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DENSITY FUNCTIONAL CALCULATIONS OF THE INFLUENCE OF SUBSTITUTION ON SINGLET–TRIPLET GAPS IN CARBENES AND VINYLIDENES

SHARON E. WORTHINGTON AND CHRISTOPHER J. CRAMER*

Department of Chemistry and Supercomputer Institute, 207 Pleasant St SE, Minneapolis, Minnesota 55455–0431, USA

Density functional theory calculations of multiplet splittings are presented that agree closely with experimental measurements for six carbenes and six vinylidenes. The calculations are further analyzed to gauge the relative importance of different factors influencing the stabilities of the different spin and electronic states. In the carbene series, with halogen substituents, orbital rehybridization effects and charge redistribution effects are large. The magnitude of π-conjugation (back-bonding) is calculated to be only moderately larger (6–8 kcal mol^{-1}) for singlets than for triplets based on natural bond orbital-derived conjugation energies. In the vinylidene series, substituion effects are primarily associated with through-space and through-bond inductive stabilization effects, especially hyperconjugation; π-conjugation effects are found to be small © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Organic molecules having an even number of electrons are rarely characterized by high-spin ground states.[1] Certain carbenes are an exception to this rule.[2,3] A carbene has a hypovalent, formally neutral carbon atom. Thus, in a Lewis sense, the carbene carbon has two electrons not involved in bonding and two non-bonding orbitals into which to place those electrons (Figure 1). When the electrons reside in the same orbital, they are necessarily spin-paired, and a closed-shell singlet electronic state is created. If the electrons reside one in each non-bonding orbital, the spin multiplicity may be either triplet or singlet (the latter sometimes called an open-shell singlet or singlet diradical). Because of favorable exchange interactions in the triplet not present in the open-shell singlet, the former state is usually lower in energy.[4]

The energy gap between the closed-shell singlet and triplet states (S–T gap) is critically dependent on the energetic separation between the two non-bonding orbitals (hereafter, unless otherwise specified, 'singlet' will imply 'closed-shell singlet'). If that gap is small, Hund's rule[5] applies, and the triplet state is preferred. As the separation between the two orbitals increases, it eventually outweighs the greater Coulomb repulsion between the two electrons in the singlet state, and the latter becomes the ground state. Methylene (CH_2) is the paradigmatic carbene,[6–10] and it has a triplet ground state with an S–T gap of 0·39 eV.[11,12] It is convenient to consider the effects of substituents on the orbital energy separation for a given carbene as a perturbation on the methylene system.

Substituents can modify the orbital energies in two related ways. First, there may be one or more conjugative or hyperconjugative stabilizing interactions between filled orbitals on the substituent and an empty orbital on the carbene (or vice versa). For example, the conjugation of aligned nitrogen lone pair orbitals with an empty carbon p orbital at the carbene center rationalizes the remarkable stability of substituted singlet diaminocarbenes.[13–15] Similarly, conjugative interactions with an extended π-system, for instance, can be stabilizing by permitting substantial delocalization of charge. Although, this latter effect can be very important in nitrenium cations (which are isoelectronic to carbenes), it is less clear that it will play much of a role in neutral carbenes.[16–19]

The second manner in which substituents can affect the

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energetic separation between the formally non-bonding orbitals is by changing the orbital hybridizations at the carbene carbon. This effect may arise either from electronegativity differences between the carbene carbon and its substituents, or from geometric constraints placed on the carbene valence angle. Thus, for example, the carbene carbon might be expected to reduce its s character in a bonding orbital to fluorine and provide a corresponding increase in s character to its other in-plane orbitals (an electronegativity effect—this effect includes an increase in splitting between the carbon 2s and 2p orbitals as partial positive charge builds up on the carbon atom[20]). Alternatively, two bulky substituents will require a larger valence angle at the carbene center in order to reduce steric repulsion, and to maintain good overlap the carbene carbon will have to devote additional s character to its bonding orbitals at the expense of the in-plane non-bonding orbital.

Obviously, it is not possible to quantify rigorously the various effects described above, since the total energy separating the two states is the only physical observable. However, by various analyses of predicted molecular geometries and electronic structures within a related series of carbenes at an appropriate level of theory, it is possible to rationalize qualitatively the relative importance of these interactions for a given set of substituent groups. An improved understanding of substituent effects may be useful both for understanding carbene reactivities in organic reactions[3,21] and for the design of stable carbenes having either high- or low-spin ground states.[1] Goddard and co-workers[22–24] have been particularly active in the area of developing predictive models and have suggested certain simple, empirically-corrected computational approaches to estimate S–T gaps, particularly for halo-substituted carbenes.[24]

We report here density functional theory (DFT) calculations for a number of structurally related carbenes for which very high quality experimental S–T gaps are available, specifically CH_2,[11,22–34] CHF,[22–25,30,35–39] CHCl,[22–25,30,36,39–41] CHBr,[24,25,36,39,40] CHI,[24,36,39,42] CF_2,[22–25,29,30,36,43,44] the vinylidenes $H_2C{=}C$,[45–50] HFC=C,[51,52] $F_2C{=}C$,[51] *tert*-butylvinylidene,[53] vinylvinylidene[54] and propadienylidene $H_2C{=}C{=}C$[44,55–63] (in several instances, prior theoretical studies have also been reported). Our approach is to gauge the quality of the calculations by comparison with the experimentally measured multiplet splitting, and to analyze suitable calculations in order to elucidate the effects of substitution and/or incorporation of the hypovalent carbon atom into a formal multiple bond by conjugation. All of the vinylidenes (including propadienylidene) have two symmetry-distinct triplet states of similar energy, one corresponding to an $n_C \rightarrow p_C$ promotion from the singlet, and one corresponding to a $\pi_{CC} \rightarrow p_C$ promotion from the singlet (Figure 1). The differential sensitivities to substitution of these two triplets can provide additional insight into the

