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Carbene Proton Attachment Energies: Theoretical Study

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The geometries and electronic energies of six singlet carbenes, with methyl and phenyl substituents, and the corresponding carbenium ions were obtained using several density functional theory (DFT) variants and the second-order Møller−Plesset method for electron correlation and compared with G3 results, with the aim to determine a relatively low-cost computational protocol that is sufficiently accurate for the specific molecules and ions of interest. Some additional calculations were performed at the CCSD(T) level. Results for diphenylcarbene, methylphenylcarbene, and their cations, which were not previously investigated by ab initio methods, are reported as are calculations on methylene, methylcarbene, dimethylcarbene, and phenylcarbene. The MPW3LYP/6-311+G(d,p) hybrid DFT level was found to give results that were in close agreement with those obtained using G3 theory, with a mean absolute deviation (MAD) of 1.76 kcal/mol for the calculated proton attachment energies (PAEs). Equilibrium geometries obtained with this method were compared with those obtained at the MP2/6-311G(d,p) level of theory, and bond lengths and bond angles had MADs of 0.005 Å and 1.0°, respectively. Harmonic vibrational frequencies of all the carbene molecules and the corresponding ions were computed to verify that the stationary points were true minima, to obtain zero-point corrected energies, to assist in infrared studies of the molecules. The recommended combination of method and basis set is expected to be a useful framework that uses modest amounts of computer resources to obtain usable thermochemical data on moderate-sized hydrocarbons and hydrocarbon cations, including coal-mimetic species.

I. Introduction

For over five decades, carbenes have been recognized to play an important role as transient intermediates.[1] They were introduced into synthetic organic and organometallic chemistry by Doering[2] and Fischer,[3] respectively, in the 1950s and 1960s, where they have since been utilized in many reactions. In the past several years, the understanding of carbenes has advanced dramatically with the preparation of persistent triplet diarylcarbenes and the isolation of heteroatom-substituted singlet carbenes (cf. ref 1 and references therein). Recent advances in laser flash photolysis experiments have made it easier to generate these carbenes, typically from diazo compounds, as well as being able to observe and characterize the corresponding carbenium ions by UV−vis spectroscopy in protic solvents.[4]

There has been a significant amount of theoretical interest in carbenes (see, e.g., refs 5–15), particularly methylene, whose singlet−triplet energy separation has been the source of great controversy, both experimentally[16,17] and theoretically (ref 14 and references therein). A major focus of most of the theoretical studies on carbenes has been the singlet−triplet energy splitting, exemplified by studies on methylcarbene,[5,12,13] dimethylcarbene,[6–8] phenylcarbene,[9,10] and diphenylcarbene.[9] Spectroscopic studies on carbenes include work on methylene,[18] methylcarbene,[19,20] dimethylcarbene,[8] and phenylcarbene.[21] Besides the singlet−triplet energy splitting of carbenes, substituent group effect (particularly, the β-silicon effect) on the stability of singlet carbenes has also been studied in detail,[11] and electron-donating groups are known to stabilize the singlet state of carbenes. Closely related to carbenes, and of relevance to the present study, are carbenium and/or carbonium ions. Some of these have also been studied theoretically[22–26] and experimentally,[4] either because of their involvement in atmospheric and/or combustion chemistry[25] or because of their importance as useful intermediates in chemical reactions.[23,27] However, we are not aware of any reported studies of the proton capture reaction by carbenes to form carbenium ions (i.e., to determine their proton attachment energies). Such information is of intrinsic interest, but it is also relevant to modeling combustion processes, including, e.g., reactions of coal combustion products with flue gas components on activated carbon.

One of the major technological solutions to the control of mercury emissions in power plants is the injection of powdered activated carbon into the flue gas stream. The reactions of gas-phase elemental mercury with the flue gas components are largely heterogeneous on the carbon sorbent surface. However, the actual mechanisms by which these reactions occur are unknown. The development of such mechanisms is expected to lead to useful predictions of new designs and/or modifications in sorbent technology that promote mercury oxidation and chemisorption. Recently, one such mechanistic model has been proposed by several of the authors[28] to explain the capture/oxidation of elemental mercury on an activated carbon surface. In fact, that model is the first specific structural mechanism for mercury and coal known in the literature to predict a zigzag carbene site on a carbon edge that can function as a Lewis basic site when it reacts with the acidic flue gas components (e.g.,

