Lawrence Berkeley National Laboratory

Recent Work

**Title**
STRUCTURE and ENERGETICS OF SIMPLE CARBENES. CH2, CHF, CHC, CHBr, CF, CCA

**Permalink**
https://escholarship.org/uc/item/52d9n4wt

**Author**
Bauschlicher Jr., C.W.

**Publication Date**
1976-03-01
Submitted to Journal of the American Chemical Society

RECEIVED

LAWRENCE BERKELEY LABORATORY

JUL 19 1976

LIBRARY AND DOCUMENTS SECTION

STRUCTURE AND ENERGETICS OF SIMPLE CARBENES.
CH₂, CHF, CHCl, CHBr, CF₂, CCl₂

Charles W. Bauschlicher Jr., Henry F. Schaefer III, and Paul S. Bagus

March 1976

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Structure and Energetics of Simple Carbenes.

\[ \text{CH}_2, \text{CHF}, \text{CHCl}, \text{CHBr}, \text{CF}_2, \text{CCl}_2 \]

Charles W. Bauschlicher Jr. and Henry F. Schaefer III

Department of Chemistry and Lawrence Berkeley Laboratory*

University of California

Berkeley, California 94720

and

Paul S. Bagus

IBM Research Laboratory

Monterey and Cottle Roads

San Jose, California 95193

* This work was done with support from the U.S. Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of the Lawrence Berkeley Laboratory nor of the U.S. Energy Research and Development Administration.
Abstract

Very few carbene singlet-triplet separations are known with any degree of reliability from experiment (CH₂ is a distinct exception) and in many cases there are not even estimates available. For this reason a consistent level of ab initio electronic structure theory has been applied to the CH₂, CHF, CHCl, CHBr, CF₂, and CCl₂ molecules. Double zeta basis sets, augmented by a set of optimized d functions on the central carbon atom, have been used in conjunction with one- and two-configuration self-consistent-field wave functions. Where experimental data is available, the theoretical equilibrium geometries agree well. A semi-empirical procedure for estimating the singlet-triplet separations predicts 19.5 kcal (the experimental value for CH₂), -2 (CHF), + 6 (CHCl), + 8 (CHBr), - 36 (CF₂), and - 6 (CCl₂), where negative separations imply a singlet ground state. These separations are readily correlated with the carbon atom Mulliken populations.
Introduction

The flourishing of carbene chemistry\textsuperscript{1,2} in recent years has been one of the most interesting experimental developments in organic chemistry. Concurrently there has been a considerable amount of theoretical research\textsuperscript{3-22} concerning the simplest carbene, the methylene free radical CH\textsubscript{2}. These theoretical studies have handsomely complimented the experimental literature in providing reliable information concerning the geometries, potential energy surfaces, and chemical reactions of the ground and excited electronic states of CH\textsubscript{2}. Despite the importance of these prototype studies, it is perhaps well to keep in mind that in synthetic and mechanistic experimental studies, substituted methylenes are often more convenient to use than the elementary CH\textsubscript{2} itself. As just one example, we point out that much of Skell's pioneering work\textsuperscript{23} on the stereospecificity of carbene reactions was carried out using dibromocarbene, CBr\textsubscript{2}. However, as was the case until very recently for CH\textsubscript{2}, there are no precise experimental measurements of the singlet-triplet separation in CBr\textsubscript{2} and other halocarbenes. Since the singlet-triplet separation is essential to any reasonably complete understanding of the chemistry of a particular carbene, an obvious goal of theoretical studies is the prediction of carbene energetics. In this vein we report in the present paper \textit{ab initio} predictions of the structures and energetics of a number of halocarbenes CHX and CX\textsubscript{2}.

The inability of experimentalists to concur on the CH\textsubscript{2} $^3\text{B}_1-^1\text{A}_1$ separation $\Delta E$ continues even to the present. For several years there have been two conflicting sets of $\Delta E$ values, the high value\textsuperscript{24-28} (8-9 kcal/mole) and the low value\textsuperscript{29-31} (0-3 kcal/mole). Recent theoretical predictions\textsuperscript{18,32-35}
have invariably supported the high value, but the very recent laser photodetachment studies of Lineberger and co-workers\textsuperscript{36} yield an even higher separation, $19.5 \pm 0.7$ kcal/mole. Furthermore Lineberger's experiment represents the only "direct" measurement to date, i.e., it does not depend in any way upon assumed thermochemical data. Hence one is forced to conclude that the most reliable value of $\Delta E$ is the one\textsuperscript{36} that differs radically from all previous experimental values.\textsuperscript{24-31}