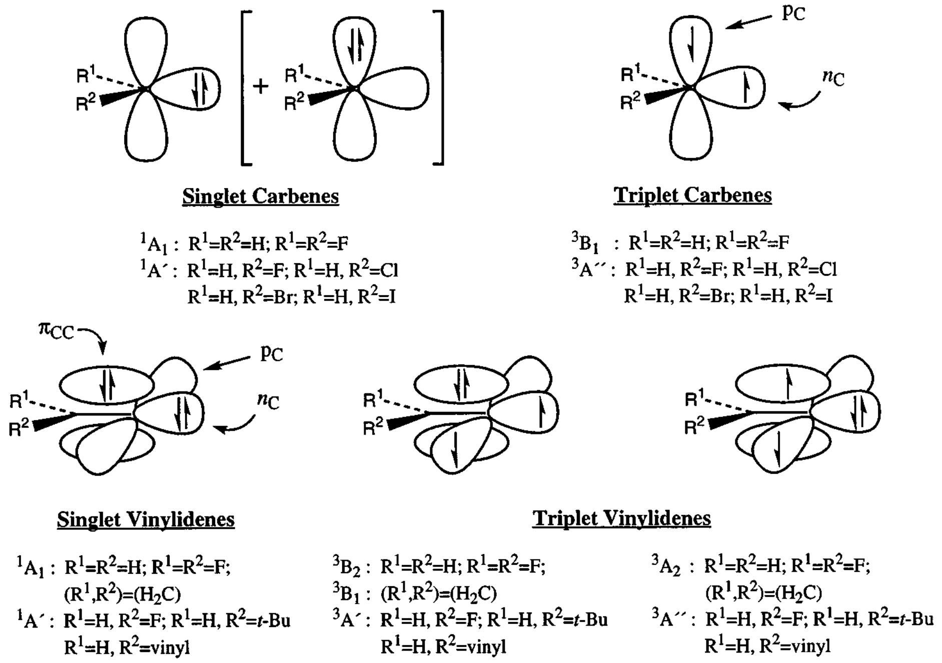

Figure 1. Orbital occupation, orbital labels and electronic state symmetries for the different carbenes and vinylidenes discussed in this paper. The singlet carbene in brackets represents a configuration that can mix into the ground state singlet to varying degrees, depending on substitution. Such mixing of excited configurations can also occur for all of the other species in this figure, but the effect is probably largest for singlet carbenes

physics underlying the substituent effects in the vinylidene systems. To further our analysis in all of these systems, we will make extensive use of natural bond orbital (NBO) methods for quantifying conjugation energies and orbital hybridizations.[64–66]

DFT has proven to be an extremely useful tool for other carbenes and isoelectronic systems.[13,17,18,29,33,42,67–76] The accuracy of various DFT functionals in the prediction of S–T gaps appears to derive from their ability to account for important non-dynamic correlation effects in the hypovalent systems (that is, the extent to which multiple configurations having the same state symmetry mix into the final state representation; see Figure 1). DFT, by construction, also accounts for dynamic correlation effects in an approximate fashion, and accomplishes all of this within what amounts to a single-determinant formalism. This stands in contrast to Hartree–Fock theory, another single-determinant formalism, which cannot be used for the estimation of S–T gaps in carbenes because of its failure to account for these important electron correlation effects. Within the context of a molecular orbital approach, multiconfiguration self-consistent-field (MCSCF) methods are required for useful accuracy, and this level of theory also finds some application in this paper.

THEORETICAL METHODS

Molecular structures were optimized at the DFT level using two different functionals. The first, referred to as BLYP, combines Becke's gradient-corrected exchange functional[77] with the gradient-corrected correlation functional developed by Lee *et al.*[78] The second functional, referred to as BVWN5, also makes use of Becke's gradient-corrected exchange functional, in this case combined with the local correlation functional of Vosko *et al.*[79] The key difference between these two is that BLYP employs a gradient-corrected correlation functional while BVWN5 has a simpler spin-density dependence for the correlation energy.

Optimizations were performed using the correlation-consistent polarized valence triple-ξ (cc-pVTZ) basis set[80] except for HCBr, HCI and *tert*-butylvinylidene. Calculations for the former two molecules employed the correlation-consistent polarized valence double-ξ (cc-pVDZ) basis set of Dunning[80] for H and C and the double-ξ effective core potential (ECP) basis of Hay and Wadt[81–83] for Br and I. Russo *et al.*[84] have shown such ECP basis sets to be useful for DFT calculations even though they were not designed for use with that level of theory. For vinylvinylidene, optimization was performed only with the BVWN5 functional; the BLYP level predicts the hydrogen migration to form vinylacetylene to proceed without barrier. For *tert*-butylvinylidene, geometries were optimized using the STO-3G basis set[85] since DFT calculations with more complete basis sets predicted hydrogen migration to form *tert*-butylacetylene to proceed without barrier; subsequent energy calculations were performed using the correlation-consistent polarized valence triple-ξ (cc-pVTZ) basis set.[80] All structures were verified as local minima by inspection of calculated analytical force constants. These frequencies were also used to calculate zero-point vibrational energies, and all reported multiplet splittings include zero-point corrections (i.e. they correspond to ΔT_0 measurements).

For vinylidene, we also carried out geometry optimizations at the MCSCF level, using the cc-pVDZ basis set and taking the entire valence space as the active space (ten electrons/ten orbitals). Similar calculations were carried out for methylene, where the full valence space is six electrons/six orbitals. All MCSCF calculations were of the complete active space (CAS) variety.[86]

Coupled cluster[87,88] energies including all single and double excitations together with a perturbative estimate for triples, CCSD(T), were calculated for the BLYP and BVWN5 geometries of singlet mono- and difluorovinylidene.

The BLYP densities were further analyzed using the NBO approach of Reed and co-workers.[64–66] The NBO formalism calculates (hyper)conjugative stabilization energies by second-order perturbation theory analysis of off-diagonal Kohn–Sham matrix elements corresponding to filled and empty orbitals in the NBO basis. NBO analysis was originally developed within the context of Hartree–Fock theory, but its extension to DFT is trivial.

Calculations were carried out using the Gaussian94[89] (including NBO version 3·1[90]) and GAMESS[91] program suites.

RESULTS

Structures

Optimized geometries for the carbenes and vinylidenes are provided in Tables 1 and 2, respectively. Agreement between calculated and experimental geometries is satisfactory for the parent systems CH_2 and vinylidene. In CHF, CHCl, and CF_2, on the other hand, the C—X bonds in the singlets are calculated to be too long by 0·03, 0·05, and 0·03 Å, respectively, at the DFT level. There do not appear to be any ambiguities in the experiments; moreover, Rodriquez and Hopkinson[30] found predicted bond lengths at the MP2/6–311++G** level to be in very good agreement with the experimental results for CHF,[92] CHCl[93] and CF_2.[94] Although these discrepancies may be a cause for some concern when using DFT to predict geometries in similar systems, they do not appear to degrade the predictive abilities of DFT with respect to the S–T gap (see below). Experimental geometries are not available for the singlets of HCBr or HCI. Our predicted DFT C—Br bond length is within 0·01 Å of the prediction of Scuseria *et al.*[40] using MCSCF methods. Our predicted DFT C—I bond length is 0·05 Å shorter than the HF/STO-3G* result of Gilles *et al.*,[39] but the latter level of theory is too low to be regarded as a trustworthy benchmark. Our DFT geometries for HCI agree closely with those calculated by Russo *et al.*[42] using similar levels of DFT. Russo *et al.*[42] noted that the vibrational frequencies predicted at the DFT level were in much better agreement with experiment[39] than those derived from the HF/STO-3G* calculations of Gilles *et al*.[39] Hence, the current DFT singlet geometries for HCBr and HCI appear reasonable.

No experimental data are available for the halogenated triplet geometries. Agreement is good (±0·01 Å in bond lengths, ±2° in angles), however, between the current predictions and either the MCSCF calculations of Scuseria *et al*.[40] or the DFT calculations of Russo *et al*.[42]

Experimental data are unavailable for the substituted vinylidenes. We are unaware of any other calculations on *tert*-butylvinylidene, for which the structures of the various electronic states are unremarkable.

