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Ab initio Calculation of the Lowest Singlet and Triplet States in CH_2, CHF, CF_2, and $CHCH_3$

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The lowest singlet and triplet states of the radicals CH_2, CHF, CF_2, and $CHCH_3$ have been investigated both in SCF and IEPA approximation ("independent electron pair approach" to account for electron correlation). The SCF calculations yield triplet ground states for CH_2, CHF, and $CHCH_3$, and a singlet ground state for CF_2. Electron correlation stabilizes the singlet state by about 14 kcal/mole with respect to the triplet for all four radicals leading to a singlet ground state also for CHF. The final triplet-singlet energy separations are 10, 6, −11, −47 kcal/mole for CH_2, $CHCH_3$, CHF, CF_2, respectively. Values for equilibrium bond angles, ionization potentials and bond energies are also given.

Key words: Small carbene radicals – Singlet-triplet energy separation – Pair correlation energies – Equilibrium bond angles

1. Introduction

Carbenes are of great importance as reactive intermediates in organic chemistry [1]. They are characterized by a formally divalent carbon center and two unpaired electrons. Such a configuration gives rise to four low-lying electronic states – a triplet and three singlets – which behave completely different in chemical reactions.

For the simplest carbene (CH_2, methylene) it is known both from experiment (ESR spectroscopy [2, 3], kinetics and thermodynamics of methylene reactions [4]) and from quantum chemical calculations [5] that the triplet state ($^3B_1$) is the ground state being about 10 kcal/mole below the lowest singlet state ($^1A_1$). From UV spectroscopy one concludes that CHF and CF_2 have singlet ground states [6–10] which is supported by SCF calculations in the case of CF_2, but not for CHF [11]. Whether carbenes with more extended substituents behave like singlets or triplets depends strongly on the electronegativity and the electronic structure of the substituents [1, 12].

In this paper we report on quantum chemical *ab initio* calculations for the systems CHF, CF_2, and $CHCH_3$, including the effects of electron correlation. The purpose of our investigation is to answer the following three questions:

1) How much are the properties of the divalent carbon center in CH_2 changed if the H-atom is substituted?

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2) How important is the influence of electron correlation on the relative stability of the lowest singlet and triplet states of CHF, CF_2, and $CHCH_3$ compared to CH_2?

3) Are the ground states of CHF and $CHCH_3$ singlet or triplet states?

Former theoretical investigations on these systems have been performed in the SCF-approximation [11, 13, 14] or with minimal CI [11] for CF_2 and CHF. $CHCH_3$ has only been studied with extended Hückel [12, 15] or MINDO/2 methods [16]. These calculations quite successfully reproduced the spectroscopical values for equilibrium bond lengths and angles for CF_2 and CHF as far as they are known experimentally [6–10, 17–19]. But they are not able to give answers to the above questions.

2. Method of Calculation

The quantum chemical method that we have used for this investigation is the "independent electron pair approach" combined with the calculation of "pair natural orbitals" (IEPA-PNO). Since this method has been described elsewhere in great detail for closed and open shell states [20–22] we just scetch its basic ideas:

1) The starting point is a restricted (closed or open shell) SCF-calculation in the Roothaan [23] or McWeeny [24] scheme.

A one-determinant SCF-wavefunction

$$\phi_0 = |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\ldots\varphi_n\bar{\varphi}_n\varphi_{n+1}\ldots\varphi_{n+p}|$$

where n is the number of doubly, p the number of singly occupied orbitals, is adequate for the lowest singlet and triplet states of the systems considered here. The higher singlet states require two-determinant SCF-wavefunctions for symmetry reasons.

The SCF-energy E_{SCF} corresponding to the SCF-wavefunction ϕ_0 is an upper bound to the true energy E of the state under consideration, the difference generally is called correlation energy

$$E_{\text{corr}} = E - E_{\text{SCF}}\,.$$

2) The occupied SCF-orbitals φ_i are transformed to localized ones ψ_i according to Boys' criterion [25]. Such a transformation is possible only within the doubly occupied and the singly occupied orbitals, respectively, but must not mix the two sets among each other.

2) For each pair i, j of localized orbitals a "pair correlation energy" ε_{ij} is calculated by means of the pair natural orbitals (PNO's) [26] of this pair. One distinguishes between *intra*pair correlation energies ε_{ii} and singlet or triplet *inter*pair correlation energies ${}^1\varepsilon_{ij}$ and ${}^3\varepsilon_{ij}$ for $i \neq j$. All ε_{ij} are calculated independently from each other.

4) The sum of the individual pair correlation energies ε_{ij} is regarded as an approximation to the correlation energy of the system, i.e.

$$E_{\text{corr}} \approx E_{\text{corr}}(\text{IEPA}) = \sum_i \varepsilon_{ii} + \sum_{i<j} ({}^1\varepsilon_{ij} + {}^3\varepsilon_{ij})$$

("independent electron pair approach", IEPA).

Though the IEPA-scheme does not yield upper bounds to the true energy IEPA-results for binding energies, excitation energies etc. of first row atoms [22] and hydrides [27] are generally an order of magnitude more reliable than SCF-results. The residual errors for hydrocarbons in most cases are in the order of 0.1–0.15 eV. This is the consequence of certain error cancellations and of the fact that the error of simply adding up pair correlation energies does not change very strongly with geometry and state. The implications of the IEPA approximation and corrections to it are currently discussed by Meyer [28] and Kutzelnigg and coworkers [29].

3. The Orbital Basis Set

For all calculations reported here we used an orbital basis of contracted Gaussian lobe functions. *p*-functions are constructed from two lobes with equal exponents η and an off-center distance d such that $d\sqrt{\eta}=0.1$. *d*-functions are constructed similarly from four lobes with $d\sqrt{\eta}=0.2$, except for d_{z^2} which consists of three lobes with almost equal exponents, the weighting factors 1.0, -2.0, 1.0 and $d\sqrt{\eta}=0.2\sqrt{2}$ for the outer lobes. For details see [30].

