry optimization of both species gives the adiabatic ( $IP_a$ ), ignoring the geometry change upon ionization (which is achieved through a single-point energy calculation on the geometrical structure of the neutral for  $(N-1)$  electrons) gives the vertical ( $IP_v$ ) ionization potential. These calculated values are compared to those taken from the PE spectra to evaluate their quality. In recent years, models have been developed that give accurate energies and are therefore well suited to predict IPs (6). These models, like the G2 (7) and CBS (8) series, are very costly in terms of computational resources and can only be applied to molecules having a small number of heavy atoms (8).

Our goal was to find a method that can provide us with good predictions for first IPs of even relatively large carbenes in a reasonably short time. For future work, such a method could then be applied to the detection of unstable carbenes in our pyrolytic studies. In this paper, we present semiempirical and ab initio calculations of the first  $IP_a$  and  $IP_v$  of carbenes **1–5** as well as of "stable" carbenes **6–8**. Experimental values for **1–6** are taken from the literature (1–3, 9–11); He(I) PE spectra of **7** and **8** are presented here for the first time.

## Experimental

HF (12), CBS-4 (8), Becke3LYP (13a, 13b), and Becke3PW91 (13b, 13c) calculations were carried out on IBM RS/6000 model 39H, 350, and 530 computers with GAUSSIAN 94 (14). Semiempirical PM3 (15) calculations were performed with the

**Table 1.** Experimental and calculated (HAM/3) vertical ionization potentials IP (eV) and Becke3LYP/6-31+G\*\*/Becke3LYP/3-21G orbital energies  $\epsilon$  (eV) of carbenes **6–8**.

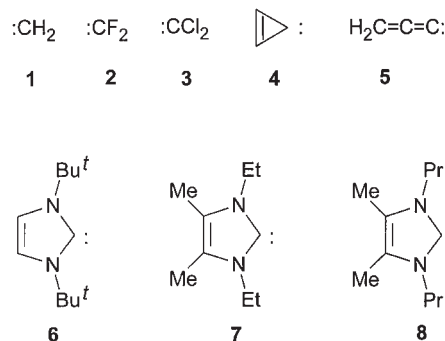
<b>6</b>			<b>7</b>			<b>8</b>		
IP			IP			IP		
Exp. <sup>a</sup>	Calcd.	$-\epsilon$	Exp.	Calcd.	$-\epsilon$	Exp.	Calcd.	$-\epsilon$
7.68	7.97	5.69	7.71	7.87	5.72	7.56	7.81	5.64
8.22	8.17	6.16	7.71	7.92	5.77	7.56	7.84	5.65
9.24	9.31	7.16	9.06	9.19	7.03	8.89	9.08	6.95
11.21	11.27	8.98	11.4	11.33	9.43	11.1	11.10	9.08

<sup>a</sup>Taken from ref. 9.

MOPAC (16) program package (version 6.00) on an IBM RS/6000 model 320H computer. All semiempirical geometry optimizations used the keyword PRECISE to tighten the convergence criteria. The equilibrium geometries obtained with PM3 were used in the HAM/3 (17) calculations on the IBM RS/6000 model 320H computer. Graphical representations of the calculationally determined eigenvectors (PM3//Becke3LYP/6-31+G\*; these were checked against Becke3LYP/6-31+G\*\*/Becke3LYP/6-31+G\* eigenvectors and were found to compare well) were plotted from HyperChem 5.<sup>3</sup>

PE spectra were measured with a locally built instrument (18) by signal averaging 12 scans with nitrogen (15.6 eV) as the calibrant. Linearity of the scale was ensured through calibrations with methyl iodide (9.54 and 10.16 eV) and O<sub>2</sub> (12.30 eV) performed prior to the experiments.

1,3-Diethyl-4,5-dimethylimidazol-2-ylidene (**7**) and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**8**) were prepared according to the literature (19).