For the case of vinylvinylidene, we have considered only the *s-trans* structure. Gunion *et al*.[54] performed extensive

Table 1. Optimized geometries of methylene and halogenated derivatives[a]

Molecule	Electronic state	Coordinate[b]	BVWN5	BLYP	Experiment
CH_2	$^1A_1$	rCH	1·115	1·120	1·110[c]
		∠HCH	101·0	100·8	102·0[c]
	$^3B_1$	rCH	1·079	1·084	
		∠HCH	134·8	135·4	134·0[c]
HCF	$^1A'$	rCH	1·129	1·135	1·130[d]
		rCF	1·334	1·329	1·305[d]
		∠HCF	101·6	101·6	103·0[d]
	$^3A''$	rCH	1·091	1·097	
		rCF	1·332	1·328	
		∠HCF	121·4	121·3	
HCCl	$^1A'$	rCH	1·114	1·119	1·130[e]
		rCCl	1·738	1·732	1·687[e]
		∠HCCl	101·1	101·0	105·0[e]
	$^3A''$	rCH	1·085	1·090	
		rCCl	1·682	1·676	
		∠HCCl	126·1	126·1	
HCBr	$^1A'$	rCH	1·134	1·139	
		rCBr	1·974	1·968	
		∠HCBr	98·4	98·3	
	$^3A''$	rCH	1·102	1·107	
		rCBr	1·897	1·892	
		∠HCBr	125·1	124·8	
HCl	$^1A'$	rCH	1·135	1·140	
		rCI	2·152	2·147	
		∠HCI	98·4	98·1	
	$^3A''$	rCH	1·102	1·107	
		rCI	2·056	2·052	
		∠HCI	127·2	126·9	
CF_2	$^1A_1$	rCF	1·330	1·326	1·300[f]
		∠FCF	104·5	104·4	104·9[f]
	$^3B_1$	rCF	1·338	1·336	
		∠FCF	120·1	119·9	

[a] See Theoretical Methods for basis sets employed.
[b] Bond lengths in Å, valence angles in degrees.
[c] Ref. 11.
[d] Ref. 92.
[e] Ref. 93.
[f] Ref. 94.

Table 2. Optimized geometries of vinylidenes and propadienylidene[a]

Molecule	Electronic state	Coordinate[b]	BVWN5	BLYP	Experiment
H_2CC	$^1A_1$	rCH	1·093	1·093	1·098[c]
		rCC	1·300	1·299	1·294[c]
		∠HCC	120·9	120·8	120·0[c]
	$^3B_2$	rCH	1·093	1·098	1·079[c]
		rCC	1·318	1·317	1·343[c]
		∠HCC	121·3	121·3	118·0[c]
	$^3A_2$	rCH	1·098	1·103	
		rCC	1·437	1·436	
		∠HCC	123·0	122·9	
H(*t*-Bu)CC	$^1A'$	rCC$(CH_3)_3$	1·580	1·573	
		rCC	1·352	1·349	
		∠CCC	128·2	127·1	
	$^3A'$	rCC$(CH_3)_3$	1·593	1·585	
		rCC	1·341	1·339	
		∠CCC	125·7	125·4	
	$^3A''$	rCC$(CH_3)_3$	1·576	1·567	
		rCC	1·514	1·510	
		∠CCC	127·4	126·9	
$H(H_2CCH)CC$	$^1A'$	rCC(H_2CCH)	1·461		
		rCC	1·307		
		∠CCC	137·9		
	$^3A'$	rCC(H_2CCH)	1·470	1·468	
		rCC	1·333	1·333	
		∠CCC	125·1	125·0	
	$^3A''$	rCC(H_2CCH)	1·422	1·420	
		rCC	1·430	1·428	
		∠CCC	122·7	122·5	
HFCC	$^1A'$	rCH	1·102	1·121	
		rCF	1·347	1·335	
		rCC	1·323	1·313	
		∠HCC	108·4	98·9	
		∠FCC	135·1	143·3	
	$^3A'$	rCH	1·087	1·093	
		rCF	1·378	1·373	
		rCC	1·313	1·315	
		∠HCC	125·0	124·6	
		∠FCC	123·3	123·4	
	$^3A''$	rCH	1·092	1·098	
		rCF	1·361	1·358	
		rCC	1·412	1·411	
		∠HCC	128·0	128·2	
		∠FCC	122·4	122·2	
F_2CC	$^1A_1$	rCF	1·338	1·335	
		rCC	1·352	1·352	
		∠FCC	120·9	120·8	
	$^3B_2$	rCF	1·350	1·347	
		rCC	1·306	1·307	
		∠FCC	125·3	125·3	
	$^3A_2$	rCF	1·334	1·331	
		rCC	1·418	1·417	
		∠FCC	125·7	125·7	
H_2CCC	$^1A_1$	rCH	1·089	1·093	
		$r(H_2)$CC	1·330	1·330	
		rCC	1·290	1·291	
		∠HCC	121·9	121·8	
	$^3B_1$	rCH	1·083	1·087	
		$r(H_2)$CC	1·364	1·364	
		rCC	1·238	1·240	

Table 2. Continued.

Molecule	Electronic state	Coordinate[b]	BVWN5	BLYP	Experiment
		∠HCC	120·8	120·8	
	$^3A_2$	*r*CH	1·086	1·091	
		r(H_2)CC	1·342	1·340	
		*r*CC	1·333	1·334	
		∠HCC	121·2	121·3	

[a] See Theoretical Methods for basis sets employed.

[b] Bond lengths in Å, valence angles in degrees.

[c] Ref. 50.

calculations on this molecule at the CISD level with a double-ξ basis set and showed that the *s-trans* radical anion is 5 kcal mol^{-1} lower in energy than the *s-cis* radical anion. Since the measured S–T gap derives from photoelectron detachment from the radical anion, the *s-cis* singlet and triplet structures of vinylvinylidene are not relevant to the experimental measurement. Our calculated singlet structure is in good accord with the CISD results of Gunion *et al.*[54] they did not report computational results for the triplets.

With respect to HFCC, DeLeeuw *et al.*[52] have performed very high-level CISD/TZ2P optimizations for all states of this molecule. For the triplets, the current DFT predictions are within 2° on all bond angles and within 0·015 Å for the C=C bond length and continue to overestimate the C—F bond length by about 0·03 Å. (This latter phenomenon may be general for fluorine bonded to a formally sp^2 carbon, and this merits further study since it would be desirable to address this issue in the development of future density functionals.) For singlet HFCC, there is a substantial difference between the geometries predicted at the BVWN5 and BLYP levels. It derives from the large exoergicity and very low barrier for HFCC to isomerize to fluoroacetylene (estimated at 0·8 kcal mol^{-1} by DeLeeuw *et al.*[52] and 2 ± 1 kcal mol^{-1} by Gilles *et al.*[51]). The fluorovinylidene minimum is found reasonably advanced along the reaction path for 1,2-hydrogen migration. This can be seen in the distorted bond angles—substantially less than 120° for CCH and substantially larger than 120° for CCF—and also in the surprisingly short C—F bond, which derives from the increased carbon s character in the C—F bond orbital of the incipient fluoroacetylene. Since this reaction coordinate is very flat, it is very sensitive to level of theory. Although the calculated bond lengths at both DFT levels are in good agreement, both internally and also with the CISD results of DeLeeuw *et al.*,[52] the latter level of theory predicts CCH and CCF bond angles of 128·0 and 114·8°, respectively. This is in much better agreement with the BVWN5 geometry. The agreement improves if we compare to CCSD(T)/TZ2P results of DeLeeuw *et al.*,[52] although the deviation in bond angles is still 5°. Our own CCSD(T)/cc-pVDZ energies calculated for the BVWN5 and BLYP structures shows the latter to be only 0·4 kcal mol^{-1} higher in energy than the former, illustrating how flat the hydrogen transfer coordinate is. Moreover, as discussed below, the large difference in geometries has no apparent impact on the calculated S—T gaps.