From our experience with CH_2 [5] we know that the inclusion of polarization functions both on C and H is of much greater importance to get good values for the triplet-singlet energy separation and the correct angular dependence of the total energies of both states than the use of extended *s*- and *p*-basis sets. (See also [31].) Because of the necessity to use much smaller basis sets for systems with two or three "heavy" atoms than it is possible for CH_2 the present calculations are performed with an orbital basis set of double zeta quality plus one set of polarization functions. Our basis consisted of

a) a 8*s*, 4*p* Huzinaga basis [32] contracted to four *s* and two *p* groups with (5, 1, 1, 1) and (3, 1) contraction, respectively, both for C and F,

Table 1. Orbital basis set for carbene calculations. The exponents η and contraction coefficients c are taken from [32]

Sym.	Nr.	C		F		H	
		η	c	η	c	η	c
s	1	2779.4685	0.002056	6507.3241	0.001988	33.6444	0.00612
		417.66068	0.015639	979.61474	0.015108	5.05796	0.04575
		95.487919	0.075238	225.07995	0.072292	1.14680	0.20572
		27.079569	0.245001	64.607431	0.236486	0.321144	0.50822
		8.749239	0.466899	21.150915	0.461240		
	2	3.043590	1.0	7.394198	1.0	0.101301	1.0
	3	0.527582	1.0	1.351308	1.0		
	4	0.161372	1.0	0.399218	1.0		
p	1	9.689473	0.036774	22.879625	0.044295	0.65	1.0
		2.053692	0.204112	5.021402	0.233797		
		0.558755	0.505244	1.357981	0.507854		
	2	0.154484	1.0	0.349390	1.0		
d	1	0.7	1.0	1.2	1.0		

b) a set of five *d*-functions with $\eta = 0.7$ for C and $\eta = 1.2$ for F,

c) a 5*s* Huzinaga basis [32] for H, contracted to two groups with (4, 1) contraction,

d) a set of three *p*-functions with $\eta = 0.65$ for H.

The exponents of the polarization functions were chosen reasonably, but were not fully optimized. The final basis set is given in Table 1.

For $CHCH_3$ we dropped the polarization functions at the H-atoms of the CH_3-group since we were not interested in special properties of this group. With this limitation the final size of the basis sets for the four radicals was: 73 lobes in 25 groups for CH_2, 113 lobes in 35 groups for CHF, 153 lobes in 45 groups for CF_2, and 128 lobes in 41 groups for $CHCH_3$.

4. SCF-Calculations

According to elementary MO-theory a divalent carbon center in a linear carbene radical R_1CR_2 has an electronic π^2 configuration. Because of the twofold degeneracy of the π-MO this configuration gives rise to three electronic states $^3\Sigma$, $^1\Delta$, and $^1\Sigma$. If the bond angle ϑ at the carbene center deviates from 180° the degeneracy of the π-MO is removed. Generally, the component in the R_1CR_2 plane is called σ, the one orthogonal to this plane is called π. (We shall adopt thi notation though some confusion is possible with the notation σ, π, ... for linea molecules). σ and π corresponds to $3a_1$ and $1b_1$ in CH_2, to $7a'$ and $2a''$ in CHF and $CHCH_3$, and to $6a_1$ and $2b_1$ for CF_2.

According to Walsh's rules [33] for AH_2, HAB, and AB_2 molecules the σ orbital is stabilized with decreasing bond angle ϑ whereas π remains nonbonding. Therefore, we expect the following correlation diagram for carbene radical

linear ($\vartheta = 180°$)			bent ($\vartheta < 180°$)	
$^1\Sigma$	$(\sigma^2 + \pi^2)$	$\longrightarrow$	$^1A_1^*$ $(^1A'^*)$	(π^2)
$^1\Delta$	$\left\{\begin{matrix}\sigma^2 - \pi^2 \\ \sigma\pi\end{matrix}\right\}$	$\longrightarrow$	$^1B_1$ $(^1A'')$	$(\sigma\pi)$
		$\longrightarrow$	$^1A_1$ $(^1A')$	(σ^2)
$^3\Sigma$	$(\sigma\pi)$	$\longrightarrow$	$^3B_1$ $(^3A'')$	$(\sigma\pi)$

A_1 and B_1 correspond to the C_{2v} symmetry of CH_2 and CF_2, A' and A'' to the C_s symmetry of CHF and $CHCH_3$. For 180° the σ-π degeneracy causes the $^3\Sigma$ state to be the ground state (Hund's rule), for $\vartheta < 180°$ the amount of stabilization of the σ orbital decides whether the triplet state with the $\sigma\pi$ configuration remains the ground state or the lowest singlet state with σ^2 becomes lower in energy.

The first step in the investigation of the relative stabilities of the lowest triplet and singlet states of the four systems are restricted SCF-calculations for different bond angles ϑ and fixed bond distances. All calculations were performed with $r_{CH} = 1.11$ Å and $r_{CF} = 1.30$ Å which are close to the experimental values [7–10] (see Table 2). For $CHCH_3$ which has not yet been observed spectroscopically the value for r_{CC} and the geometry of the CH_3 group were taken from ethane.

Our SCF-results are given in Table 3 and Fig. 1. All the curves in Fig. 1 are shifted such that the energies are measured relative to the energies of the single

Table 2. Experimental geometries for CH_2, CHF, CF_2 and ethane (C_2H_6)

Molecule	State	Distances	Bond angles	Ref.
CH_2	$\tilde{X}\,^3B_1$ $\tilde{a}\,^1A_1$	$r_{CH} = 1.078$ Å $r_{CH} = 1.11$ Å	136 ± 8^0 102.4^0	[2, 3, 34] [35]
CHF	$\tilde{X}\,^1A'$	$r_{CF} = 1.314$ Å $r_{CH} = 1.121$ Å[a]	101.6^0	[7]
CF_2	$\tilde{X}\,^1A_1$	$r_{CF} = 1.300$ Å	104.9^0	[8–10]
C_2H_6 (ethane)		$r_{CC} = 1.543$ Å $r_{CH} = 1.102$ Å	$\vartheta_{CCH} = 109.3^0$	[36]

[a] Estimated.