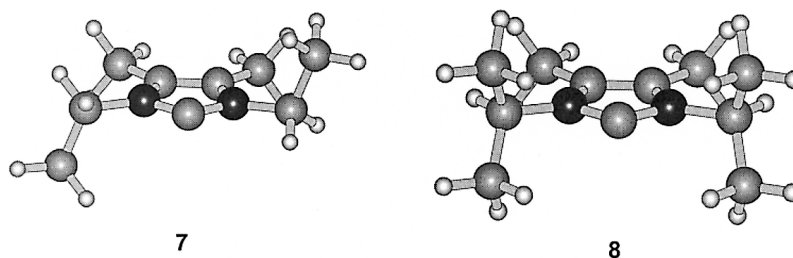
## Results and discussion

### Photoelectron spectra of stable carbenes **6–8**

Ultraviolet PE spectra of carbenes **7** and **8** are depicted in Fig. 1. The spectra show great similarity with the He(I) PE spectrum of **6** (9): all three spectra exhibit two low-energy bands well separated from the main group of  $\sigma$  bands, which has a shoulder on the low-energy side, and the first band in each of the spectra is made up of two ionizations. The first four ionizations of **7** and **8** ( $IP_{\text{exp}}$ ) are listed in Table 1 along with those reported for **6** (9). While for the *tert*-butyl substituted carbene **6** the separation of the first two ionizations is large

<sup>3</sup> Hypercube, Inc., Waterloo, Ont. 1996.

**Fig. 2.** Most stable conformations for carbenes **7** (Becke3LYP/6-31+G\*) and **8** (Becke3LYP/3-21G\*).



enough to give rise to two discrete maxima, for the ethyl and isopropyl analogues **7** and **8**, respectively, this difference is smaller and thus leads to one broad band for which only one maximum can be given. As can be seen in Table 1, Becke3LYP/6-31+G\*/Becke3LYP/3-21G orbital energies  $\epsilon$  for **6–8** (the lowest energy conformation for **7** and **8** is given in Fig. 2) mirror the experimental relative energy differences perfectly (the absolute deviation between  $-\epsilon$  and  $IP_{\text{exp}}$  is about 2 eV, a value not unusual for Becke3LYP calculations). While on going from **6** to **7** there is little change in the HOMO energy, HOMO-1 is destabilized by 0.4 eV. This fact confirms the character of HOMO and HOMO-1 of carbene **6** as given by Arduengo et al. (9). The HOMO is the in-plane lone pair on the carbene carbon  $n_C$  rather than a ring  $\pi$  orbital (as suggested for the unsubstituted parent carbene (20)): in the sequence **6–7**, a  $\pi$  orbital would exhibit a destabilization due to methyl substitution on the ring, a behavior that is observed for HOMO-1 ( $\pi_3$ ). Methyl substitution affects HOMO-2 ( $\pi_2$ ) in the same way as HOMO-1 whereas HOMO-3 (mostly  $\sigma$ -type electron density on nitrogen substituents) is stabilized when *tert*-butyl groups are exchanged for ethyl groups. So the orbital sequence in carbenes **6–8**, in accord with Arduengo et al. (9), is  $n_C > \pi_3 > \pi_2 > \sigma$ , which is confirmed by the PE spectra.

The semiempirical HAM/3 method gives ionization potentials directly. In Table 1  $IP_v$ 's are given for PM3 optimized geometries. For **6** and **7** these geometries do not differ significantly from those obtained with ab initio methods; for **8** the

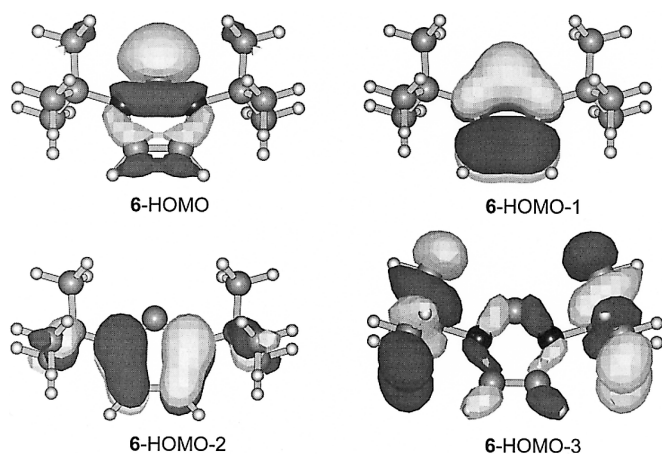
yet this does not much affect the calculated ionization potentials). HAM/3 IPs show a very good correlation with the experimental data.