DFT methods are known sometimes to be unreliable for estimating the barrier to hydrogen transfer reactions,[95] and it appears based on HFCC that the gradient-corrected LYP correlation functional has a lower barrier for the vinylidene to acetylene transformation than is the case for the local correlation functional VWN5. This is further demonstrated in the cases of vinyl- and *tert*-butylvinylidene, as discussed further below. In the vinylvinylidene case, the singlet is stationary only at the BVWN5 level of theory. For the case of *tert*-butylvinylidene, with *both* DFT functionals the singlet is stationary only if small, unpolarized basis sets are used (e.g. STO-3G, 3–21G). The resulting geometries give good S–T gaps when single-point calculations are carried out with more complete basis sets, but this is obviously not the most desirable way to have to approach this problem.

When singlet difluorovinylidene is optimized within the constraints of C_{2v} symmetry, a very small imaginary frequency is calculated at the BLYP level (all frequencies are positive at the BVWN5 level). The imaginary mode corresponds to pyramidalization of the CF_2 carbon, with an optimized out-of-plane angle of about 9°. However, BLYP and CCSD(T) single-point calculations indicate this structure to be less than 0·1 kcal mol^{-1} lower in energy. Since the first vibrational level will clearly be above this barrier, we have used the C_{2v} structure throughout. Gallo and Schaefer[96] have calculated the singlet structure to have C_{2v} symmetry at the SCF and CCSD levels. At the CCSD/DZP level they calculate the C=C and C—F bond lengths to be 1·362 and 1·322 Å, respectively, and the CCF bond angle to be 123·4°, in reasonable agreement with the DFT calculations. It may be that the inclusion of triple excitations would improve the structural agreement, given the multiconfigurational character of the vinylidene, but as noted above, it may also be that the DFT estimates of the C—F bond length may be too long.

Finally, with respect to propadienylidene, our calculated structures for the $^1A_1$ state are in good agreement with the MP2/6–31G* results of Jonas *et al.*[44] and in excellent agreement with the CCSD/TZ2P results of Stanton *et al.*[63] Jonas *et al.*[44] also calculated one triplet, but did not provide the electronic state. Its geometry agrees well with our DFT-calculated $^3B_1$ geometry (which itself is different from the $^3A_2$ geometry), so we assume that the triplet reported by those authors is the $^3B_1$. We actually find the $^3A_2$ state to be the lower energy of the two by about 1·5 kcal mol^{-1} (see below). Its geometry involves a much longer C=C bond to the vinylidene center since it formally has only a single π electron. This same lengthening is present in all of the vinylidene $^3A_2$ states, which are all similarly π deficient in bonding.

Table 3. Triplet energies relative to singlets (eV) for methylene and halogenated derivatives[a]

Molecule	BVWN5[b]	BLYP[c]	Experiment
CH_2	−0·40	−0·42	−0·39 ± 0·003[d]
HCF	0·61	0·58	0·65 ± 0·02[e]
HCCl	0·29	0·27	0·18 ± 0·11[e]
HCBr	0·31	0·28	0·11 ± 0·10[e]
HCI	0·23	0·21	−0·26 ± 0·17[e]
CF_2	2·34	2·35	2·45[f]

[a] See Theoretical Methods for basis sets employed.

[b] Absolute energies (hartree) of singlets in this column: −39·361 03, −138·963 71, −499·628 37, −52·059 21, −50·272 75, −238·583 14.

[c] Absolute energies (hartree) of singlets in this column: −39·110 39, −138·430 12, −498·777 66, −51·667 21, −49·888 77, −237·769 38.

[d] Ref. 27.

[e] Ref. 39.

[f] Ref. 103.

Multiplet splittings

Tables 3 and 4 list the energies of the triplet states relative to the singlets for the methylenes and vinylidenes, respectively. All of the experimental data derive from photoionization spectroscopy, with the exception of methylene, where other measurements are also available. The various methods all agree extremely closely on the methylene S–T splitting.[11,12,27]

The multiplet splittings predicted by the two different DFT functionals typically agree very closely with one another. The largest deviation is 1·5 kcal mol^{-1} for the $^3A_2$ state of vinylidene (where the splitting itself is the largest discussed in this work, 63·4 kcal mol^{-1})—the average difference between the two is only about 0·5 kcal mol^{-1}. Evidently there is no advantage to using a gradient-corrected correlation functional (LYP) over a simpler one (VWN5) in this context.

The DFT predictions compare very favorably with experiment for the methylene series. The deviation of theory from experiment is about 0·5 kcal mol^{-1} for CH_2, 1 kcal mol^{-1} for HCF, within the experimental error bars for HCCl, and about 2 kcal mol^{-1} for CF_2 (where the gap is very large, 56·6 kcal mol^{-1}). Our CF_2 predictions agree closely with those of Gutsev and Ziegler[29] employing a different gradient-corrected DFT functional; Jonas *et al.*[44] predicted a splitting of 57·1 kcal mol^{-1} with projected fourth-order Møller–Plesset theory (PMP4) using a large basis set. For HCBr and HCI, the experimental assignments of the multiplet splittings rely on Franck–Condon simulations of the observed vibrational progressions in the photoelectron spectra. To carry out these simulations, structures and force constants were calculated at levels of electronic structure theory that would not be expected to be particularly trustworthy, and Gilles *et al.*[39] noted that this could lead to substantial error in the assigned multiplet splittings. The present DFT predictions are in reasonable agreement with the different gradient-corrected DFT prediction of Russo *et al.*[42] (within 0·16 eV) and the empirically

Table 4. Triplet energies relative to singlets (eV) for vinylidene, substituted vinylidenes and propadienylidene[a]

Molecule	Electronic state	BVWN5[b]	BLYP[c]	Experiment
H_2CC	$^3B_2$	2·09	2·10	2·065 ± 0·006[d]
	$^3A_2$	2·52	2·59	2·754 ± 0·020[d]
H(*t*-Bu)CC	$^3A'$	1·98	2·03	1·975 ± 0·015[f]
	$^3A''$	2·28	2·31	Unassigned
$H(H_2CCH)CC$	$^3A'$	2·05		1·923 ± 0·015[g]
	$^3A''$	1·85		2·035 ± 0·030[g]
HFCC	$^3A'$	1·44	1·44	1·358 ± 0·009[e]
	$^3A''$	1·34	1·37	1·320 ± 0·009[e]
F_2CC	$^3B_2$	1·25	1·24	> 1·09[e]
	$^3A_2$	0·64	0·64	0·924 ± 0·009[e]
H_2CCC	$^3B_1$	1·45	1·44	1·290 ± 0·009[h]
	$^3A_2$	1·37	1·37	Unassigned

[a] See Theoretical Methods for geometries and basis sets employed.