Table 3. Angular dependence of the SCF energies of CH_2, CHF, CF_2, and $CHCH_3$ (all energies in atomic units)

Molecule	State	90^0	105^0	120^0	135^0	150^0	165°	180^0
CH_2	$^1A_1$	− 38.87005	− 38.87412	− 38.86680	− 38.85163	− 38.83351	− 38.81867	− 38.81285
	$^3B_1$	− 38.88167	− 38.90335	− 38.91327	− 38.91363	− 38.90720	− 38.89820	− 38.89354
CHF	$^1A'$	−137.73165	−137.74052	−137.72674	−137.69657	−137.65711	−137.62066	−137.60524
	$^3A''$	−137.71048	−137.73720	−137.74586	−137.74003	−137.72285	−137.69883	−137.68223
CF_2	$^1A_1$	−236.60725	−236.63013	−236.61037	−236.56310	−236.49367	−236.40489	−236.34456
	$^3B_1$	−236.51960	−236.56634	−236.57616	−236.56420	−236.53582	−236.49319	−236.42119
$CHCH_3$	$^1A'$	− 77.90048	− 77.90842	− 77.90179	− 77.88542	− 77.86506	− 77.84787	− 77.84092
	$^3A''$	− 77.90349	− 77.92959	− 77.94123	− 77.94176	− 77.93456	− 77.92429	− 77.91885

Bond lengths as given in Table 2.

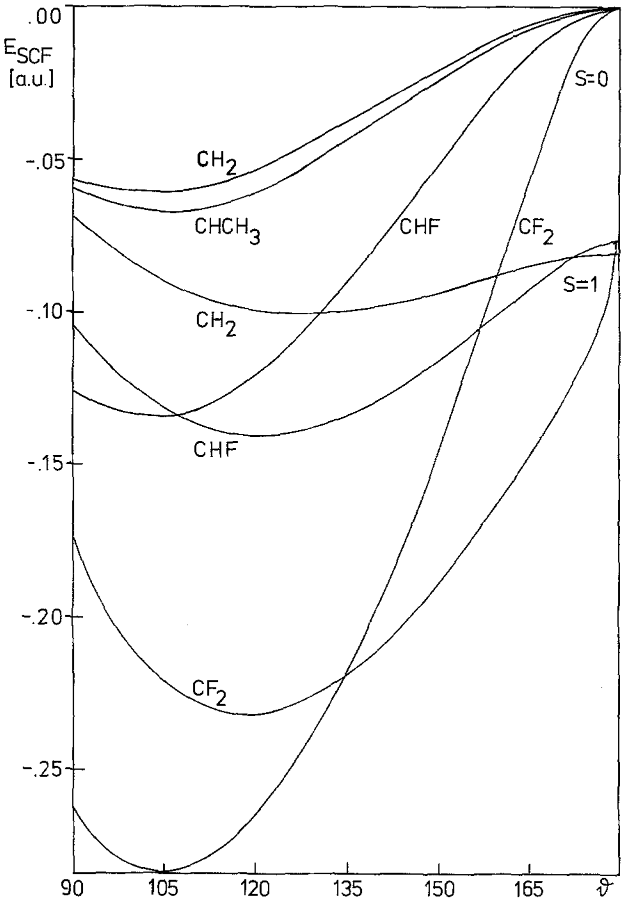

Fig. 1. SCF energies of the lowest singlet ($S=0$) and triplet ($S=1$) states of CH_2, CHF, CF_2, an $CHCH_3$ (all energies relative to E_{SCF} for $S=0$, $\vartheta=180^0$; fixed distances $R_{CH}=2.1a_0 \cdot R_{CF}=2.457a$ $R_{CC}=2.916a_0$)

states at 180°. The curve for the $^3A''$ state of $CHCH_3$ has been omitted since i almost coincides with the $^3B_1$ curve of CH_2. One observes the following characteristic features:

1) Though the SCF-energies of both states of CH_2 are considerably higher (b about 0.015 a.u.) than those obtained in earlier calculations with much mor extended basis sets [5] the triplet-singlet energy separation, the angula dependence of the energies, and the equilibrium bond angles are nearly th same as in [5]. We expect our less extended basis set to give reliable result also for the substituted methylenes.
2) For 180° the triplet states are lower than the singlets by about 0.08 a.u ≈ 50 kcal/mole for all four systems (0.0807 a.u. for CH_2, 0.0770 a.u. for CHF 0.0766 a.u. for CF_2, 0.0779 a.u. for $CHCH_3$). This can be explained by th fact that in the linear case the energy difference of the configurations $\ldots\sigma$

and $\ldots\sigma\pi$ (triplet) is given by the combination

$$(\pi\pi|\sigma\sigma)-(\pi\sigma|\sigma\pi)-(\sigma\sigma|\sigma\sigma)$$

of Coulomb and exchange integrals only involving the highest σ and π orbitals, provided that the σ orbital is identical in the two configurations. Since both the σ and the π orbital are localized mainly on the carbon atom the triplet-singlet energy difference in carbenes at 180° is an inherent property of the carbene *C*-atom and not much influenced by substitution.

3) In all four systems the SCF energy of the singlet state is lowered with decreasing ϑ about twice as much as that of the triplet. This is easily explained by means of the Walsh diagrams [33]: The stabilization of the σ-orbital with decreasing ϑ affects the $\ldots\sigma^2$ configuration twice as much as $\ldots\sigma\pi$.
4) Despite of the large stabilization of the singlet states with decreasing ϑ only CF_2 has a singlet ground state. In the SCF-approximation the triplet-singlet energy separations are 0.040 a.u. for CH_2, 0.005 a.u. for CHF, -0.054 a.u. for CF_2, and 0.034 a.u. for $CHCH_3$, respectively. For CHF, the singlet and triplet state have almost the same SCF-energy which has been observed previously by Harrison [11].