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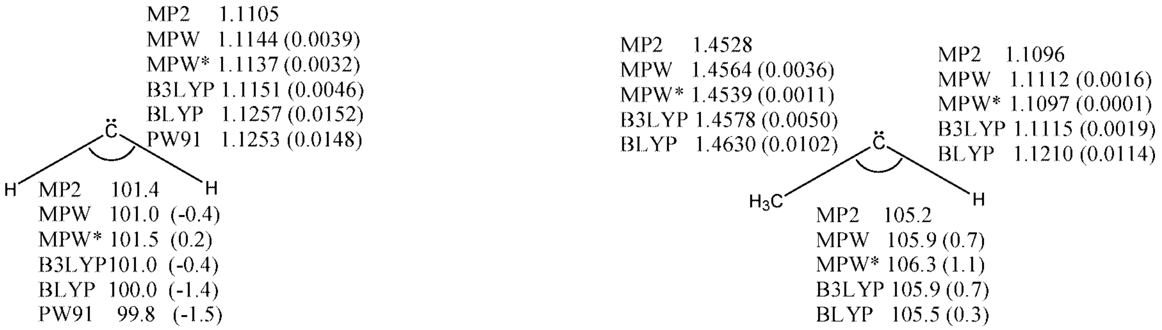
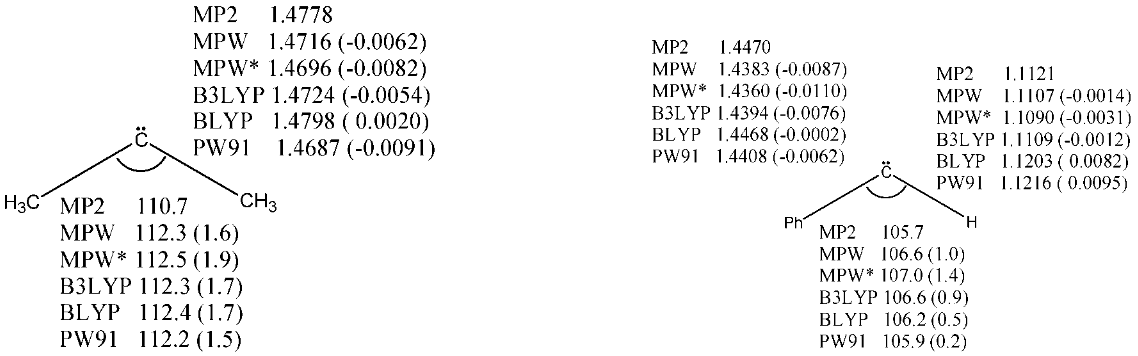


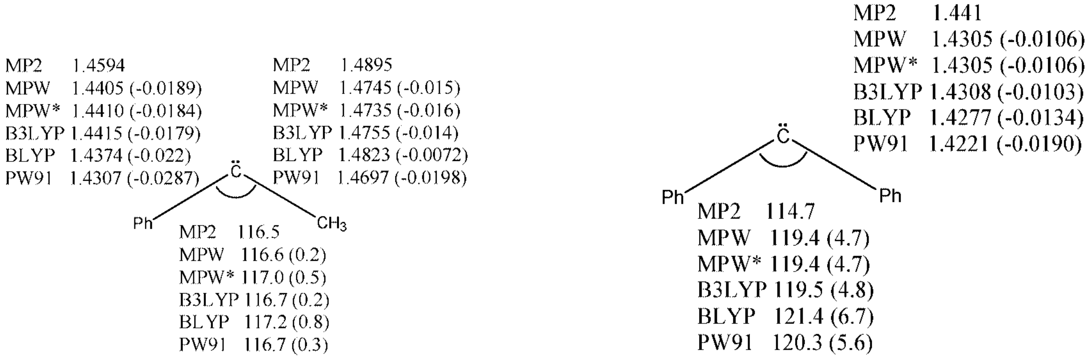
Methylene

Methylcarbene



Dimethylcarbene

Phenylcarbene



Methylphenylcarbene

Diphenylcarbene

Figure 1. Selected optimized geometric parameters near the carbene carbon obtained at the MP2 and various DFT levels using the 6-311G(d,p) basis set. Deviations of the DFT variants from MP2 values are given in parentheses. MPW and MPW* represent MPW3LYP values obtained using the 6-311G(d,p) and 6-311+G(d,p) basis sets, respectively.

HCl, H_2SO_4) or when it reacts with oxidized forms of mercury in the flue gas. Olson and co-workers[28] have demonstrated experimentally that this mechanism explains, at least in part, the oxidation of elemental mercury on activated carbon. Because of the difficulty in obtaining quantitative measurements of thermochemical data on transient species, computational models appear to be an attractive alternative. Unfortunately, essentially unambiguously reliable electronic structure methods for thermochemistry, such as G3 theory,[29] are prohibitively expensive[30] for considering larger models of the surface, hence necessitating assessment of other methods that are significantly less computationally intensive yet produce results that are sufficiently close to those obtained by G3 theory to answer specific questions about a specific set of molecules. This study, therefore, focuses on the assessment of electronic structure methods based on molecular geometries and proton attachment energies (PAEs) of some representative carbenes—methylene, methylcarbene (MC), dimethylcarbene (DMC), phenylcarbene (PC), methylphenylcarbene (MPC), and diphenylcarbene (DPC) (cf. Figure 1)—to find a suitable theoretical level that is computationally less expensive yet accurate enough to be useful in modeling larger coal-mimetic molecules. The singlet electronic states of these carbenes are specifically considered in this study, since these are expected to show enhanced Lewis basicity on the carbon graphene edge structures as proposed in the mechanistic model.

The paper is organized such that the computational details are given in section II, the results are presented and discussed in section III, and the conclusions are given in section IV.

II. Computational Details

Second-order Møller—Plesset perturbation theory (MP2)[31–34] and the B3LYP,[35–37] PW91PW91,[38–42] and BLYP[36,37,43] variants of the density functional theory (DFT) method, as well as the newer MPW3LYP variant of DFT developed by Truhlar and