Among the molecules studied in the present research, CHF and CF$_2$ have been the subject of two previous theoretical studies.\textsuperscript{15,37} Of these, the more recent results of Staemmler are the more reliable. Using a double zeta plus polarization basis set,\textsuperscript{15} Staemmler carried out SCF and pair correlation studies of CHF and CF$_2$. With fixed bond distances $r(\text{CH}) = 1.11$ Å and $r(\text{CF}) = 1.30$, he predicted the bond angles of the lowest singlet and triplet states, and the singlet-triplet separations, $-11$ kcal (CHF) and $-47$ kcal (CF$_2$), with the singlet state lying lower in both cases. Incidentally, while these $\Delta E$ values are not known from experiment, the ground state singlet structures of CHF\textsuperscript{38} $[r(\text{CF}) = 1.314$ Å, $r(\text{CH}) = 1.121$ Å, $\theta = 101.6^\circ]$ and CF$_2$\textsuperscript{39-41} $[r(\text{CF}) = 1.300$ Å, $\theta = 104.9^\circ]$ are known. The structure of the lowest singlet state of CHCl is also known from experiment,\textsuperscript{42} $r(\text{CCl}) = 1.689$ Å, $r(\text{CH}) = 1.12$ Å, $\theta = 103.4^\circ$. Although electronic spectra have been recorded for all three of the above molecules, apparently no triplet state transitions have been observed, resulting in the lack of experimental singlet-triplet separations.

Although the CCl$_2$ and CBr$_2$ species have been studied extensively by matrix isolation spectroscopy,\textsuperscript{43-45} their molecular structures are not known. Although again the $\Delta E$ values are not known, a singlet ground state
is presumed based on the failure to observe nonstereospecificity in the addition reactions to olefins.\textsuperscript{46} Finally although the CHBr molecule has not been observed by electronic or vibrational spectroscopy, it is readily generated from the corresponding diazo compound and its reactions have been investigated in some detail.\textsuperscript{2,47}

**Theoretical Approach**

The present research builds upon previous theoretical work\textsuperscript{22,32-35} on CH\textsubscript{2} which suggests that quite reliable structures and reasonable singlet-triplet separations may be obtained from rather simple wave functions. For CH\textsubscript{2} the triplet state is approximated by a single determinant self-consistent-field (SCF) wave function

\[
\begin{align*}
1a_1^2 & 2a_1^2 & 1b_2^2 & 3a_1 & lb_1 & 3B_1
\end{align*}
\tag{1}
\]

while a two-configuration SCF description of the singlet state

\[
\begin{align*}
c_1 & 1a_1^2 & 2a_1^2 & 1b_2^2 & 3a_1^2 \\
c_2 & 1a_1^2 & 2a_1^2 & 1b_2^2 & lb_1
\end{align*}
\tag{2}
\]

is appropriate. The key features of this approach is to treat the 3a\textsubscript{1} and lb\textsubscript{1} orbitals on an equal footing for both electronic states. Near the Hartree-Fock limit (saturated basis set), this level of theory predicts\textsuperscript{22} 10.9 kcal/mole for \(\Delta E\). At the time this research was carried out, the latter value \((\Delta E = 10.9\) kcal\) appeared to represent a reasonable compromise between the best available configuration interaction (CI) result\textsuperscript{33} (14.1 kcal)
and the most reliable experimental value \(^{24-28}\) (8-9 kcal). In any case, the use of a two-configuration singlet and one-configuration triplet description does provide a consistent picture of the singlet-triplet separation. As we point out later, a semi-empirical correlation can be readily made to allow agreement with the very recent Lineberger experiments. For all carbenes considered in the present paper, the triplet (one configuration) and singlet (two configurations) states were

(continued on page 4)
treated in an analogous fashion. Of course CHF, CHCl, and CHBr have only a plane of symmetry and hence the corresponding term symbols are \(3\text{A}''\) and \(1\text{A}'\). If one assumes that Lineberger's experimental value for the CH\(_2\) singlet-triplet separation is correct, then it is clear that our two-configuration description of the singlet state overcompensates for the fact that the \(1\text{A}_1\) state has more correlation energy than the \(3\text{B}_1\) state. In fact Lineberger's result is somewhat closer to the 24.8 kcal \(\Delta E\) obtained when a one-configuration Hartree-Fock description of the \(1\text{A}_1\) state is adopted. To be even more precise the Lineberger results lies 60\% of the way from the two-configuration separation to the one-configuration value. We should certainly keep this in mind when attempting to estimate singlet-triplet separations where no experimental data is available.