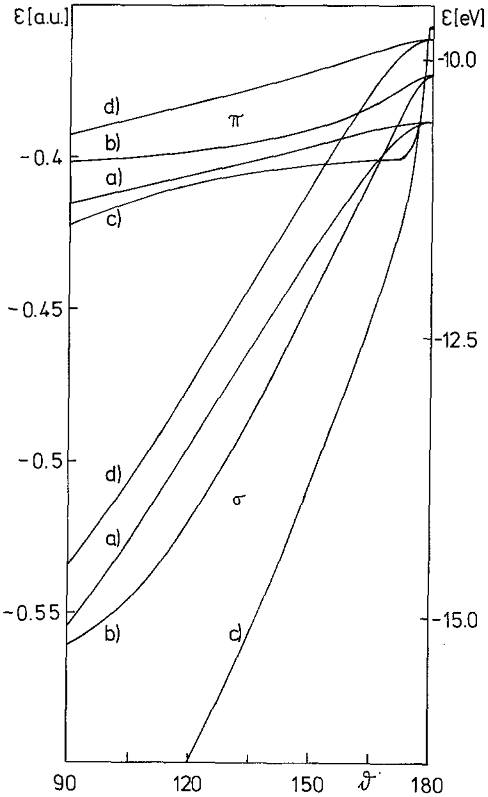

Fig. 2. Orbital energies of the highest occupied σ an πMOs of the triplet states of a) CH_2, b) CHF, c) CF_2, and d) $CHCH_3$ (fixed distances)

The differences in the angular dependence of the SCF-energies of the fou radicals can be explained by means of the following arguments:

1) The substituents (F, CH_3) possess low-lying occupied π-orbitals interactin with the carbon π-orbital. This conjugation leads to a slight delocalizatio of the π-orbitals: The lower one becomes weakly bonding, the upper one – whic is still localized mainly on the carbon atom – becomes weakly antibonding Therefore, the highest occupied carbon orbitals are destabilized with respec to CH_2 (resonance effect, $+R$ [37]).
2) The high electronegativity of the F-atom causes the C–F σ-bond to be polarize towards the F-atom and the C-atom to bear an effective positive charge This stabilizes the highest carbon σ- and π-orbitals (inductive effect, $-I_\sigma$ $+I_\pi$ [37]).
3) The stabilization of the carbon σ-orbital with decreasing ϑ as predicted b Walsh [33] is enhanced very strongly by electronegative substituents (compar the discussion in Ref. [38]).

Figure 2 shows the SCF orbital energies of the highest occupied σ- and π-orbital as calculated for the triplet states. For $CHCH_3$ the resonance effect predominate such that the orbital energies are higher than those of CH_2 for all ϑ. For CH and CF_2 the competition of the three effects leads to a strong stabilization of th σ-orbital, whereas the π-orbital is influenced only slightly. The F-atom is actin as a σ-acceptor and a weak π-donator. Similar diagrams for the $^1A_1$ state of CF have been published by Sachs *et al.* [13].

5. Influence of Electron Correlation

It is well known from quantum chemical calculations on CH_2 [5] that electron correlation is of great importance for the triplet-singlet energy separation. To investigate whether this is true also for substituted methylenes we calculated valence shell correlation energies for CHF, CF_2, and $CHCH_3$ within the IEPA model as scetched in Section 2. For CH_2 we repeated the IEPA calculations of [5] with the smaller basis set used here to estimate the influence of the basis on the numerical values of pair correlation energies. The calculations were performed for $90^0 \leqq \vartheta \leqq 180^0$ and fixed distances as given in Section 4.

To save computation time we calculated pair correlation energies only fo pairs of localized orbitals that both involve the carbene center. This is expected to be a good approximation since a) the correlation within the CH_3 group o among the F lone pairs is almost independent from ϑ and b) interpair correlation energies between carbon valence shell orbitals and the lone pairs on F or th C–H bonds are small and change only slightly with ϑ. Some pilot calculation have shown that both assumptions are quite good; the inclusion of all possibl pairs which is of course very time-consuming changes the final results by abou 5% or less. The sum of the carbon valence shell pair correlation energies will b denoted by E^{CV}_{corr}.

The results of these calculations are given in the Tables 4–7. It must be note that we did not perform the IEPA calculations for the singlet state at $\vartheta = 180°$ Because of the degeneracy of the σ and π-orbitals for 180° the singlet states hav to be described by two-determinant SCF-wavefunctions and the IEPA schem based on one-determinant SCF-wavefunctions yields less satisfactory results

Table 4. Valence shell pair correlation energies of CH_2 ($R = 2.10a_0$ fixed, all energies negative in a.u.)

State		n	90^0	105^0	120^0	135^0	150^0	165^0	180^0
$^1A_1$	E_{SCF}		38.87005	38.87412	38.86680	38.85163	38.83351	38.81867	38.81285
	$\varepsilon(b^2)$	2	0.03046	0.03061	0.03071	0.03070	0.03042	0.02995	
	$\varepsilon(\sigma^2)$	1	0.03542	0.03488	0.03393	0.03247	0.03043	0.02809	
	$\varepsilon(bb')$	1	0.01764	0.01633	0.01566	0.01538	0.01530	0.01534	
	$\varepsilon(b, \sigma)$	2	0.02120	0.02120	0.02153	0.02211	0.02293	0.02414	
	E_{corr}^{CV}		0.15638	0.15483	0.15407	0.15347	0.15243	0.15161	
	$E_{SCF} + E_{corr}^{CV}$		39.02643	39.02895	39.02087	39.00510	38.98594	38.97028	
$^3B_1$	E_{SCF}		38.88167	38.90335	38.91327	38.91363	38.90720	38.89820	38.89354
	$\varepsilon(b^2)$	2	0.02799	0.02763	0.02736	0.02719	0.02711	0.02702	0.02692
	$\varepsilon(bb')$	1	0.01334	0.01185	0.01086	0.01020	0.00972	0.00936	0.00919
	$\varepsilon(b, \sigma)$	2	0.01184	0.01205	0.01264	0.01356	0.01497	0.01694	0.01869
	$\varepsilon(b, \pi)$	2	0.01561	0.01574	0.01602	0.01645	0.01712	0.01803	0.01869
	$^3\varepsilon(\sigma, \pi)$	1	0.00650	0.00664	0.00679	0.00693	0.00703	0.00697	0.00762
	E_{corr}^{CV}		0.13072	0.12933	0.12969	0.13153	0.13515	0.14031	0.14541
	$E_{SCF} + E_{corr}^{CV}$		39.01239	39.03268	39.04296	39.04516	39.04235	39.03851	39.03895