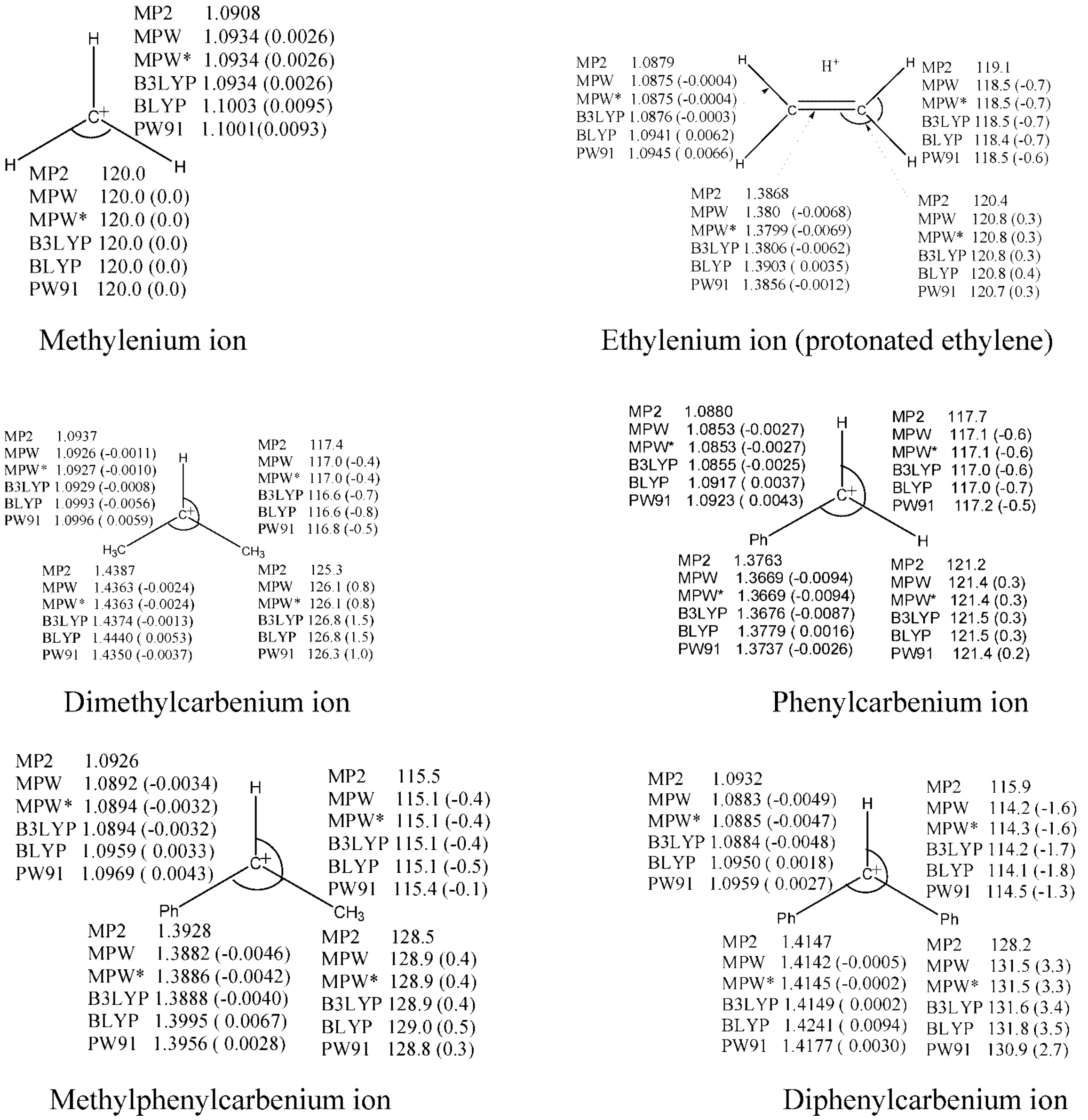


Figure 2. Selected optimized geometric parameters of carbenium ions obtained at the MP2 and various DFT levels using the 6-311G(d,p) basis set. Deviations of the DFT variants from MP2 values are given in parentheses. MPW and MPW* represent MPW3LYP values obtained using the 6-311G(d,p) and 6-311+G(d,p) basis sets, respectively.

co-workers[44] for thermochemistry, were compared with G3 theory[29] for predictions of proton attachment energies for the selected carbenes. The following protonation reactions were considered:

$$H_2C: + H^+ \rightarrow CH_3^+ \quad (1)$$

$$CH_3HC: + H^+ \rightarrow CH_3CH_2^+ \quad (2)$$

$$(CH_3)_2CH: + H^+ \rightarrow (CH_3)_2CH^+ \quad (3)$$

$$PhHC: + H^+ \rightarrow PhCH_2^+ \quad (4)$$

$$PhCH_3C: + H^+ \rightarrow PhCH_3CH^+ \quad (5)$$

Although too expensive to be used in studies of larger systems, coupled-cluster singles and doubles with inclusion of perturbative triples correction (CCSD(T))[45–49] calculations were also performed on these molecules.

Prior to the calculations that included electron correlation, geometry optimizations and harmonic vibrational frequencies were calculated for all molecules at the restricted Hartree−Fock (RHF) level using the 6-31G(d) basis set. All structures (cf. Figure 1) were optimized without using point group symmetry, except for methylene and the corresponding methylenium ion, which belong to the C_{2v} and D_{3h} point groups, respectively. The stationary points were confirmed to be true minima by ascertaining that there were no imaginary frequencies when second-derivative calculations were performed.