### Calculation of the first adiabatic ionization potential

The limitation for the number of carbenes studied in this work is the number of carbene PE spectra available. We took PE spectroscopic literature values for the first adiabatic ionization potentials of singlet (21) carbenes **2–5** (1–3). To include a triplet carbene, the  $IP_a$  of the parent methylene (**1**) determined from a mass spectrometric experiment (10.35 eV) (11) as well as from the Rydberg series in its VUV spectrum (10.40 eV) (10) was also considered. For these carbenes, we performed calculations for first  $IP_a$ 's using the compound computational model CBS-4. While being the smallest — and fastest — model in the CBS/PNO (complete basis set/pair natural orbitals) series, this model still gives accurate molecular energies on a UHF/3-21G(\*) optimized geometry (the mean absolute deviation from experimental IPs for the G2 test set (22) is 2.2 kcal mol<sup>-1</sup> or 0.1 eV; the maximum error is 6.1 kcal mol<sup>-1</sup> or 0.3 eV for hydrogen fluoride) (8). Total energies from which  $IP_a$ 's are computed are listed in Table 2. As can be seen in Table 3, CBS-4 values for carbenes **1–3** and **5** differ from experiment by less than 0.2 eV; the difference for **4** is only slightly larger. The mean absolute deviation is 0.13 eV, a figure against which other calculational methods can be evaluated.

There have been previous attempts at calculating first adiabatic IPs of carbenes in the literature. Using an electron propagator method (MCSTEP), Nichols et al. (23) in 1994 applied adiabatic corrections to calculated vertical ionization potentials of **1**. Rodriguez, Bohme, and Hopkinson (24) in 1996 employed fourth-order Møller–Plesset theory and QCISD(T) to obtain enthalpies of formation for **1** and **3** and from these deduce  $IP_a$ 's. In 1989, Wong and Radom (25) used the CISD/6-31G\* level of theory to predict the, at that time unknown,  $IP_a$  of **4** to be 8.8 eV, a value that is still 0.35 eV off. Russo, Sicilia, and Toscano (26) in 1992 used a density functional approach (LCGTO-LSD/NLC) to the  $IP_a$ 's of **1–3**. They report 10.69 eV for **1**, 11.56 eV for **2**, and 9.55 eV for **3**, which, compared to the experimental data stated in this paper, give differences of 0.29, 0.14, and 0.28 eV, respectively. These values seem to suggest that density functional theory is suitable for our purpose.

Tables 2 and 3 give results from semiempirical PM3 and ab initio HF, Becke3LYP, and Becke3PW91 methods. PM3  $IP_a$ 's (Table 3) for difluoro carbene (**2**), dichloro carbene (**3**), and propadienyldiene (**5**) are unacceptably low and even though those of methylene (**1**) and cyclopropenyldiene (**4**) are very close to the experimental values, PM3 cannot be used for our



methine hydrogens are twisted 47° out of the plane with PM3 (the in-plane ab initio conformation for **8** is shown in Fig. 2,

**Table 2.** Ab initio total energies (hartrees) and PM3 heats of formation (kcal mol<sup>-1</sup>) for optimized geometries for carbenes **1–5** with *N* and *N*–1 electrons.