Table 5. Valence shell pair correlation energies of CHF ($R_{CH} = 2.10a_0$, $R_{CF} = 2.457a_0$ fixed, all energies negative, in a.u.)

State		n	90⁰	105⁰	120⁰	135⁰	150⁰	165⁰	180⁰
$^1A'$	E_{SCF}		137.73165	137.74052	137.72674	137.69657	137.65711	137.62066	137.60524
	$\varepsilon(b_1^2)$[a]	1	0.03175	0.03169	0.03193	0.03242	0.03279	0.03176	
	$\varepsilon(b_2^2)$	1	0.02432	0.02452	0.02501	0.02566	0.02638	0.02677	
	$\varepsilon(\sigma^2)$	1	0.03659	0.03630	0.03575	0.03472	0.03273	0.02972	
	$\varepsilon(b_1 b_2)$	1	0.00965	0.00794	0.00767	0.00767	0.00785	0.00813	
	$\varepsilon(b_1 \sigma)$	1	0.02000	0.02017	0.02072	0.02160	0.02293	0.02544	
	$\varepsilon(b_2 \sigma)$	1	0.00860	0.00979	0.01005	0.01041	0.01093	0.01157	
	E_{corr}^{CV}		0.13082	0.13041	0.13113	0.13248	0.13361	0.13339	
	$E_{SCF} + E_{corr}^{CV}$		137.86274	137.87093	137.85787	137.82905	137.79072	137.75405	
$^3A''$	E_{SCF}		137.71048	137.73720	137.74586	137.74003	137.72285	137.69883	137.68223
	$\varepsilon(b_1^2)$	1	0.02671	0.02650	0.02631	0.02626	0.02637	0.02640	0.02568
	$\varepsilon(b_2^2)$	1	0.02468	0.02470	0.02484	0.02515	0.02563	0.02631	0.02683
	$\varepsilon(b_1 b_2)$	1	0.00720	0.00647	0.00607	0.00584	0.00569	0.00560	0.00546
	$\varepsilon(b_1 \sigma)$	1	0.01236	0.01204	0.01225	0.01284	0.01398	0.01660	0.02180
	$\varepsilon(b_1 \pi)$	1	0.01615	0.01614	0.01634	0.01691	0.01782	0.01929	0.02180
	$\varepsilon(b_2 \sigma)$	1	0.00681	0.00680	0.00697	0.00728	0.00779	0.00874	0.01034
	$\varepsilon(b_2 \pi)$	1	0.00847	0.00852	0.00865	0.00891	0.00920	0.00968	0.01034
	$^3\varepsilon(\sigma\pi)$	1	0.00602	0.00608	0.00618	0.00631	0.00646	0.00660	0.00733
	E_{corr}^{CV}		0.10840	0.10725	0.10761	0.10950	0.11294	0.11922	0.12958
	$E_{SCF} + E_{corr}^{CV}$		137.81888	137.84445	137.85347	137.84953	137.83579	137.81805	137.81181

[a] b_1 and b_2 are the C–H and C–F σ-bond orbitals.

Table 6. Valence shell pair correlation energies of CF_2 ($R_{CF} = 2.457 a_0$ fixed, all energies in a.u., negative)

State		n	90⁰	105⁰	120⁰	135⁰	150⁰	165⁰	180⁰
$^1A_1$	E_{SCF}		236.60725	236.63013	236.61037	236.56310	236.49367	236.40489	236.34456
	$\varepsilon(b^2)$	2	0.02464	0.02465	0.02508	0.02588	0.02704	0.02873	
	$\varepsilon(\sigma^2)$	1	0.03782	0.03751	0.03731	0.03732	0.03755	0.03698	
	$\varepsilon(bb')$	1	0.00467	0.00427	0.00411	0.00409	0.00418	0.00441	
	$\varepsilon(b\sigma)$	2	0.00995	0.00994	0.01017	0.01056	0.01110	0.01193	
	E_{corr}^{CV}		0.11167	0.11096	0.11192	0.11429	0.11801	0.12271	
	$E_{SCF} + E_{corr}^{CV}$		236.71892	236.74109	236.72229	236.67739	236.61168	236.52760	
$^3B_1$	E_{SCF}		236.51960	236.56634	236.57616	236.56420	236.53582	236.49319	236.42119
	$\varepsilon(b^2)$	2	0.02520	0.02470	0.02454	0.02468	0.02504	0.02555	0.02822
	$\varepsilon(bb')$	1	0.00404	0.00365	0.00349	0.00344	0.00343	0.00345	0.00337
	$\varepsilon(b\sigma)$	2	0.00611	0.00634	0.00665	0.00704	0.00751	0.00807	0.01338
	$\varepsilon(b\pi)$	2	0.00834	0.00850	0.00872	0.00894	0.00926	0.00946	0.01338
	$^3\varepsilon(\sigma\pi)$	1	0.00493	0.00498	0.00503	0.00509	0.00514	0.00517	0.00699
	E_{corr}^{CV}		0.08872	0.08771	0.08834	0.08985	0.09219	0.09478	0.12032
	$E_{SCF} + E_{corr}^{CV}$		236.60787	236.65405	236.66450	236.65405	236.62801	236.58797	236.54151