In G3 theory, geometry optimization is performed at the MP2(FU)/6-31G(d) level and then the energy is further improved by several additional single point calculations using high-level correlation methods with increasingly larger basis sets.[27] In general, G3 results have an overall mean absolute deviation (MAD) from experiment of only 1.07 kcal/mol.[50] Recently, a modification of G3 theory to incorporate use of improved geometries and zero-point energies obtained at the B3LYP/6-31G(2df,p) level and addition of a *g* polarization function to the G3Large basis set for second-row atoms at the Hartree−Fock level gives an extension of G3 theory called G3X.[50] This new

TABLE 1: PAEs and Deviations of PAEs from G3 (ΔPAEs) for the Methods Considered in This Work (in kcal/mol)

	MP2		CCSD(T)		B3LYP		BLYP		PW91PW91		MPW3LYP		G3
reaction	PAE	ΔPAE	PAE	ΔPAE	PAE	ΔPAE	PAE	ΔPAE	PAE	ΔPAE	PAE	ΔPAE	PAE
1	−220.73	6.34	−217.73	3.33	−217.76	3.39	−215.84	1.44	−216.58	2.20	−217.34	2.95	−214.38
2	−249.23	5.21	−246.03	2.01	−246.86	2.82	−245.74	1.69	−246.82	2.82	−245.38	1.38	−244.03
3	−255.12	3.26	−253.62	1.76	−256.32	4.46	−257.81	5.96	−257.12	5.27	−255.94	4.08	−251.87
4	−272.73	3.51	−272.27	3.01	−273.95	4.71	−274.40	5.21	−274.13	4.89	−273.74	4.52	−269.23
5	−278.50	4.52	−277.61	3.64	−279.71	5.77	−278.63	4.64	−278.28	4.33	−278.81	4.83	−273.96
MAD		4.58		2.76		4.20		3.77		3.89		3.56	

theory (G3X) has an overall MAD from experiment of 0.95 kcal/mol based on the G3/99 test set of 376 reaction energies. However, due to the large basis sets and high levels of correlation used in G3 theory or its extension G3X, calculations on larger coal-mimetic molecules become computationally inaccessible. Hence, prototypes were considered in our assessment studies that were small enough so that G3 calculations could be completed without undue strain on computational resources and large enough that the larger ones would begin to mimic some features of the coal surface.

For the selected carbenes, proton attachment energies (PAEs) obtained by the considered methods were calculated using variously augmented 6-31G(d,p)[51] polarized valence double-ζ and 6-311G(d,p)[52] polarized valence triple-ζ basis sets. In one set of studies, the geometries of the molecules were first optimized using the 6-31G(d)[51] basis set at the RHF level and the energies were improved by performing single point calculations with the 6-311G(d,p) basis at higher correlated levels. Recognizing that dynamic electron correlation can have a significant effect on predictions of molecular equilibrium geometry, full geometry optimizations were also carried out at the MP2/6-311G(d,p) level and at the various DFT levels.

To further analyze sensitivity to basis set and in particular the role of diffuse functions, the MPW3LYP variant of DFT, for which the closest agreement with G3 theory was obtained, was used to perform additional calculations with different basis sets, including two main categories of the Pople-type basis sets of valence double- and triple-ζ quality. Beginning with double-ζ 6-31G(d), basis sets were increased by adding polarization and/or diffuse functions up to and including the triple-ζ 6-311++G(d,p). The complete list of basis sets used for this analysis is 6-31G(d), 6-31G(d,p), 6-31+G(d,p),[51] 6-31++G(d,p),[53] 6-311G(d,p),[52] 6-311+G(d,p), and 6-311++G(d,p).[52,54] All the calculations reported herein were performed using the Gaussian 03 program package.[55]

III. Results and Discussion

The geometries in the proximity of the carbene carbon for the optimized structures are presented in Figures 1 and 2 for the carbenes and their corresponding carbenium ions, respectively. The energy changes associated with reactions 1–5 [i.e., proton attachment energies (PAEs)] were calculated using the electronic structure methods discussed in section II and compared with those obtained by G3 theory. The results of this comparison are presented in Table 1. Harmonic vibrational frequencies were calculated at the MPW3LYP/6-311+G(d,p) level and compared with available literature values. Selected frequencies with large IR intensities are presented here, and full tables of the frequencies are given in the Supporting Information. Optimized geometries and proton attachment energies are discussed in sections III.A and III.B, respectively, and section III.C examines the harmonic frequencies.

III.A. Geometries. Selected parameters of the optimized geometries obtained at the MP2/6-311G(d,p) level and at various DFT levels are given in Figures 1 and 2 for the carbenes and carbenium ions, respectively. Deviations from MP2 geometries of the DFT methods are given in parentheses. Although MP2/6-311G(d,p) geometries are not definitive, they are expected to be sufficiently accurate to serve as reference points, and calculations on methylene support this assumption.

The experimental C−H bond length and H−C−H bond angle for methylene reported by Petek et al.[18] as 1.107 Å and 102.4°, respectively, are in close agreement with the values obtain in this work at the MP2 level (1.111 Å and 101.4°). The configuration interaction (CI) results of Bauschlicher et al.,[56] which report the bond length and angle as 1.110 Å and 102.0°, respectively, are among the best theoretical results for methylene, and our MP2 values show close agreement with these as well. The geometries obtained by hybrid DFT methods show better agreement with those obtained by MP2 than do the pure DFT methods BLYP and PW91PW91, which have slightly larger errors of about 1.5° for bond angle and 0.015 Å for bond length. In the case of methylcarbene (MC) and dimethylcarbene (DMC), our calculated values for selected parameters near the carbene carbon are, in general, close to those obtained in the rather few previous theoretical studies.[5,7,8,13] The bond angle for MC is reported as 104.9° and the C−H and C−C bond lengths are 1.106 and 1.470 Å, respectively, computed at the CCSD/TZ2P(f+d) level,[13] while the C−C distance and bond angle in DMC were obtained as 1.473 Å and 111.5° at the CISD/TZ2P+f level of theory.[7] In these two cases, our MP2 values are close to previous theory, with a mean absolute deviation of about 0.007 Å for bond length and 0.7° for angles. The DFT methods have slightly larger differences from MP2 results and previous theory in the case of DMC, where the bond angle is in error by about 2° although the bond lengths remain close to MP2 values with a mean absolute deviation of 0.006 Å.