	Number of electrons	1	2	3	4	5
CBS-4	<i>N</i>	–39.077 579	–237.487 215	–957.413 803	–115.158 279	–115.132 313
	<i>N</i> –1	–38.693 913	–237.064 719	–957.079 771	–114.814 424	–114.753 286
PM3	<i>N</i>	71.64	–49.09	57.45	136.17	139.37
	<i>N</i> –1	310.58	201.15	212.80	350.76	362.70
HF/6-31+G*	<i>N</i>	–38.923 719	–236.671 751	–956.715 811	–114.627 381	–114.599 271
	<i>N</i> –1	–38.566 493	–236.289 448	–956.408 058	–114.335 510	–114.272 080
B3LYP/3-21G	<i>N</i>	–38.936 055	–236.393 390	–953.755 592 <sup>a</sup>	–114.690 050	–114.694 755
	<i>N</i> –1	–38.555 452	–235.977 747	–953.386 355 <sup>b</sup>	–114.359 722	–114.319 198
B3LYP/6-31+G*	<i>N</i>	–39.154 890	–237.711 308	–958.388 918	–115.361 684	–115.342 591
	<i>N</i> –1	–38.772 761	–237.289 913	–958.050 779	–115.027 242	–114.957 802
( +ZPVE) <sup>c</sup>	<i>N</i>	–39.137 542	–237.704 573	–958.384 919	–115.329 432	–115.311 348
	<i>N</i> –1	–38.756 218	–237.281 601	–958.045 505	–114.994 425	–114.926 986
B3LYP/6-31+G*// B3LYP/3-21G(*)	<i>N</i>	–39.154 864	–237.709 291	–958.377 853	–115.359 662	–115.342 492
	<i>N</i> –1	–38.772 757	–237.286 859	–958.044 394	–115.026 737	–114.957 752
B3PW91/3-21G(*)	<i>N</i>	–38.922 924	–236.307 901	–953.864 982	–114.641 021	–114.640 063
	<i>N</i> –1	–38.535 457	–235.891 058	–953.528 919	–114.309 362	–114.260 035
B3PW91/6-31+G*	<i>N</i>	–39.140 743	–237.618 323	–958.264 337	–115.312 328	–115.286 037
	<i>N</i> –1	–38.753 605	–237.202 117	–957.928 944	–114.979 628	–114.907 511
B3PW91/6-31+G*// B3PW91/3-21G(*)	<i>N</i>	–39.140 721	–237.616 022	–958.263 159	–115.310 130	–115.285 950
	<i>N</i> –1	–38.753 603	–237.198 761	–957.928 933	–114.979 004	–114.907 381

<sup>a</sup>B3LYP/3-21G\* value is –953.991 570.<sup>b</sup>B3LYP/3-21G\* value is –953.655 543.<sup>c</sup>ZPVE (not scaled) corrected B3LYP/6-31+G\* total energies.**Table 3.** Observed and calculated first adiabatic ionization potentials (eV) of carbenes **1–8**.

	1	2	3	4	5	6	7	8
IP <sub>a,obs</sub>	10.4 <sup>a</sup>	11.42 <sup>b</sup>	9.27 <sup>c</sup>	9.15 <sup>d</sup>	10.43 <sup>d</sup>	7.2 <sup>e</sup>	7.1 <sup>f</sup>	7.0 <sup>f</sup>
CBS-4	10.44	11.50	9.09	9.36	10.31			
PM3	10.36	10.85	6.74	9.31	9.68	7.88	8.14	8.07
HF/6-31+G*	9.72	10.40	8.37	7.94	8.90			
B3LYP/3-21G	10.36	11.31	10.05 <sup>g</sup>	8.99	10.22	6.84	6.91	6.81
B3LYP/6-31+G* ( +ZPVE) <sup>h</sup>	10.40	11.47	9.20	9.10	10.47	7.14	7.26	
	10.38	11.51	9.24	9.12	10.46			
B3LYP/6-31+G*// B3LYP/3-21G(*)	10.40	11.50	9.18	9.06	10.47	7.12	7.24	7.06
B3PW91/3-21G(*)	10.54	11.34	9.14	9.02	10.34	6.85	6.92	6.83
B3PW91/6-31+G*	10.53	11.32	9.13	9.05	10.30			
B3PW91/6-31+G*// B3PW91/3-21G(*)	10.53	11.35	9.09	9.01	10.30	7.32	7.57	7.00

<sup>a</sup>References 10, 11.<sup>b</sup>Reference 3.<sup>c</sup>Reference 1.<sup>d</sup>Reference 2.<sup>e</sup>Estimated from ref. 9.<sup>f</sup>This work.<sup>g</sup>B3LYP/3-21G\* value is 9.14 eV.<sup>h</sup>ZPVE (not scaled) corrected B3LYP/6-31+G\* total energies.

purpose. HF with a 6-31+G\* basis set performs much worse; all IP<sub>a</sub>'s are prohibitively low. Becke3LYP, on the other hand, with as small a basis set as 3-21G, gives very good agreement with experiment, the only exception being for dichloro carbene (**3**). This is obviously due to the presence of third-row chlorine atoms and is corrected by including polarization functions in the basis set (Table 3). The resulting mean absolute deviation

is an amazing 0.13 eV, the same value that we obtained using CBS-4. With the 6-31+G\* basis set it even drops to 0.04 eV for this set of five carbenes, which is considerably better than the CBS-4 value.