[b] Absolute energies (hartree) of singlets in this column: −77·677 51, −235·714 17, −155·465 05, −177·213 16, −276·769 40, −115·937 27.

[c] Absolute energies (hartree) of singlets in this column: −77·238 86, −234·317 82, −176·491 53, −275·764 05, −115·307 77.

[d] Ref. 50.

[e] Ref. 51.

[f] Ref. 53.

[g] Ref. 54.

[h] Ref. 61; the assignment of this splitting to the $^3B_1$ state is ambiguous.

corrected generalized valence bond results of Irikura *et al.*[24] (within 0·033 eV).

For vinylidene, the relative energy of the $^3B_2$ state is well predicted by DFT, but the error in the $^3A_2$ relative energy is rather large, about 5 kcal mol^{-1} at the BVWN level. While this is less than 10% of the total multiplet splitting, it is still disappointing. On the other hand, full valence CAS/cc-pVDZ calculations predict the energies of the $^3B_2$ and $^3A_2$ states relative to $^1A_1$ to be 1·65 and 2·50 eV, respectively. Thus, DFT is more accurate than a fairly sizable CAS calculation (and requires much less CPU time).

In *tert*-butylvinylidene, the DFT predicted relative energy of the $^3A'$ state is excellent being less than 1 kcal mol^{-1} from the experimental value reported. Although the $^3A''$ state is not observed experimentally, a range is reported for the appearance of the band. The relative energy predicted by DFT is in good agreement with the experimental expected value for this latter state.

The DFT predictions for vinylvinylidene are reasonable for the two triplet states if the experimental assignment is correct (this situation is assumed in Table 4). The agreement would be improved (and consistent with the accuracy of the other vinylidene predictions) if the experimental assignment of the two triplet origins were reversed. For the $^3A'$ state, the energy splitting is within 3 kcal mol^{-1} of the assigned experimental value, but within 0·4 kcal mol^{-1} of the splitting assigned to the $^3A''$ state. The error in the calculated DFT relative energy for the experimentally assigned $^3A''$ state is about 4 kcal mol^{-1}, but if the triplet states have been misassigned experimentally, the error reduces to 2 kcal-mol^{-1}. Gunion *et al.*[54] noted that the assignment of the origin peak for the $^3A''$ state is ambiguous, so it is possible that the appearance of misassignment is coincidental. Further analysis would require a more complete vibrational analysis, for which data are currently lacking.

The DFT predictions are fairly good for the energies above singlet of the two triplet states of HFCC, being off by less than 2 kcal mol^{-1}. Interestingly, DeLeeuw *et al.*[52] calculated the relative state energies of $^3A'$ and $^3A''$ to be 1·30 and 1·42 eV, respectively, at the CCSD(T)/TZ2P level. That is, the triplet state energies are reversed compared with the DFT predictions and the experimental assignment. DeLeeuw *et al.* noted that their predicted $^3A''$ state energy would place the (0,0) transition for this state directly under a vibrational absorption in the $^3A'$ envelope (although they also pointed out that this suggestion cannot explain the low intensity peak that Gilles *et al.*[51] *did* assign as the $^3A''$ origin). The DFT results are consonant with the experimental assignment, and this may indicate that the single-reference CCSD(T) method does not accurately order these states.

In F_2CC, the predicted energy of the $^3B_2$ state exceeds the lower bound established by experiment, but the $^3A_2$ state is predicted to be 6·5 kcal mol^{-1} lower in energy relative to $^1A_1$ than is observed experimentally. The experimental assignment of the (0,0) band in the photoelectron spectrum may possibly be flawed. No vibrational progression is observed for the $^3A_2$ signal, so the single observed peak could correspond to a contaminating species. Moreover, were the actual splitting to be close to the DFT prediction, its experimental identification would be complicated by the long vibrational progression of the $^1A_1$ band, which extends beyond the calculated splitting. On the other hand, the splitting predicted by DFT for the $^3A_2$ state of vinylidene is also too low, and by a similar margin to the F_2CC case (if we assume that the experimental peak assignment in F_2CC is correct). Application of alternative theoretical methods (e.g. MCSCF) will be helpful in resolving this issue.

Finally, in the case of propadienylidene, DFT predicts the $^3B_1$ and $^3A_2$ states to be separated by less than 0·1 eV, with the latter predicted to be within 2 kcal mol^{-1} of the experimentally assigned splitting. Robinson *et al.*[61] assign the triplet band in the photoelectron spectrum to the $^3B_1$ state without any discussion of the $^3A_2$ state. No vibrational analysis was performed for this triplet state. Given how close the two triplet states are calculated to be at the DFT level, it may be that the distinct shoulder on the lower energy side of the assigned triplet origin corresponds to the $^3A_2$ state, which DFT does find to be about 1·5 kcal mol^{-1} lower in energy. We calculate the radical anion that is the photodetachment precursor to propadienylidene to have C=C: and $(H_2)C{=}C$ bond lengths of 1·290 and 1·387 Å, respectively, at the BVWN5/aug-cc-pVDZ level (diffuse functions added to the basis set since this is an anion). This C=C: bond length is roughly half way between those calculated for the two diffferent triplet states, and the $H_2C{=}C$ bond length is 0·023 Å longer than that calculated for the $^3B_1$ state and 0·045 Å longer than that calculated for the $^3A_2$ state. This suggests that the Franck–Condon intensity expected for the $^3B_1$ state would be larger than that for the $^3A_2$ state. This analysis is consistent with the smaller intensity of the shoulder suggested above as the possible origin for the latter triplet state.

DISCUSSION

Overall, the ability of the density functional calculations to predict accurately the state energy splittings for the studied carbenes is excellent. This suggests that analyses of other properties relevant to the state energies at this level of theory will also be productive. We begin with a consideration of the carbene orbital hybridizations and conjugation energies for the halo-substituted methylenes. Table 5 presents these hybridizations as derived from NBO analysis.

One possible explanation for the observed trend in the S–T gaps in these systems is that more electronegative halogen atoms cause the carbon atom to devote more s character to its in-plane non-bonding orbital (n_C) in order to minimize positive charge build-up on carbon. This makes the promotion energy to the out-of-plane p orbital larger, and thereby increases the S–T gap. Inspection of Table 4 reveals, however, that the percentage of s character in n_C in the singlets increases in order $HCI < HCBr \approx$

Table 5. NBO orbital hybridizations at the carbene carbon in substituted methylenes[a]

Molecule	Electronic state	n_C	σ_{CH}	σ_{CX}
CH_2	$^1A_1$	$sp^{0\cdot6}$	$sp^{4\cdot2}$	
	$^3B_1$	$sp^{2\cdot0}$	$sp^{2\cdot0}$	
HCF	$^1A'$	$sp^{0\cdot5}$	$sp^{5\cdot5}$	$sp^{5\cdot1}$
	$^3A''$	$sp^{0\cdot8}$	$sp^{2\cdot9}$	$sp^{4\cdot0}$
HCCl	$^1A'$	$sp^{0\cdot5}$	$sp^{4\cdot4}$	$sp^{6\cdot3}$
	$^3A''$	$sp^{1\cdot1}$	$sp^{2\cdot4}$	$sp^{3\cdot5}$
HCBr	$^1A'$	$sp^{0\cdot4}$	$sp^{4\cdot3}$	$sp^{11\cdot2}$
	$^3A''$	$sp^{0\cdot9}$	$sp^{2\cdot4}$	$sp^{4\cdot9}$
HCI	$^1A'$	$sp^{0\cdot3}$	$sp^{4\cdot3}$	$sp^{13\cdot2}$
	$^3A''$	$sp^{0\cdot9}$	$sp^{2\cdot3}$	$sp^{4\cdot9}$
CF_2	$^1A_1$	$sp^{0\cdot4}$		$sp^{5\cdot5}$
	$^3B_1$	$sp^{0\cdot5}$		$sp^{4\cdot1}$

[a] Contributions from d functions are less than 0·5% in all cases.