We were unable to obtain a methylcarbene (MC) structure using the PW91PW91 functional, so this entry is omitted in Figure 1. Instead, we observed rearrangement to ethylene with a C−C bond length of 1.3333 Å, a C−H bond length of 1.0913 Å, and a central bond angle of 121.7°. With other methods, we obtained an MC structure and found that the bond lengths of the C−H bonds in the CH_3 group of MC are not equal; i.e., they are 1.090, 1.135, and 1.096 Å at the MP2 level. The elongation of one of these C−H bonds indicates the propensity of hydrogen to migrate to the carbene carbon to form ethylene, analogous to the well-known rearrangement of methylnitrene to methyleneimine.[57,58] This rearrangement of MC to form ethylene has been observed by Schaefer and co-workers[12] and is known to proceed over a very small barrier of 1.2 kcal/mol at 0 K. Similarly, Fuelscher and co-workers[8] reported that DMC rearranges to propene with a predicted barrier of 8.5 kcal/mol. Despite the low barriers to rearrangement, these species (MC and DMC) were found to be true minima on their respective potential energy surfaces.[7,8,12] Our calculated geometries are consistent with the singlet structures obtained in these previous calculations, with the already noted exception of the PW91PW91 functional results for MC.

While there is still reasonable agreement between our MP2 geometries and those obtained by DFT methods for phenylcarbene (PC) and methylphenylcarbene (MPC), there is a larger difference of about 5° in the bond angle at the carbene carbon for diphenylcarbene (DPC). The values obtained by the DFT methods agree with a previous Hartree−Fock calculation using the 6-31G(d) basis set.[10] Results obtained in this study for PC are also in good agreement with previous results obtained at different levels of theory.[59–61] The Ph−C−H angle was found to be 105.9°, 106.3°, 106.8°, and 106.3° at the BLYP,[59] MP2,[61] CASSCF(8,8),[60] and B3LYP[60] levels of theory, respectively, using the 6-31G(d) basis set; the Ph−C bond length was obtained as 1.451, 1.445, 1.462, and 1.443 Å at the BLYP, MP2, CASSCF, and B3LYP levels, respectively. At the CISD/DZd[60] level, the angle and bond length were obtained as 106.9° and 1.450 Å, respectively. These values can be compared with the MP2 results obtained in this study (cf. Figure 1) using the 6-311G(d,p) basis set, 105.7° and 1.4470 Å, and the MPW3LYP/6-311+G(d,p) bond angle and bond length, 107.0°and 1.4360 Å. Results obtained using the other DFT methods considered in this study (cf. Figure 1) are also in good agreement with previous theoretical results. No higher level ab initio method results could be found in the literature for diphenylcarbene and methylphenylcarbene.

For the carbenium ions, previous theoretical data on equilibrium geometries are available only for the methyl cation (methylenium ion), ethyl cation (ethylenium ion), and isopropyl cation (dimethylcarbenium ion). We could not find any previous theoretical results on phenylcarbenium ion, methylphenylcarbenium ion, and diphenylcarbenium ion. Our calculated bond lengths and angles for methylenium ion using both MP2 and the different DFT variants show very good agreement (MAD less than 1%) with the experimental values (1.087 Å and 120.0°) of Croton et al.[62] The mean absolute deviation from the experimental bond length is 0.004, 0.007, and 0.014 Å for MP2, hybrid, and pure DFT variants, respectively. In fact, our calculated bond length (1.0908 Å) at the MP2/6-311G(d,p) level is an almost exact match with that reported by Dixon et al.[25] (1.0907 Å) at the CCSD(T)/aug-cc-pVTZ level. The DFT variants have a mean absolute deviation from Dixon's value of 0.005 Å.

In the case of protonated methylcarbene, the resulting methylcarbenium ion (ethyl cation) rearranges to a bridged structure, protonated ethylene (cf. Figure 2). This rearrangement has been noted previously,[22] with the observation that NDDO (neglect of diatomic differential overlap) semiempirical schemes disagree with ab initio wave function approaches as to which of ethyl cation and protonated ethylene is more stable. For example, ab initio Hartree−Fock calculations[63] for ethyl and vinyl cations show them to be more stable than the isomeric bridged structures, protonated ethylene and protonated acetylene, respectively, contrary to NDDO calculations.[64] Preuss and coworkers[65] used the SCF-MO-LC(LCGO) method, with basis set comprised of two *s* functions on hydrogen and seven *s* and two *p* sets of functions on carbon, and found that ethyl cation and protonated ethylene have the same energy. Allen and coworkers[22] argue that this was the result of using a small basis set that, in particular, does not adequately represent the hydrogen atoms. While the question of the existence of a barrier to the rearrangement of ethyl cation to protonated ethylene constitutes an interesting theoretical problem, it is clear that the barrier, if it exists, must be small and the two isomers must be very close in energy. Moreover, as noted by Kirmse[66] and McClelland,[4] carbocations are likely to rearrange to the more stable forms. We adopted the protonated ethylene form of $[C_2H_5]^+$ in further studies. The data for dimethylcarbenium ion is in good agreement with previous theory, which also used the MP2/6-311G(d,p) level.[67] The DFT bond lengths disagree by 0.006 Å or less, and the bond angles differ by no more than 1°.