For Becke3LYP calculations we omitted corrections for zero-point vibrational energies (ZPVEs) as we expected their influence to be small. A check with unscaled ZPVEs (the

**Table 4.** Ab initio total energies (hartrees) and PM3 heats of formation (kcal mol<sup>-1</sup>) for optimized geometries for carbenes 6–8 with *N* and *N*–1 electrons.

	Number of electrons	6	7	8
	PM3	<i>N</i>	14.99	16.93
	<i>N</i> –1	196.64	204.70	192.83
B3LYP/3-21G	<i>N</i>	–537.742 612	–459.541 260	–537.751 035
	<i>N</i> –1	–537.491 300	–459.287 465	–537.500 666
B3LYP/6-31+G*	<i>N</i>	–540.701 937	–462.082 812	
	<i>N</i> –1	–540.439 654	–461.816 130	
B3LYP/6-31+G*// B3LYP/3-21G(*)	<i>N</i>	–540.699 913	–462.080 961	–540.711 260
	<i>N</i> –1	–540.438 104	–461.814 873	–540.451 716
B3PW91/3-21G(*)	<i>N</i>	–537.552 549	–459.375 795	–537.559 916
	<i>N</i> –1	–537.300 717	–459.121 491	–537.308 901
B3PW91/6-31+G*// B3PW91/3-21G(*)	<i>N</i>	–540.499 975	–461.908 494	–540.511 437
	<i>N</i> –1	–540.240 705	–461.645 146	–540.254 247

**Table 5.** Observed and calculated first vertical ionization potentials (eV) of carbenes 1–8.

	1	2	3	4	5	6	7	8
IP <sub>v,obs</sub>	— <sup>a</sup>	12.27 <sup>b</sup>	9.8 <sup>c</sup>	9.4 <sup>d</sup>	10.43 <sup>d</sup>	7.68 <sup>e</sup>	7.71 <sup>f</sup>	7.56 <sup>f</sup>
HAM/3 <sup>g</sup>	9.11	12.31	— <sup>h</sup>	10.06	10.00	7.97	7.88	7.81
B3LYP/6-31+G*	10.42	12.33	10.18	9.42	10.43	7.56	7.66	— <sup>i</sup>
B3LYP/6-31+G*// B3LYP/3-21G(*)	10.43	12.60	10.43	9.61	10.41	7.69	7.82	7.59
B3PW91/6-31+G*	10.56	12.21	10.12	9.37	10.42	— <sup>i</sup>	— <sup>i</sup>	— <sup>i</sup>
B3PW91/6-31+G*// B3PW91/3-21G(*)	10.56	12.49	10.38	9.57	10.39	7.63	7.65	7.51

<sup>a</sup>Not known.<sup>b</sup>Reference 3.<sup>c</sup>Estimated from ref. 1.<sup>d</sup>Estimated from ref. 2.<sup>e</sup>Reference 9.<sup>f</sup>This work.<sup>g</sup>On PM3 optimized geometries.<sup>h</sup>HAM/3 is not parameterized for chlorine.<sup>i</sup>The carbene was not optimized at this level of theory.

factor for Becke3LYP/6-31G\* is 0.98 (6), which is close enough to 1.0; we assumed the same to be true for the 6-31+G\* basis) on Becke3LYP/6-31+G\* total energies confirmed this (Tables 2 and 3).