Table 7. Valence shell pair correlation energies for $CHCH_3$ (all energies negative, in a.u., geometry see Table 2)

State	$^1A'$	$^3A''$
	105^0	129^0
E_{SCF}	77.90842	77.94267
$\varepsilon(b_1^2)^a$	0.03085	0.02718
$\varepsilon(b_2^2)$	0.02610	0.02389
$\varepsilon(b_1 b_2)$	0.01515	0.00997
$\varepsilon(b_1 \sigma)$	0.02106	0.01298
$\varepsilon(b_2 \sigma)$	0.01957	0.01194
$\varepsilon(b_1 \pi)$		0.01609
$\varepsilon(b_2 \pi)$		0.01475
$\varepsilon(\sigma^2)$	0.03492	
$^3\varepsilon(\sigma\pi)$		0.00677
E_{corr}^{CV}	0.14765	0.12357
$E_{SCF} + E_{corr}^{CV}$	78.05607	78.06624

[a] b_1 and b_2 are the C–H and C–C σ-bond orbitals.

In the case of $CHCH_3$ we performed the IEPA calculations only for the SCF equilibrium bond angles (105° and 129°, respectively) since the resultant curves are very similar to those of CH_2. (To avoid too many lower indices we use the notation ε_{ij} and $\varepsilon(i,j)$ synonymously. Furthermore, for $i \neq j$, ε_{ij} denotes the sum of singlet and triplet interpair contributions).

Concerning the discussion of the individual pair correlation energies ε_{ij}, the angular dependence of E_{corr}^{CV}, and the difference in the valence shell correlation energies between the singlet and triplet states in CH_2 we refer to [5]. Here we are mainly interested in the influence of the substitution on the ε_{ij}. From the Tables 4–7 one can conclude:

1) Pair correlation energies of equivalent localized pairs in different systems have remarkably similar values. Up to deviations of about 0.001 a.u. we find in all systems in which the corresponding ε_{ij} occur the following values:

	Singlet states	Triplet states	
$\varepsilon(b_{CH}^2)$	−0.031 a.u.	−0.027 a.u.	almost independent of ϑ
$\varepsilon(b_{CF}^2)$	−0.025 a.u.	−0.025 a.u.	
$^3\varepsilon(\sigma, \pi)$		−0.006 a.u.	at $\vartheta = 120°$
$\varepsilon(b_{CH}, \sigma)$	−0.021 a.u.	−0.012 a.u.	
$\varepsilon(b_{CH}, \pi)$		−0.016 a.u.	
$\varepsilon(b_{CF}, \sigma)$	−0.010 a.u.	−0.007 a.u.	
$\varepsilon(b_{CF}, \pi)$		−0.009 a.u.	

2) The significant difference between $\varepsilon(b_{CH}^2)$ and $\varepsilon(b_{CF}^2)$ is explained by the fact that the C–F bonds are very strongly polarized towards the F-atom such that C–F σ-bond is almost more similar to a lone pair on F than to the non-polar C–H bond. (The intrapair correlation energy of a F lone pair in this basis is about 0.019 a.u.) The same fact is responsible for the small value of $\varepsilon(b_{CF}, b'_{CF})$

as compared to $\varepsilon(b_{CH}, b_{CF})$ or $\varepsilon(b_{CH}, b'_{CH})$, and for the difference between $\varepsilon(b_{CH}, \sigma)$, $\varepsilon(b_{CH}, \pi)$ and $\varepsilon(b_{CF}, \sigma)$, $\varepsilon(b_{CF}, \pi)$. The differential overlap between the two localized orbitals i, j involved in $\varepsilon(i, j)$ is decreased by the polarity of the C–F-bond.

The difference in $\varepsilon(b_{CH}^2)$ between the singlet and triplet states in due to the availability of the π-orbitals for excitation [26] in the singlet state. This is of minor importance for $\varepsilon(b_{CF}^2)$ where the π-orbital is localized on the C-atom, the C–F bond orbital however more on the F-atom.

3) The decrease of $|E_{corr}^{CV}|$ in the order CH_2, $CHCH_3$, CHF, CF_2 both for the singlet and triplet states is a consequence of this decrease of the individual ε_{ij} involving CF bonds. The difference of the valence shell correlation energies between singlet and triplet states at their equilibrium bond angles, however, has almost the same value for all four systems, namely -0.0233 a.u. (CH_2), -0.0241 a.u. ($CHCH_3$), -0.0228 a.u. (CHF), and -0.0226 a.u. (CF_2). That is, electron correlation stabilizes the singlet states of all four radicals by about 14 kcal/mole with respect to the triplet, this stabilization is independent of substitution.
4) The angular dependence of E_{corr}^{CV} is almost the same for all systems, except for angles close to 180°.
5) Compared to our previous calculation on CH_2 [5] with a more extended basis set the present values for the ε_{ij} of CH_2 are by about 10% smaller (in absolute value). An analogous behaviour can be expected for the substituted methylenes, too, but it must be noted that the influence of higher angular polarization functions (f-type) is much larger for F than for C.

We can conclude by stating that the influence of electron correlation on the relative stability of the singlet and triplet states and on the angular dependence of the total energies has the same absolute magnitude for all four radicals, and probably for all carbenes. But the relative importance of correlation is very different since the SCF-energies show quite a different behaviour: For CH_2 the triplet state remains the ground state even after the inclusion of correlation, but the triplet-singlet energy separation is decreased from 25 to 10 kcal/mole, and the equilibrium bond angle of the triplet state is increased considerably (compare Table 8). The same holds for $CHCH_3$. In CHF, however, correlation causes the

Table 8. Equilibrium bond angles ϑ_e and singlet-triplet energy separations of CH_2, $CHCH_3$, CHF, and CF_2