Geometric parameters for phenylcarbenium ion, methylphenylcarbenium ion, and diphenylcarbenium ion have not been previously reported. Analysis of the geometries obtained at the MP2 level and at the various DFT levels using the 6-311G(d,p) basis set indicates that the hybrid DFT methods chosen in this study are consistently close to the MP2 results and that the pure DFT methods have slightly larger deviations in some cases. However, when also taking into account proton attachment energies, which are discussed in detail in section III.B, MPW3LYP gave results that were closer to those obtained by G3 than the rest of the methods under consideration. The agreement between MPW3LYP and G3 PAEs was essentially better with the larger 6-311+G(d,p) basis set; consequently, we inquired what would be the differences between geometric parameters obtained at the MP2/6-311G(d,p) level and those obtained at the MPW3LYP/6-311+G(d,p) level. Our results show that similar deviations from MP2/6-311G(d,p) geometries were obtained for MPW3LYP using the 6-311+G(d,p) basis set as with 6-311G(d,p) (cf. Figures 1 and 2); hence, to better achieve consistency between geometry optimizations and best energy calculations, thermochemical data on all molecules were obtained with geometries optimized at the MPW3LYP/6-311+G(d,p) level.

III.B. Proton Attachment Energies. Proton attachment energies (PAEs) for all considered carbenes, except for diphenylcarbene, are given in Table 1 for all theoretical methods considered in this study. Also shown in this table are the deviations of PAEs between those obtained by G3 and those obtained by other methods (denoted by ΔPAEs) as well as the mean absolute deviations (MADs). Because of computational resource considerations, G3 results were not obtained for diphenylcarbene. We were unable to find literature results for PAEs for the studied carbenes. Considering that G3 theory is a well-established method for obtaining very good thermochemical data for small-to-moderate-sized molecules, the PAEs obtained by G3 have been used as the references by which to assess the other methods.

As stated in section II, the results in Table 1 were obtained from single point energy calculations using the 6-311G(d,p) basis set at their respective optimized geometries with the 6-31G(d) basis for the different variants of DFT, while the MP2 and CCSD(T) energies are single point energies using the 6-311G(d,p) basis set at MP2/6-31G(d) optimized geometries. These results indicate that all the DFT methods have similar deviations from G3. MP2 results agree with G3 approximately, but not quite, as well as the DFTs while CCSD(T) proves to be somewhat better (cf. Table 1, the MAD of MP2 is 4.58 kcal/mol and that for the DFT methods is about 4.0 kcal/mol). It is interesting to find that the ΔPAEs calculated by the DFT methods are not too different from the ones obtained by MP2 and are not significantly worse than those of CCSD(T) (with MAD of 2.76 kcal/mol). The somewhat better performance of MPW3LYP relative to the other considered DFT variants is not particularly surprising, since it was designed specifically for thermochemistry.[44] Based on the MADs shown in Table 1, MPW3LYP is seen to have a slight edge (ca. 0.4 kcal/mol) over

TABLE 2: Deviations of PAEs from G3 (ΔPAEs) Calculated at the MPW3LYP Level of Theory with Different Basis Sets

	ΔPAE (kcal/mol)						
reaction	6-31G*	6-31G**	6-31+G**	6-31++G**	6-311G**	6-311+G**	6-311++G**
1	6.34	6.90	2.64	2.57	2.95	1.38	1.38
2	3.70	5.40	0.31	0.13	1.38	0.38	0.44
3	7.59	8.79	2.76	2.70	4.08	2.26	2.26
4	9.41	10.10	2.45	2.38	4.52	1.82	1.82
5	9.85	10.67	3.33	3.33	4.83	2.89	2.89
MAD	7.40	8.35	2.32	2.20	3.58	1.76	1.76

TABLE 3: Vibrational Frequencies and IR Intensities of Methylene and Methylenium Ion

methylene			methylenium ion		
frequency (cm^{-1})	IR intensity (km/mol)	MRCI[a] (expt[b])	frequency (cm^{-1})	IR intensity (km/mol)	CCSD(T)[c] (expt[d])
1387	0.3	1351 (1353)	1404	20.0	1417
2895	98.4	2787 (2806)	1404	20.0	
2959	82.3	2839 (2865)	1417	11.1	1428 (1380)
			3020	0.0	3036
			3215	70.4	3246 (3108)
			3215	70.4	

[a] From ref 64, MRCI/ANO (5s4p3d2f1g/3s2p1d) [b] From ref 18. [c] From ref 25, CCSD(T)/aug-cc-pVDZ [d] From ref 56.

TABLE 4: Vibrational Frequencies and IR Intensities of Methylcarbene and Methylcarbenium Ion

methylcarbene			methylcarbenium ion	
frequency (cm^{-1})	IR intensity (km/mol)	CISD[a]	frequency (cm^{-1})	IR intensity (km/mol)
469	6.7	484	546	135.2
620	45.0	588	839	0.3
959	21.7	978	1081	0.1
1127	6.1	1128	1088	22.1
1261	19.6	1306	1140	56.4
1303	43.4	1369	1249	0.0
1345	11.9	1435	1273	1.5
1511	3.9	1560	1358	9.8
2821	15.6	3011	1474	25.1
2920	82.6	3027	1572	9.8
2991	51.6	3148	2142	44.2
3086	20.8	3226	3120	0.1
			3121	27.6
			3219	0.0
			3237	53.1

[a] From ref 13, CISD/DZP.

TABLE 5: Large Intensity Vibrational Frequencies of Dimethylcarbene and Dimethylcarbenium Ion

dimethylcarbene		dimethylcarbenium ion	
frequency (cm^{-1})	IR intensity (km/mol)	frequency (cm^{-1})	IR intensity (km/mol)
1203	20.3	710	63.0
1338	87.5	1095	73.2
2915	68.5	1244	26.1
2963	35.0	1283	240.5
2963	77.2	1437	34.4
		1482	18.0
		1543	48.5
		2862	226.2
		3038	55.4

the other DFT methods and so was chosen as the method for further studies.