Although the number of carbenes studied is small, electronically 1–5 are quite different. That Becke3LYP did an excellent job of predicting all first IP<sub>a</sub>'s was promising for an extension of the study to the so-called “stable” carbenes 6–8. Carbenes 6–8 have considerably more heavy atoms than carbenes 1–5 and obtaining optimized geometries of their radical cations using Becke3LYP/6-31+G\* is still computationally demanding. We therefore checked the possibility of doing single-point energy calculations at this level of theory using the Becke3LYP/3-21G(\*) optimized geometries. The result is a mean absolute deviation of 0.06 eV; calculated IP<sub>a</sub>'s can be seen in Table 3. So this is probably the method of choice for calculating the first IP<sub>a</sub> of carbenes of all sizes.

For a further comparison,<sup>4</sup> we repeated the above DFT calculations using the PW91 correlation functional (Tables 2 and 3). While Becke3PW91 performs slightly better than Becke3LYP

with the 3-21G(\*) basis set, it is definitely worse when the 6-31+G\* basis set is employed.

Experimental IP<sub>a</sub>'s of carbenes 6–8 as given in Table 3 were estimated from their PE spectra (onset of the first band). The calculational data (Tables 3 and 4) for these stable carbenes confirm the previous findings for the ordinary carbenes: Becke3LYP/6-31+G\*//Becke3LYP/3-21G(\*) gives excellent results.

#### Calculation of the first vertical ionization potential

Experimental first vertical IPs of carbenes 2–8 are listed in Table 5. As there are no reported IP<sub>v</sub>'s for carbenes 3–5, we estimated them from their PE spectra (maximum of the band) (1, 2). For carbenes 6–8 we have shown that IP<sub>v</sub>'s calculated with the semiempirical HAM/3 method are in very good agreement with experiment (see above). This statement was based on a total of 12 IPs for the three compounds. Yet, if only the first IP<sub>v</sub> of a carbene is considered, deviations from the experimental value can be rather large (Table 5).

A calculation of the first IP<sub>v</sub> differs from a calculation of the first IP<sub>a</sub>: while the IP<sub>a</sub> requires optimized geometries for both the carbene *and* its radical cation (relaxation), for the IP<sub>v</sub>

<sup>4</sup> We thank A.D. Becke for suggesting this comparison.

**Table 6.** Ab initio total energies (hartrees) for single-point energy calculations for  $N-1$  electrons on carbene optimized geometries for carbenes **1–8**.

	B3LYP/6-31+G*	B3LYP/6-31+G*// B3LYP/3-21G(*)	B3PW91/6-31+G*	B3PW91/6-31+G*// B3PW91/3-21G(*)
<b>1</b>	-38.771 923	-38.771 678	-38.752 788	-38.752 607
<b>2</b>	-237.258 112	-237.246 377	-237.169 708	-237.156 819
<b>3</b>	-958.014 792	-958.004 503	-957.892 397	-957.881 649
<b>4</b>	-115.015 580	-115.006 556	-114.967 917	-114.958 579
<b>5</b>	-114.959 358	-114.960 061	-114.903 182	-114.904 021
<b>6</b>	-540.424 084	-540.417 214	— <sup>a</sup>	-540.219 579
<b>7</b>	-461.801 290	-461.793 751	— <sup>a</sup>	-461.627 432
<b>8</b>	— <sup>a</sup>	-540.432 303	— <sup>a</sup>	-540.235 277

<sup>a</sup>The carbene was not optimized at this level of theory.

the energy of the radical cation is calculated on the geometry of the neutral carbene (no relaxation). As for the first  $IP_a$ , there have been attempts at calculating first vertical IPs of carbenes. In 1985, Nguyen et al. (27) performed HF, MP2, MP3, and MP4SDQ (6-31G\*\* basis) single-point energy calculations on the HF/3-21G\* geometry for **3** and obtained  $IP_v$ 's of 9.45, 9.73, 9.86, and 9.75 eV, respectively, which shows the level of theory necessary to get close to the estimated value of 9.8 eV given in Table 5. Bauschlicher and Taylor (28) in 1987 published full CI benchmark calculations for  $IP_v$ 's of **1** to which other high-level calculations were compared (X.-C. Wang and K.F. Freed in 1989 (29), Nichols et al. (23)). The work of Wong and Radom (25) includes the predicted  $IP_v$  of **4**. The reported value of 9.0 eV using CISD/6-31G\* differs from the value in Table 5 by 0.4 eV. Russo, Sicilia, and Toscano (26) give LCGTO-LSD/NLC  $IP_v$ 's for **1** (10.73 eV), **2** (12.09 eV), and **3** (10.30 eV).