The basis sets used here begin with Dunning's contracted gaussian double zeta sets. For hydrogen we use his (4s/2s) contraction\(^48\) of Huzinaga's primitive set\(^49\) (with a scale factor of 1.2); for carbon and fluorine the (9s 5p/4s 2p) contraction of Huzinaga's primitive set; for chlorine the (12s 9p/6s 4p) contraction\(^50\) of Veillard's primitive set;\(^51\) and for bromine Dunning's (14s 11p 5d/8s 6p 2d) contraction of his own primitive set.\(^52\) Since Dunning's bromine basis has never been used or reported in the literature previously, it is given in Table I. With the near Hartree-Fock energies of Clementi and Roetti\(^53\) given in parentheses, the ground state atomic SCF energies obtained with the above double zeta bases are -0.4993 (-0.5), -37.6845 (-37.6886), -99.3933 (-99.4093), -459.4706 (-459.4819), and -2572.3102 (-2572.4408) hartrees. Thus in each case we begin with a reasonably accurate SCF description of the separated atoms.
From this point the general procedure adopted was to add a set of six d-like functions ($XXe^{-\alpha^2}$, $YYe^{-\alpha^2}$, $ZZe^{-\alpha^2}$, $XXe^{-\alpha^2}$, $XZe^{-\alpha^2}$, and $YZe^{-\alpha^2}$) centered on the carbon atom. We discovered that for CH$_2$ the optimum orbital exponent $\alpha$ was 0.74 for the $^3B_1$ state, but quite different, 0.51, for the $^1A_1$ state. Therefore, for the other carbenes the singlet and triplet geometries were first optimized using these polarization function exponents (0.74 and 0.51). Then, at the predicted geometries the singlet and triplet $\alpha$ values were optimized for that particular carbene (e.g., CHCl). 

For reasons of economy, this procedure was simplified for the CHBr molecule. There the singlet and triplet geometry optimizations were carried out only at the double zeta level. Final computations were performed at these two geometries using carbon d functions with orbital exponent $\alpha = 0.4$.

A number of refinements to the above scheme were tested for CH$_2$ and CF$_2$ and are summarized in Table II. There we see that for CH$_2$ the addition of a set of p functions ($\alpha = 1.0$) to each hydrogen changes the singlet-triplet separation from 12.3 and 12.8 kcal/mole. For both the singlet and triplet state, geometry changes are minor (bond distances change by less than 0.005 Å and bond angles by less than 1°). For difluorocarbene, the addition of a set of d functions ($\alpha = 1.0$) on each F atom changes $\Delta E$ from -45.3 kcal to -44.5 kcal. Here however the addition of d functions changes the bond distance more substantially. For example the calculations including polarization functions only on carbon give $r_e$(CF) = 2.477 and $\theta_e = 117.8^\circ$ for the $^3B_1$ state. Upon addition of polarization functions to the fluorine atoms this SCF prediction changes to $r_e$(CF) = 2.463 bohrs.
and $\theta_e = 118.2^\circ$ and the total energy is lowered from $-236.6496$ hartrees to $-236.6733$ hartrees. Thus it is probably true that the absence of polarization functions on the terminal atoms becomes a more serious problem as one goes from CH$_2$ to CF$_2$ to CC$_2$ to CBr$_2$. Note also that for CF$_2$ the carbon d exponents were reoptimized after adding to fluorine polarization functions, yielding $\alpha = 0.69$ for the $^3B_1$ state and $\alpha = 0.67$ for the $^1A_1$ state.

Results and Discussion

The predicted singlet-triplet separations and equilibrium geometries are given in Tables II and III. We turn first to an evaluation of the molecular structures, since there is a fair amount of experimental data available for these. For all four experimentally known bond angles (the singlet state of CH$_2$, CHF, CHCl$_2$, and CF$_2$) the theoretical predictions are in close agreement, the differences being $0.1^\circ$, $0.6^\circ$, $1.4^\circ$, and $0.6^\circ$. Although the $^3B_1$ CH$_2$ bond angle is not known precisely from experiment, the best existing theoretical calculations $^{33,35}$ suggest a result near $134^\circ$. The apparently larger error for $^3B_1$ CH$_2$ is probably due to the relatively flat nature of that potential surface near the equilibrium geometry. For CH$_2$, CHF, and CHCl$_2$, the predicted CH bond distances agree well with experiment, the errors being $0.004$ Å, $0.010$ Å, and $0.019$ Å. Again there is a tendency for the discrepancies to become large for the larger molecules. This tendency is most apparent for the CCl bond distance in $^1A_1'$ CHCl$_2$, where
the \textit{ab initio} value 1.76 Å is a full 0.07 Å longer than experiment. We suspect that the use of polarization functions (i.e., a single set of d functions) on chlorine would remove most of this error. By comparison, for the ClF$_2$ molecule, Ungemach and Schaefer\cite{54} find that the addition of d functions on Cl decreases the predicted bond distances by 0.10 Å. Finally, we note that the C-F distances in singlet CHF and CF$_2$ are predicted in very good agreement with experiment.