Although the most thorough comparisons were performed with the 6-311G(d,p) basis set, and it is reasonable to assume that differential improvements to calculated PAEs will be small beyond the triple split valence level, the effect of increasing basis set was investigated by performing additional calculations at the MPW3LYP level (cf. Table 2). Comparing the ΔPAEs obtained by MPW3LYP shown in Table 1 to those in Table 2, one observes that (1) adding a set of diffuse functions on carbon when using a double-ζ basis set (6-31+G(d,p)) results in better PAEs than using 6-311G(d,p) (see column 4 of Table 2 and ΔPAE of MPW3LYP in Table 1), (2) adding diffuse functions on carbon when using a triple-ζ basis set (6-311+G(d,p)) leads to a further improvement in PAEs (see column 7 of Table 2 and ΔPAE of MPW3LYP in Table 1), and (3) addition of polarization and/or diffuse functions on hydrogen produces no significant change in the ΔPAEs (see Table 2, columns 2 and 3, 4 and 5, and 7 and 8). To summarize, the results shown in Table 2 seem to indicate that, for a given basis set, addition of polarization and/or diffuse functions on hydrogen is not nearly as important in improving the overall PAE as on carbon for the studied carbenes and carbenium ions.

Overall, the geometry, energy, and basis set analyses made above appear to be in support of using MPW3LYP/6-311+G(d,p) as an appropriate theoretical level for carrying out quantum chemical calculations on carbene and carbenium ion molecules. It has modest computational requirements, especially compared with MP2 and CCSD(T) ab initio methods, and yet produces results that are sufficiently close to G3 theory to be a useful tool for performing calculations on larger hydrocarbons.

III.C. Harmonic Frequencies. Harmonic vibrational frequencies were computed for all the molecules considered in this work at the MPW3LYP/6-311+G(d,p) level of theory, and these are shown in Tables 3, 4, 5, 6, 7, and 8. Theoretical harmonic frequencies have previously been reported only for methylene,[14,68] methylenium ion,[25] methylcarbene,[12,13] dimethylcarbene,[6] and phenylcarbene.[21] Experimental vibrational frequency data are known for even fewer of the molecules or molecular ions: we could only find experimental frequency data for methylene,[18] the methylenium ion,[62] and phenylcarbene.[21] Consequently, most of the frequencies have not been discussed previously in the literature. However, there is UV−vis spectroscopic information on most of the carbenium ions considered, including dimethylcarbenium ion, phenylcarbenium ion, methylphenylcarbenium ion, and diphenylcarbenium ion, which have been observed in laser flash photolysis (LFP) experiments in polar protic solvents.[4] DPC has also been observed in laser flash photolysis of diphenylchloromethane in acetonitrile or acetonitrile/water mixture.[69]

The frequencies of methylene and the methylenium ion are given in Table 3 and compared with those reported in previous experimental and theoretical studies. Our agreement with previous results is quite good, especially after applying a suitable scaling factor of 0.9613.[70] The unscaled frequencies of methylene differ from the experimental values by 34, 89, and 94 cm^{-1}, which are reduced to 20, 23, and 20 cm^{-1} when scaled. In the case of the methylenium ion, the two reported experimental frequency modes differ from the corresponding ones calculated in this study by 37 and 107 cm^{-1}; the differences

TABLE 6: Large Intensity Vibrational Frequencies of Phenylcarbene and Phenylcarbenium Ion

phenylcarbene			phenylcarbenium ion	
frequency (cm^{-1})	IR intensity (km/mol)	B3LYP[a] (expt[b])	frequency (cm^{-1})	IR intensity (km/mol)
286	37.6	347 (343)	642	50.5
530	39.6	498 (497)	800	31.1
689	47.2	669 (670)	1104	23.2
782	48.5	747 (741)	1211	20.6
1191	19.1	1161 (1160)	1383	107.3
1286	142.9	1270 (1264)	1418	24.0
1472	26.0	1429 (1428)	1476	88.4
1622	100.2	1567 (1562)	1660	258.1
2929	99.4	3049 (3035)		

[a] From ref 21, B3LYP/6-31G* scaled by 0.95. [b] From ref 21.

TABLE 7: Large Intensity Vibrational Frequencies of Methylphenylcarbene and Methylphenylcarbenium Ion

methylphenylcarbene		methylphenylcarbenium ion	
frequency (cm^{-1})	IR intensity (km/mol)	frequency (cm^{-1})	IR intensity (km/mol)
692	35.9	650	42.3
761	30.3	781	27.1
1284	120.4	795	37.5
1339	50.1	1012	36.8
1620	26.6	1216	35.8
2928	61.0	1289	22.1
2983	48.4	1353	201.1
		1374	12.1
		1408	30.0
		1438	16.8
		1444	140.9
		1477	24.3
		1500	22.9
		1586	77.8
		1643	343.8
		2999	63.7