Table 5 shows the Becke3LYP/6-31+G\*  $IP_v$ 's (total energies for the radical cations are given in Table 6) from this work for carbenes **1–7**. For **1**, there is no  $IP_v$  available, but our calculations suggest that it should be close to its  $IP_a$  of 10.4 eV.  $IP_v$ 's for **2** and **4–7** are very close to the experimental values with the largest difference of 0.12 eV for **6**. The difference for **3** with 0.38 eV is somewhat large; this might be partially due to an uncertainty in our estimation of the experimental first  $IP_v$ . As can be seen in Table 5, good results are obtained with Becke3LYP/6-31+G\*//Becke3LYP/3-21G(\*) for **1–8**, especially for carbenes with more heavy atoms. Except for dihalo carbenes **2** and **3** with a difference of 0.33 and 0.63 eV (the latter value could be smaller, see above), respectively,  $IP_v$ 's differ by less than 0.22 eV. Becke3PW91 values for the first vertical IP, in contrast to values obtained for the first adiabatic IP, are comparable to those obtained with Becke3LYP (Table 5).

## Conclusions

Recorded PE spectra of stable carbenes **7** and **8** resemble that of the *tert*-butyl substituted carbene **6**. An interpretation of the change in ionization potentials on going from **6** to **7** together with orbital energies taken from Becke3LYP/6-31+G\* calculations and the effect of methyl substitution on the ring gave the character of the four highest occupied molecular orbitals for **6–8** as  $n_C > \pi_3 > \pi_2 > \sigma$ .

The Becke3LYP method was employed in the calculation of first adiabatic and vertical ionization potentials of carbenes

**1–8**. For the  $IP_a$ 's of the small carbenes **1–5**, a mean absolute deviation of 0.04 eV was achieved with Becke3LYP/6-31+G\*; this was found to be substantially better than even the CBS-4 performance (mean absolute deviation of 0.13 eV) for this set of molecules. The Becke3LYP/6-31+G\*//Becke3LYP/3-21G(\*) level of theory was also tested and found to be sufficiently accurate (the largest absolute error was 0.14 eV for **7**, which could be due to an uncertainty in our location of the experimental  $IP_a$ ). While semiempirical PM3 and ab initio HF/6-31+G\* calculations gave unsatisfactory values for the adiabatic IP, those obtained with the Becke3PW91 method were found to be only slightly worse than Becke3LYP results.

Calculated Becke3LYP/6-31+G\* first  $IP_v$ 's of carbenes **2–7** are very close to the experimental values (less than 0.13 eV difference) with the exception of dichloro carbene (**3**) (the difference of 0.38 eV could again be attributed to an error in our prediction of the experimental  $IP_v$ ). Becke3LYP/6-31+G\*//Becke3LYP/3-21G(\*) gave similar results with a slight loss of accuracy. For  $IP_v$ 's, Becke3PW91 performs about as well as Becke3LYP.

This study has provided us with a calculational method, Becke3LYP/6-31+G\*, that gives accurate first adiabatic and vertical ionization potentials for carbenes without being computationally too demanding. Depending on the size of the carbene, 3-21G(\*) or 6-31+G\* basis sets can be employed in geometry optimizations. In future gas phase pyrolysis studies, this can aid in the interpretation of PE spectra with regard to the possible presence of carbenes.

## Acknowledgments

We gratefully acknowledge the use of the IBM SP2 computer at Queen's University granted under the auspices of an IBM Canada – Queen's University collaborative project. We thank Ms. O. Donini for assistance with operational aspects of parallel GAUSSIAN 94, and the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. We also gratefully acknowledge the usage of the SGI computing installation in the Geochemistry Labs at McMaster funded by NSERC.

## References

1. D.W. Kohn, E.S.J. Robles, C.F. Logan, and P. Chen. *J. Phys. Chem.* **97**, 4936 (1993).
2. H. Clauberg, D.W. Minsek, and P. Chen. *J. Am. Chem. Soc.* **114**, 99 (1992).