		CH_2	$CHCH_3$	CHF	CF_2
Singlet states ϑ_e	SCF	102.9	104.8	103.4	104.7
	IEPA	101.1		103.4	104.7
	exp.	102.4 [35]		101.6 [7]	104.9 [8–10]
Triplet states ϑ_e	SCF	128.0	128.1	120.9	118.1
	IEPA	134.1		122.4	118.8
	exp.	136±8 [2, 3, 34]			
E(triplet)–E(singlet) [kcal/mole]	SCF	− 25	− 21	− 3	34
	IEPA	− 10	− 6	11	47
	exp.	− 8 [4]			

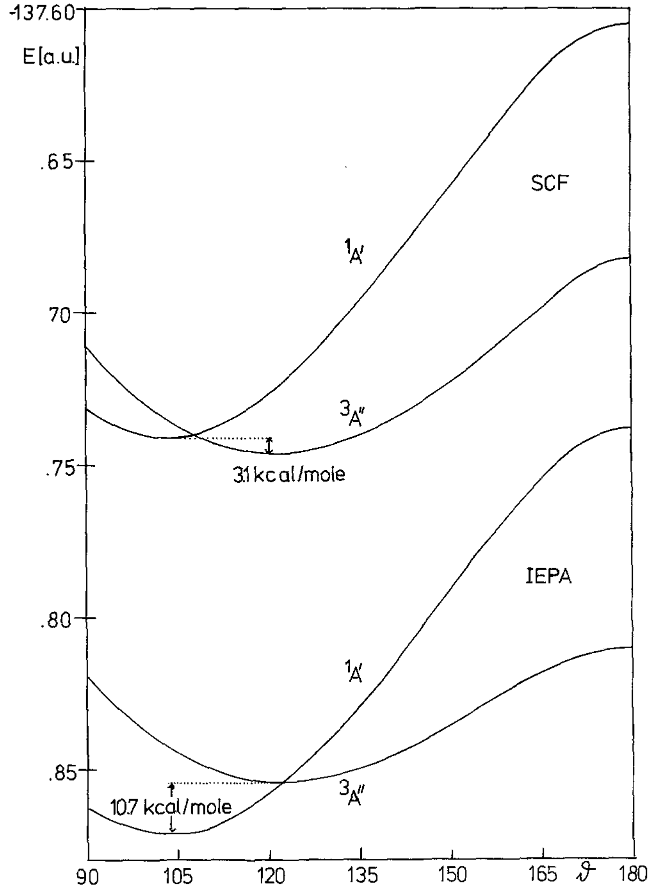

Fig. 3. Angular dependence of the SCF and IEPA energies of the two lowest states of CHF ($R_{CH} = 2.1\,a_0$ and $R_{CF} = 2.457\,a_0$ fixed)

singlet to be the ground state, the equilibrium bond angles are hardly influenced since the SCF-energies show a much stronger angular dependence than E_{corr}^{CV}. For CF_2 the singlet remains the ground state, the equilibrium bond angles are almost not influenced by correlation.

The potential energy curves of the singlet and triplet state of CHF are given in Fig. 3. For CH_2 we refer to the more accurate calculation [5]. For CF_2 the shape of the curves without and with correlation is so similar that we only give the SCF curves in Fig. 1.

6. First Ionization Potentials and Bond Energies

Tables 9 and 10 contain the results of our calculations of first ionization potentials and bond energies of carbenes. Since electron correlation is of similar importance for these properties as for excitation energies we have applied both the SCF and the IEPA approximation.

Table 9. Ionization potentials of carbenes (in eV)

	CH_2	CHF[a]	CF_2	$CHCH_3$
Neutral molecule[b] ion[b]	$^3B_1(135^0)$ $^2A_1(135^0)$	$^1A'(103.4^0)$ $^2A'(122.4^0)$	$^1A_1(105^0)$ $^2A_1(120^0)$	$^3A''(129^0)$ $^2A'(129^0)$
Koopmans theorem	10.93	10.82	12.80	10.34
SCF	9.58	9.39	10.98	8.55
IEPA	10.27	10.40	11.94	9.19
exp. [6]	10.40		12.1 13.3	

[a] The Koopmans' and SCF values for CHF are taken for $^3A''$ at 120^0.

[b] Fixed distances (see Table 2).

Table 10. Bond energies (D_e) of CH_2, CHF, CF_2(eV)

Bond	SCF	IEPA(C)[a]	IEPA[b]	exp.[c]
C–H	2.37	3.46		3.47 [42]
HC–H	4.16	4.50		4.2 [6] 5.45 [43]
H–C–H	6.53	7.96		
C–F	3.43	3.87	5.07	5.5±0.2 [42] 4.9 [43]
HC–F	3.55	3.86	5.20	
H–CF	2.50	3.45	3.59	
H–C–F	5.93	7.32	8.66	
FC–F	3.60	4.02	5.50	≦5.2 [6] 5.2±0.4 [43]
F–C–F	7.03	7.89	10.57	

[a] Only carbon valence shell taken into account.

[b] Total valence shell correlation (estimated).

[c] D_0 values; to compare with the calculated D_e values one has to enlarge D_0 by the corresponding zero point energies.

In all calculations of this section we took the bond distances of Table 2. The equilibrium bond angles for the neutral radicals are those of Table 8; the positive ions have almost the same bond angles as the triplet states since the ions have an electronic $\ldots\sigma$ configuration with the σ-orbital singly occupied as in the triplet states.

As it is observed frequently for first row atoms and molecules Koopmans' and SCF values of the first ionization potentials are in error by up to 1–2 eV, the Koopmans' values being slightly better than the SCF values (see Table 9). The errors of our IEPA results are expected to be an order of magnitude smaller, namely 0.1–0.2 eV [22]. Within this error limit the agreement with the experimental results is satisfactory; it has to be noted that the experimental figures suffer from various error sources (see [6]). In the case of CF_2 our calculations favour the lower experimental value of 12.1 eV.