TABLE 8: Large Intensity Vibrational Frequencies of Diphenylcarbene and Diphenylcarbenium Ion

diphenylcarbene		diphenylcarbenium ion	
frequency (cm^{-1})	IR intensity (km/mol)	frequency (cm^{-1})	IR intensity (km/mol)
228	32.4	497	64.3
354	59.7	579	45.9
411	29.1	674	71.1
490	102.2	783	87.1
693	45.1	959	23.4
774	121.2	1009	46.2
806	20.2	1207	143.1
1365	98.3	1251	58.1
1459	22.9	1368	99.0
1617	26.4	1381	22.0
3183	23.9	1386	186.2
3195	27.6	1459	62.6
		1481	51.4
		1559	657.0
		1587	37.5
		1623	567.2
		1642	19.9

become reduced to 18 and 17 cm^{-1} after scaling. Although no experimental frequencies could be found for methylcarbene, those calculated in this work (cf. Table 4) differ from the ones previously obtained at the CISD/DZP level of theory[13] by deviations similar to those seen for methylene. Harmonic vibrational frequencies have been calculated previously for dimethylcarbene by Matzinger et al.,[7] but these were not reported in their paper. However, they mentioned that their calculated frequencies are expected to overestimate experiment by about 10%. Since the actual values from the previous theoretical calculations were not given, it is not possible to make any comparisons with our frequency data for DMC shown in Table 5. To our knowledge, there are no previous reports of vibrational frequencies for methylcarbenium ion and dimethylcarbenium ion. For these cases, those with large IR intensities are given in Tables 4 and 5, and a full list of the frequencies is given in the Supporting Information.

Of the arylcarbenes and the corresponding arylcarbenium ions considered in this study, harmonic frequencies could only be found for phenylcarbene.[21] The largest intensity frequency modes are given in Table 6 as well as the corresponding literature values from ref 21 and the full spectrum is given in the Supporting Information. A detailed comparison with the full spectrum shows that there is good agreement between the frequencies obtained in this work and those from previous theoretical calculations[21] and experimental measurements.[21] When our results are scaled by a factor of 0.9613,[70] the agreement is even better; the MAD between frequencies from this work and experiment reduces from 45, 43, and 106 to 28, 13, and 84, for frequencies in the regions <1000 cm^{-1}, [1000, 3000 cm^{-1}], and >3000 cm^{-1}, respectively. The largest error in the >3000 range comes from the mode at 2929 cm^{-1}, which shows a difference of 106 cm^{-1} from the experimental value (3035 cm^{-1}) before scaling; this difference becomes larger after scaling (219 cm^{-1}). The experimentally measured modes at 3060 and 3073 cm^{-1} are actually only 18 and 14 cm^{-1} different from the scaled values (3042 and 3059 cm^{-1}, respectively) from this work. The frequencies of the remaining molecules and their corresponding carbenium ions, methylphenylcarbene and diphenylcarbene, and the phenylcarbenium ion, have been calculated for the first time; those with largest intensities are given in Tables 6, 7, and 8. A full listing of the frequencies for these species is given in the Supporting Information.

IV. Conclusions

In this study, a number of quantum chemical methods and basis sets have been assessed for the description of aliphatic and aromatic substituted carbenes and carbenium ions. The MPW3LYP hybrid DFT method of Truhlar and co-workers[44] with the 6-311+G(d,p) basis set gave the best results. The calculated PAEs at the MPW3LYP/6-311+G(d,p) level were in close agreement (MAD of 1.76 kcal/mol) with those obtained by G3 theory. To obtain accurate thermodynamic data for these molecules, it was found that one needs polarized valence triple-ζ basis sets with additional diffuse functions. However, polarization and diffuse functions are not as important for H atoms as for C atoms in the case of the studied carbenes and carbenium ions.

Equilibrium geometries calculated at the MPW3LYP/6-311+G(d,p) were found to be in good agreement with those obtained at the MP2/6-311G(d,p) level, with a mean absolute deviation of only 0.005 Å for bond lengths and 1.0° for bond angles. It was found that effects on geometry of methyl and phenyl substituents for the larger carbene structures are qualitatively the same as for the smaller ones. Namely, the methyl and phenyl groups open the central angle by about 4° in passing from methylene to methylcarbene and phenylcarbene, respectively. Then, the addition of another methyl increases the central angle by about 6° (in passing from methylcarbene to dimethylcarbene) or 11° if a phenyl were added (in passing from methylcarbene to methylphenylcarbene). Finally, the formation of a diphenyl substituted carbene leads to an increase in the central angle of approximately 9° (in passing from phenylcarbene to diphenylcarbene).

Protonation occurred as expected at the carbene carbon for all carbenes studied except one. In the case of methylcarbene, the ethylenium ion was found to have the structure of protonated ethylene, with H−C−C and H−C−H bond angles of approximately 120° and the existence of a distinct bridged hydrogen. For methylene, dimethylcarbene, phenylcarbene, methylphenylcarbene, and diphenylcarbene, the corresponding cations had shorter bond lengths between the carbene carbon and the substituted carbon than in the neutral molecules.

To assist in IR spectroscopic identification, we obtained harmonic vibrational frequencies at the MPW3LYP/6-311+G(d,p) level, which were found to have reasonable agreement with theoretical and experimental values that were available for methylene, methylenium ion, methylcarbene, and phenylcarbene. Theoretical harmonic vibrational frequencies were reported for the first time for the methylcarbenium and dimethylcarbenium ions and for methylphenylcarbene, diphenylcarbene, and their corresponding carbenium ions.

Since the prototype molecules chosen for this study represent a wide variety of carbenes, the results obtained are expected to provide useful insights into computational modeling of coal combustion reactions.

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Supporting Information Available: Full listings of harmonic vibrational frequencies of dimethylcarbene, dimethylcarbenium ion, phenylcarbene, phenylcarbenium ion, methylphenylcarbene, methylphenylcarbenium ion, diphenylcarbene, and diphenylcarbenium ion in Tables 5−8. This material is available free of charge via the Internet at http://pubs.acs.org.

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