$CF_2 < HCCl \approx HCF < CH_2$. This does not correlate at all with the observed S–T gap progression. The trouble with this analysis is that it ignores the different requirements for bonding between carbon and another second-row atom compared to a fourth- or fifth-row atom. In order to maximize overlap with iodine bonding orbitals, for instance, carbon must devote very significant p character to the σ_{CI} orbital, and indeed this effect is apparent from the carbon σ_{CX} hybridizations listed in Table 4. Thus, the dominant influence on carbene orbital hybridization is not electronegativity but atomic size.

However, this does not invalidate arguments for the influence of electronegativity on the S–T splitting. Rather, the influence must be inferred from a different analysis. In particular, if we examine the *change* in the n_C and σ_{CX} orbital hybridizations on passing from the singlet to the triplet, the effect of electronegative substituents is apparent. In the case of iodine, with a roughly equal electronegativity to carbon, promotion of one electron from n_C to p_C leads to a 10% increase in the s character of the σ_{CI} orbital. This reduces the descreening of the carbon nucleus brought about by $n_C \rightarrow p_C$ promotion. This increase in σ_{CX} s character drops to 8% for HCBr and HCCl and 4% for HCF and CF_2.

Moreover, the different electron-withdrawing powers of the halogen atoms affect the charge at the carbene carbon. The natural population analysis[64] (NPA) charge on the singlet carbon atom calculated at the BLYP/cc-pVDZ level is −0·33 for HCI, −0·22 for HCBr, −0·13 for HCCl, −0·12 for CH_2, 0·27 for CHF and 0·61 for CF_2. Increasing charge at carbon increases the separation between the s and p orbital energies, and hence increases the S–T gap. Irikura *et al.*[24] have emphasized the predictive utility of an empirical charge scheme for estimating S–T gaps in carbenes. In terms of the physical effects of halogen substitution, however, there is clearly a complex synergism between orbital hybridization and charge withdrawal.

Another substituent influence that has been suggested to affect splitting between the singlet and triplet states is stabilizing π donation from substituents into the empty p orbital in the singlet state, in other words, conjugation. Irikura *et al.*[24] noted that the contribution of halogen p orbitals to the delocalized molecular orbital nominally called p_C increases with increasing π donor character. However, that does not necessarily indicate this to be net stabilizing for the singlet over the triplet. It must be noted that the singlet will derive more stabilization from this particular conjugation because the acceptor p_C is formally empty, whereas in the triplet it is singly occupied. On the other hand, the triplet has only a single electron occupying the *in-plane* orbital, which also can conjugate with substituent halogen atoms. It is not obvious that the sum of the two one-electron conjugation energies in the triplet will not be equal to the two-electron conjugation energy for the singlet.

To examine this issue, we have calculated the conjugation energies via second-order perturbation theory on the off-diagonal elements of the Kohn–Sham matrix expressed in the NBO basis. One important technical aspect of this analysis is that in order for the conjugation energy in the singlet not to be overestimated, it is critical that the degree to which the doubly excited singlet configuration contributes to the ground state wave function be well represented. At the Hartree–Fock level, which is single-determinant in nature, this would be expected to be very poorly represented. DFT is also formally a single determinant methodology, but by minimizing the energy with respect to the electron density, this level of theory is able to distribute density into regions of space associated with the doubly excited configuration in a natural way, so NBO analysis at this level is expected to be more informative than at the HF level. This analysis is further illustrated in Figure 2, which presents electron probability difference maps for both of these levels of theory with a full valence CAS calculation (all calculations for the identical molecular geometry). As expected, the HF level overestimates the in-plane density and underestimates the out-of-plane density much more severely than the DFT level. There is some remaining discrepancy with the CAS density, however, so singlet conjugation energies may still be somewhat overestimated.

In any case, the total calculated NBO conjugation energies for the halo-substituted methylene singlets are 4·22, 4·44, 4·24, 3·04 and 2·78 eV for CF_2, HCF, HCCl, HCBr and HCI, respectively. For the triplet states, on the other hand, these same total conjugation energies are 3·88, 4·08, 4·28, 2·86 and 2·52 eV, respectively. That is, there is a moderate difference in the NBO stabilization energies associated with conjugation predicted for the different spin states amounting to about 8 kcal mol^{-1} for the fluorinated carbenes and less than 6 kcal mol^{-1} for the other carbenes. For comparison, Khodabandeh and Carter[31] and Lim *et al.*[18] considered the importance of analogous hyperconjugative donor interactions in stabilizing the singlet state of methylcarbene, and Parasuk and Cramer[97] discussed the importance of phenyl conjugation in stabilizing singlet phenylcarbene—both groups concluded that the energetic