In the ionization process only the valence shell of the carbene carbon center is involved, not the F-atoms or the CH_3 group. Therefore, it is sufficient to take into account the difference between the carbon valence shell correlation energies of the neutral radicals and the ions (in the same way as for the angular dependence of the total energies of the lowest triplet and singlet states, see Section 5). The influence of the remaining pair correlation energies can be neglected. This is not possible, however, for the calculation of bond energies of fluorated carbenes (Table 10). During the formation of a C–F bond the change in the correlation energy of the F-atom itself and the interatomic correlation contributions are of the same or even greater importance than that of the carbon valence shell. We therefore have to consider the total valence shell correlation energy of the whole system. To save computer time this quantity was estimated in the following way: a) IEPA calculation of the carbon valence shell correlation energy, b) IEPA calculation of the valence shell correlation energies of F and CF, c) transfer of equivalent pair correlation energies from CF to CHF and CF_2 and estimate of the remaining ε_{ij} for pairs localized far away from each other (e.g. C–H σ-bonds and F lone pairs). The comparison of the ε_{ij} of equivalent localized orbitals in Section 5 and other experience show this to be an acceptable procedure.

The SCF and valence shell correlation energies of the individual subunits calculated with the present basis set are

	E_{SCF}	E^V_{corr}	
$H(^2S)$	$-$ 0.49981 a.u.	0.0	
$C(^3P)$	$-$ 37.67395 a.u.	-0.07924 a.u.	
$F(^2P)$	$-$ 99.34896 a.u.	-0.17372 a.u.	
$CH(^2\Pi)$	$-$ 38.26096 a.u.	-0.11918 a.u.	($r_{CH} = 2.1\,a_0$)
$CF(^2\Pi)$	-137.14880 a.u.	-0.31340 a.u.	($r_{CF} = 2.457\,a_0$)

Our values of E^V_{corr} of the constituent atoms are about 20–30% smaller (in absolute value) than the "experimental" valence shell correlation energies [39].

Table 10 shows that the SCF values of bond energies are in error by 1–2 eV. In CHF and CF_2 the carbon valence shell correlation can only partly account for this difference. Our – more semiempirical – estimate of the total valence shell correlation energy, however, yields rather satisfactory results with an error in the order of 0.1–0.3 eV. This supports the general experience that IEPA results for bond energies, excitation energies etc. are an order of magnitude more reliable than SCF results.

We have to mention that the additivity errors of the IEPA scheme increase with the number of electrons; the cancellation between these errors and the deficiencies of the basis is better in small molecules than in atoms. Due to this effect IEPA correlation energies of molecules often are "more accurate" than those of the constituent atoms. In our calculations we account for about 80–90% of molecular valence shell correlation energies, but only for 70–80% for the atoms. In CH for instance, our value of -0.03994 a.u. for the change in correlation energy between CH and C + H is only 10% smaller than the "experimental" value [40, 41] of -0.043 a.u.

7. Some Properties of $CHCH_3$

In the present paper we have calculated the energy difference between the lowest triplet and singlet states of $CHCH_3$.

Further calculations on the hypersurfaces of the two states are in progress, in particular to investigate the rearrangement of $CHCH_3$ to ethylene. Here we report preliminarily on some properties of $CHCH_3$ apart from those already mentioned in the Tables 8–10. (The C–C distance of 2.916 a_0 was taken though the MINDO/2 investigations predict an appreciably shorter distance which would change the results slightly.)

The SCF energies of both the singlet and triplet states of $CHCH_3$ are much higher than that of the ethylene ground state in its equilibrium geometry. With the present basis we get for ethylene $E_{SCF} = -78.01930$ a.u. which is 0.11088 a.u. = 69.6 kcal/mole below the $CHCH_3$ singlet and still 0.07663 a.u. = 48.1 kcal/mole below the $CHCH_3$ triplet. (Since our basis set for $CHCH_3$ contains *p*-functions only for one H-atom we have to take for ethylene the weighted average between the SCF-energies of −78.01596 a.u. without and −78.02931 a.u. with *p*-functions at all H-atoms.)

The valence shell correlation energy is estimated [44] to be about 0.02 to 0.03 a.u. larger in ethylene than in singlet $CHCH_3$ such that totally C_2H_4 is about 85 kcal/mole below singlet $CHCH_3$ and 80 kcal/mole below triplet $CHCH_3$. The rotation barrier of $CHCH_3$ with respect to rotation through the C–C bond is quite different for the two states: 0.44 kcal/mole in the triplet state (at 129°) and 2.19 kcal/mole in the singlet (at 105°), both in SCF-approximation. This difference is due to a) the larger bond angle in triplet $CHCH_3$ which reduces the rotation barrier and b) to the fact that in the triplet state the –CH group is more isotropic than in the singlet. Though the present basis set is too poor to allow for very accurate predictions this behaviour fits nicely into the compilation of experimental and calculated rotation barriers of organic molecules published recently by Radom and Pople [45]. The much smaller values for the rotation barriers in $CHCH_3$ found by Bodor and Dewar [16] and Hoffmann *et al.* [15] may be due to the deficiencies of the MINDO/2 and extended Hückel methods.

8. Conclusions

The main results of the present investigation with regard to the questions of the introduction may be stated as follows:

a) The behaviour of the SCF-energies of carbenes (angular dependence, relative stability of singlet and triplet states) is influenced very strongly by the substituents. This can be explained in terms of overlap and substituent effects (inductive, resonance effect) as discussed in textbooks on valence theory [37].

b) Electron correlation has a large influence on the value of the triplet-singlet energy separation. In the case of CHF it even leads to a singlet ground state whereas the SCF-approximation gives a triplet one. The angular dependence of the correlation energies, however, is not very important and does not change the shape of the potential curves very much.

c) The difference in correlation energy for the singlet and triplet state is nearly the same in all carbenes. This is a consequence of the fact that this difference depends on the highest occupied σ and π-MO's which are mainly localized on the carbene C-atom. In the same way the triplet-singlet splitting at 180° in SCF approximation is a property of the carbon atom and not much influenced by substitution.

d) We expect that similar arguments are also valid for carbenes others than the four considered here; substitution of the H-atoms of methylene by electronegative substituents stabilizes the singlet state with respect to the triplet.

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