3. J.M. Dyke, L. Golob, N. Jonathan, A. Morris, and M. Okuda. *J. Chem. Soc. Faraday Trans. 2*, **70**, 1828 (1974).
4. P. Chen. *Unimol. Bimol. Ion-Mol. React. Dyn.* 371 (1994).
5. T. Koopmans. *Physica*, **1**, 104 (1933).
6. J.B. Foresman and A. Frisch. *Exploring chemistry with electronic structure methods*. 2nd ed. Gaussian, Inc., Pittsburgh, Pa. 1996.
7. L.A. Curtiss, K. Raghavachari, G.W. Trucks, and J.A. Pople. *J. Chem. Phys.* **94**, 7221 (1991); *J. Chem. Phys.* **98**, 1293 (1993).
8. J.W. Ochterski, G.A. Petersson, and J.A. Montgomery, Jr. *J. Chem. Phys.* **104**, 2598 (1996).
9. A.J. Arduengo III, H. Bock, H. Chen, M. Denk, D.A. Dixon, J.C. Green, W.A. Herrmann, N.L. Jones, M. Wagner, and R. West. *J. Am. Chem. Soc.* **116**, 6641 (1994).
10. G. Herzberg. *Can. J. Phys.* **39**, 1511 (1961).
11. W. Reineke and K. Strein. *Ber. Bunsen-Ges. Phys. Chem.* **80**, 343 (1976).
12. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople. *Ab initio molecular orbital theory*. John Wiley & Sons, New York. 1986.
13. (a) A.D. Becke. *J. Chem. Phys.* **98**, 5648 (1993); (b) C. Lee, W. Yang, and R.G. Parr. *Phys. Rev. B: Condens. Matter*, **37**, 785 (1988); (c) J.P. Perdew and Y. Wang. *Phys. Rev. B: Condens. Matter*, **45**, 13244 (1992).
14. M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, and J.A. Pople. *Gaussian 94*, Revision B.3. Gaussian, Inc., Pittsburgh, Pa. 1995.
15. J.J.P. Stewart. *J. Comput. Chem.* **10**, 209 (1989).
16. J.J.P. Stewart. *QCPE*, 455, (1983).
17. L. Åsbrink, C. Fridh, and E. Lindholm. *HAM/3*, *QCPE Bull.* **13**, 393 (1981).
18. N.H. Werstiuk, D.N. Butler, and E. Shahid. *Can. J. Chem.* **65**, 760 (1986).
19. N. Kuhn and T. Kratz. *Synthesis*, 561 (1993).
20. C. Heinemann and W. Thiel. *Chem. Phys. Lett.* **217**, 11 (1994).
21. O.M. Nefedov, M.P. Egorov, A.I. Ioffe, L.G. Menchikov, P.S. Zuev, V.I. Minkin, B.Ya. Simkin, and M.N. Glukhovtsev. *Pure Appl. Chem.* **64**, 265 (1992).
22. L.A. Curtis, K. Raghavachari, G.W. Trucks, and J.A. Pople. *J. Chem. Phys.* **94**, 7221 (1991).
23. J.A. Nichols, D. Heryadi, D.L. Yeager, and J.T. Golab. *J. Chem. Phys.* **100**, 2947 (1994).
24. C.F. Rodriguez, D.K. Bohme, and A.C. Hopkinson. *J. Phys. Chem.* **100**, 2942 (1996).
25. M.W. Wong and L. Radom. *Org. Mass Spectrom.* **24**, 539 (1989).
26. N. Russo, E. Sicilia, and M. Toscano. *J. Chem. Phys.* **97**, 5031 (1992).
27. M.T. Nguyen, M.C. Kerins, A.F. Hegarty, and N.J. Fitzpatrick. *Chem. Phys. Lett.* **117**, 295 (1985).
28. C.W. Bauschlicher, Jr. and P.R. Taylor. *J. Chem. Phys.* **86**, 2844 (1987).
29. X.-C. Wang and K.F. Freed. *J. Chem. Phys.* **91**, 1142 (1989).