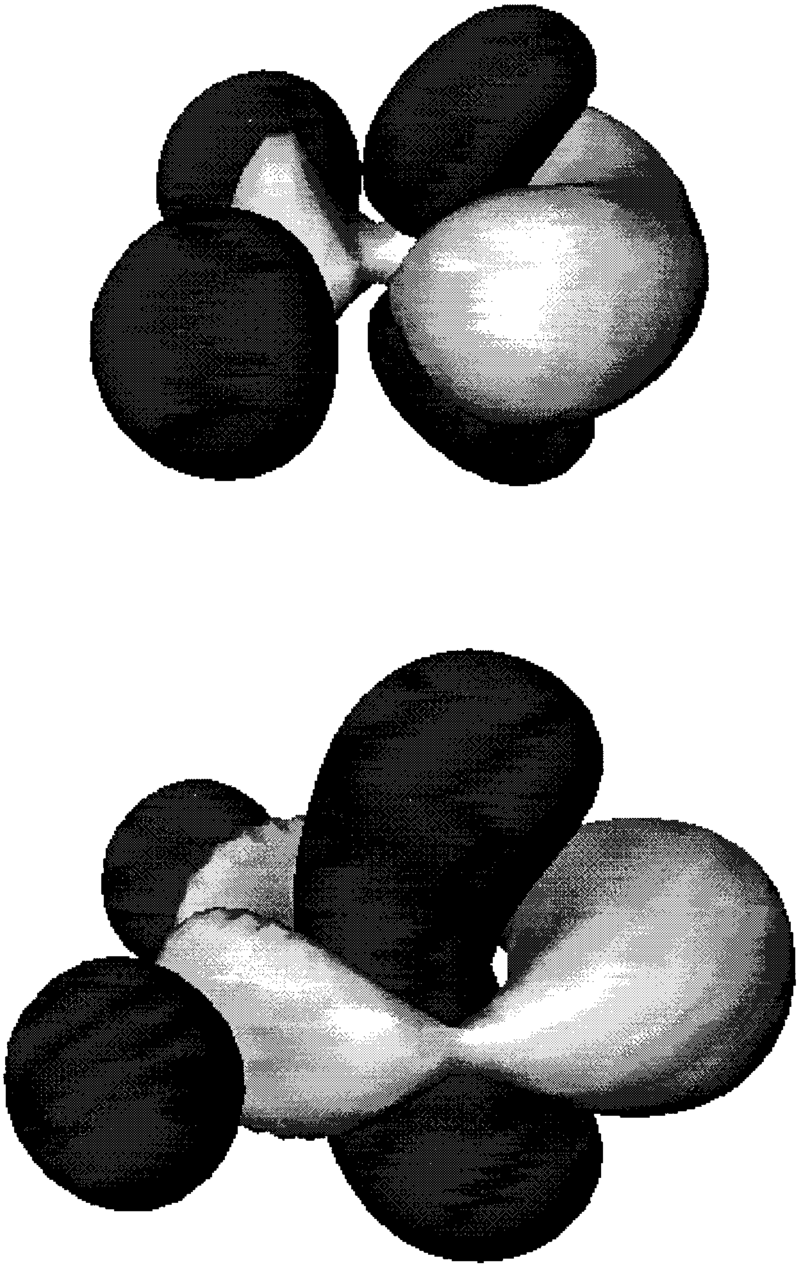

Figure 2. Difference maps in the electron probability density for methylene as calculated at different levels of theory. The upper map shows the difference between full valence CAS/cc-pVDZ and BLYC/cc-pVDZ. The lower map shows the difference between full valence CAS/cc-pVDZ and HF/cc-pVDZ. All calculations used the same geometry for methylene. The maps depict ±0·0025 isodensity contours, with light gray indicating excess density relative to the CAS level and dark gray indicating depleted density relative to the CAS level

effect of (hyper)conjugation were negligible. These carbene analyses are in marked contrast to the situation with isoelectronic nitrenes and nitrenium ions, where the same groups (methyl and phenyl) can show differential stabilization effects of 20 to 50 kcal mol^{-1}.[16–18,76,97] Evidently significant (hyper)conjugative stabilization of singlet states requires either a large formal charge on the hypovalent atom or a reasonably powerful π donor, and the halogen-substituted carbenes are so characterized only to a moderate degree.

Our finding that conjugation does not strongly stabilize the singlet state at first glance seems to be at odds with various other studies on substituted carbenes. For instance, Feller *et al.*[43] concluded that conjugation was the dominant factor influencing S–T splittings for the C_{2v} (planar) geometries of $C(NH_2)_2$, $C(OH)_2$ and $C(FH)_2^{2+}$ (the geometry at which conjugation into the carbon p orbital would be expected to be maximized). In qualitative agreement with the earlier results of Feller *et al.*[43] at less reliable levels of theory, we calculate the S–T splittings to be 3·56, 2·78 and 2·27 eV for planar $C(NH_2)_2$, $C(OH)_2$ and $C(FH)_2^{2+}$, respectively, at the BVWN5/cc-pVDZ level. The last two molecules represent a particularly interesting comparison insofar as they are isoelectronic, and one would expect the FH^+ substituents to be much stronger than OH in a σ withdrawing sense, but weaker in a π donating sense. Since the σ withdrawing power of the substituents *increases* along this series, but the S–T splitting *decreases*, Feller *et al.*[43] concluded that π conjugation is the dominant influence on the S–T splitting. NBO analysis is entirely consistent with this conclusion. For the planar structures, we calculate the difference in conjugation energies for singlet vs triplet to be 2·27 eV for $C(OH)_2$ and only 0·24 eV for $C(FH)_2^{2+}$ [with $C(NH_2)_2$ the comparison is less obvious, since there is no lone pair on nitrogen to conjugate with the carbene σ orbital in the triplet]. Thus, as noted above for *uncharged* halogen-substituted carbenes, π conjugation does not significantly stabilize one state over the other in $C(FH)_2^{2+}$, and the absolute splitting is dictated by σ inductive effects. However, with OH as a substituent, π conjugation becomes a significant factor, and apparently considerably outweighs the smaller inductive effect. In other words, the NBO analysis presented thus far does not imply that π conjugation is unimportant when it comes to trends in S–T gaps for *rows* of the Periodic Table, but rather that it is of mitigated importance for the halogen *column* of the Periodic Table, consistent with halogens being viewed as very weak π donors (we speculate moreover, that carbenes substituted with third and lower row atoms will also show low sensitivity to π conjugation, since the interaction of those atoms lone pairs with a carbon 2p orbital is expected to be substantially reduced).

A referee has pointed out that this analysis fails to explain why the S–T splitting for $C(FH)_2^{2+}$ is not substantially larger than for CF_2, since both show only small differences in π-conjugation energies for singlet and triplet states, but FH^+ should be much more inductively withdrawing than F. This point is well taken and difficult to address unambiguously, since any decomposition of total energies is necessarily arbitrary and model dependent. It may be that other effects not present in CF_2 destabilize the singlet state of $C(FH)_2^{2+}$. For instance, Coulomb repulsion in the charged singlet is expected to be larger than for the charged triplet, since the bond angle is smaller. A calculation of the FCF bending coordinate for the charged system does show it to be less steep for opening the angle than is the case for the neutral, but the extent of that difference is only about 5 kcal mol^{-1} over 20°, which does not dramatically increase the difference in the S–T gaps between the two molecules. Our experience with NBO analysis suggests that it is a useful method for analyzing conjugative and hyperconjugative interactions,[98] but in this instance it is not sufficient in and of itself to explain the apparent discrepancy noted by the referee.

Turning now to the vinylidene series, substitution decreases both S–T gaps in the order t-Bu < vinyl < F < F_2 (propadienylidene is discussed as a special case below). This ordering holds for both triplets, but the total decrease is much larger for the n^1p^1 triplets than for the $p^1\pi^1$ triplets (see Figure 1 for orbital labeling). Lineberger and co-workers[51,53] have noted that this effect is associated with a large destabilization of the singlet states along this series relative to the doublet radical anions (as measured by the electron affinity of the singlets), a smaller destabilization of the n^1p^1 triplets and weak stabilization of the $p^1\pi^1$ triplets. DeLeeuw *et al.*[52] obtained good agreement at the CCSD(T) level with the reported electron affinities[51] for the different states of HFCC.

Phrased slightly differently, we may say that all of the substituents studied have their strongest influence on the p_C orbital, and that influence is an inductive one, so a substituted vinylidene state with this orbital occupied is stabilized more than a state where it is not (all relative to unsubstituted vinylidene)—hence the observation by Lineberger and co-workers[51,53] that substitution destabilizes the singlet (unoccupied p) relative to the radical anion (singly occupied p). The next strongest interaction is with the n_C orbital, and that is also stabilizing for all substituents considered here, and the weakest interaction is with the π_{CC} orbital, with this being slightly destabilizing. This analysis is consistent with most of the substituents being σ-electron-withdrawing groups (so they can hyperconjugatively delocalize p and n_C density) and π-electron-donating groups (so they have net destabilizing interactions with the C=C π system); the influence of the σ effects are much more significant at the carbenic center than are the π effects.

To provide a quantitative estimate of the σ-electron-withdrawing effects, we again make use of NBO analysis, focusing on the hyperconjugative interactions between the p_C orbital and the parallel σ^*_{CX} acceptor orbitals at the other end of the C=C bond. Table 6 provides these stabilization energies separated into σ^*_{CH} and $\sigma^*_{CC}/\sigma^*_{CF}$ components. It is clear that there is significantly enhanced hyperconjugative stabilization as the σ^*-accepting character of the substituent

Table 6. NBO stabilization energies (kcal mol^{-1}) from hyperconjugation for substituted vinylidenes[a]

Molecule	Electronic state	$p_C \rightarrow \sigma^*_{CH}$	$p_C \rightarrow \sigma^*_{CX}$
H_2CC	$^3B_2$	10·5 (each H)	
	$^3A_2$	8·7 (each H)	
H(*t*-Bu)CC	$^3A'$	11·4	10·8
	$^3A''$	7·9	7·4
$H(H_2CCH)CC$	$^3A'$	10·9	9·4
	$^3A''$	10·0	7·5
HFCC	$^3A'$	11·9	35·8
	$^3A''$	7·8	28·7
F_2CC	$^3B_2$		41·7 (each F)
	$^3A_2$		31·4 (each F)

[a] Calculated at BLYP/cc-pVTZ level.

increases. The effect is weak for *tert*-butyl, larger for vinyl and largest of all for fluoro and difluoro. This trend is the same in both triplet states, but the magnitudes of the stabilizations are smaller for the $p^1\pi^1$ triplets. This presumably derives from the longer C=C bonds in these triplets. With only one π-bonding electron, the C=C bond lengthens and overlap between the p_C and σ^* acceptor orbitals is reduced, thereby reducing the energies of their interactions. The magnitude of the difference in effects between the two triplet states is proportional overall to the strength of the interaction with the substituent.

These same trends are observed for $n_C \rightarrow \sigma^*$ stabilization energies (one could alternatively call these through-bond inductive stabilization energies), but the magnitudes are smaller because of the weaker overlap between these orbitals. The greater increase in hyperconjugative stabilization energies for the p_C orbitals compared with the n_C orbitals as a function of substitution thus decreases the S–T gaps for the n^1p^1 triplets, since this gap correlates with the $n \rightarrow p$ promotion energy, i.e. there is more stabilization available to the n^1p^1 triplet than to the n^2 singlet.

The triplet–triplet gap, to continue this analysis, decreases (and indeed inverts) with substitution by increasingly powerful σ-electron-withdrawing groups. This gap corresponds to the promotion energy for a $\pi \rightarrow n$ electron transfer (note that π is below n for vinylidene). As noted above, the energy of the n_C orbital drops with substitution because of its hyperconjugative interactions with in-plane σ^* acceptors. The energy of the π orbital, on the other hand, is only weakly affected by substitution. All of the substituents considered here are weak π donors (vinyl being the strongest) and as such will slightly increase the energy of the π_{CC} orbital relative to n_C when compared with vinylidene. This analysis is borne out by inspection of UHF one-electron-orbital eigenvalues for the $p^1\pi^1$ triplets, for instance—the π_{CC}–n_C orbital energy splitting decreases in the order $H_2CC > HFCC > F_2CC$. Thus, whereas the lower energy triplet for H_2CC is the . . . $n^1p^1\pi^2$ $^3B_2$ state, hyperconjugation lowers the energy of the n_C orbital sufficiently in FHCC (and F_2CC) that the lowest energy triplet becomes the . . . $n^2p^1\pi^1$ $^3A''$ state ($^3A_2$ for F_2CC).

One interesting feature of F_2CC is how low the calculated excitation energy is to go from the $^1A_1$ to the $^3A_2$ state. The singlet state has the proper π orbital occupation to be Y-aromatic[99] (i.e. six π electrons in the four-orbital system derived from the two carbon and two fluorine p orbitals). However, there does not appear to be any particularly large stabilization of this electronic structure over the five π electron triplet state $^3A_2$: the S–T gap conforms to what would be expected given the observed trend for other vinylidene substitution patterns. This is consistent with the conclusions reached by various groups that the isoelectronic trimethylenemethane dianion does not enjoy any Y-aromatic stabilization.[100–102] More refined calculations on this system would be needed to evaluate this issue quantitatively, however.

Finally, propadienylidene provides an interesting example of the effects of an orbital hybridization difference between two different triplet states, namely the $^3B_1$ and $^3A_2$ states. In the $^3B_1$ state, the n_C orbital is only half-filled, and the terminal carbon atom redistributes s character to the only remaining bond, the C—C multiple bond. This redistribution, together with the one full and one partial π bonds in the cumulenic system, reduces the C—C distance to 1·24 Å. This has the effect of adding propargyl-like character to the system, i.e. it resembles the diradical of methylacetylene derived from abstraction of the acetylenic hydrogen atom and one methyl hydrogen atom. This is different from the geometry of the $^3A_2$ state, which has a reasonably standard allene-like geometry since the n_C orbital is doubly occupied. This difference can be further quantified by examination of the degree of spin density located on the CH_2 group. The Fermi contact integral at the $C(H_2)$ carbon is 0·030 au for the $^3B_1$ state, but only −0·012 au for the $^3A_2$ state. This difference may prove useful should identification of either or both of these triplet species by ESR ever be attempted.

CONCLUSIONS

Density functional theory shows great promise as an inexpensive method for the calculation of multiplet splittings in carbene and vinylidene systems. Its single determinant formalism offers various opportunities for analysis of the computations in order to gain further insight into substituent effects for these molecules.

By examination of conjugation energies within a natural bond orbital formalism, we conclude that the relative importance of π conjugation in stabilizing halogen-substituted carbene singlets is of reduced importance compared with other effects, in particular orbital rehybridization and charge build-up at the carbene carbon. Both of the latter effects depend critically on substituent electron-withdrawing power. In order to analyze the importance of orbital rehybridization, it is critical to study both the singlet *and* the triplet orbitals, since the absolute degree of s character in individual carbene orbitals is more a function of the principal quantum number of the substituent valence orbitals, but the change in s character with change in spin multiplicity is a more sensitive measure of substituent electronegativity.

Substitution effects on vinylidene multiplet splittings are dominated by σ-electron-withdrawing interactions that can stabilize the p_C orbital preferentially. This strongly stabilizes both possible triplet states relative to the singlet. The relative energies of the two triplet states are further affected by a combination of σ-withdrawing and π-donating effects. For all of the experimentally known systems, these two effects operate in concert to decrease, and ultimately invert, the energy separating these two states as increasingly powerful σ-donors/π-acceptors are substituted on to the system.

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