For the reasons mentioned in the previous paragraph, we expect the CCl bond distance to be 0.08 Å larger than the exact (unknown) bond distance. Similarly the predicted CBr separation in CHBr is expected to be somewhat larger than would be the case if a true Hartree-Fock (complete basis set) calculation were carried out.

In addition for CHBr the lack of a geometry optimization with carbon d functions also will have some effect. Comparisons for CHCl suggest that the CH distance and bond angle are relatively independent of the carbon polarization functions. However, the CCl distances in singlet and triplet CHCl were reduced by 0.08 and 0.04 Å by geometry optimization with carbon d functions. The other predicted carbene structural parameters should be quite reliable.

Inspection of Table III shows several fairly clear trends. Perhaps the most obvious is the well known fact that the singlet bond angles are much less than their triplet counterparts. Less obvious but consistent with the above is the observation that with one exception (CF$_2$) the triplet carbene bond distances are less than those of the corresponding singlet states. The magnitudes of the triplet bond angles span a fairly narrow range, from $117.8^\circ$ (CF$_2$) to $128.8^\circ$ (CH$_2$) and the same is true of the singlet
bond angles which vary from 102.0° (CHCl) to 109.4° (CCl₂). On the whole, then, one arrives at a very consistent picture of the structures of these molecules.

As mentioned earlier, the theoretical singlet-triplet separations, given in Table II, must be weighed with respect to the latest experimental value for CH₂, namely 19.5 ± 0.7 kcal. In fact our value of 23.0 kcal in the absence of polarization functions is closer to Lineberger's result than is the 12.3 kcal value obtained with d functions on carbon. If we note that the former theoretical value for CH₂ places the singlet state 3.5 kcal too high and the latter 7.2 kcal too low, we can have some idea of the uncertainty of the present predictions. To tackle the easy cases first, it appears clear that CF₂ and CCl₂ have 1A₁ ground states. For CF₂ the separation is quite large, with the singlet lying perhaps ~36 kcal lower. CCl₂ is more treacherous due to the potential importance of Cl polarization functions but a plausible suggestion is ~-6 kcal. For CHF, CHCl, and CHBr definitive predictions of the ground states are not possible, but semi-empirical estimates along the lines suggested above are -2 kcal (singlet lower) for CHF, 6 kcal (triplet lower) for CHCl, and 8 kcal (again, triplet lower) for CHBr.

We do not ascribe a high degree of reliability to the above predictions. However it is certainly a good omen that in the six cases considered the differences between the singlet-triplet separation obtained without polarization functions and that with d functions are 10.7, 10.9, 10.8, 10.1, 13.4, and 10.6 kcal. Furthermore it would seem better to have a rough theoretical estimate of these separations than no separation at all.
Finally, we ask the question, is it possible to understand this rather broad range of singlet-triplet separations (+19.5 to -36 kcal) in terms of a simple picture of the electronic structures. In fact the original motivation for our research was the hope that it would be possible to correlate the electron density near the carbon atom with the predicted singlet-triplet separations. With this in mind, we give in Table IV the calculated Mulliken populations for the molecules studied. Such Mulliken populations should only be used for rough qualitative comparisons, since they tend to be basis dependent. For the latter reason the populations given in Table IV are those obtained with straight double zeta basis sets, no polarization functions included. The inclusion of polarization functions on carbon tends to detract from the balanced character that is mandatory for a basis set to yield chemically reasonably Mulliken populations.

The singlet-triplet separation $\Delta E$ in carbenes is determined by the interplay of the relative stability of the highest occupied (both are occupied in the triplet state SCF wave functions) $a_1$ and $b_1$ orbitals with the pairing energy, an admittedly ill-defined quantity. For CH$_2$ (as in nearly all carbenes) the $3a_1$ orbital has a lower orbital energy, but the pairing energy is sufficient to produce a ground state triplet. Analysis of the $3a_1$ orbital for the $^1A_1$ state shows it to be localized on carbon with a sizeable amount of relatively diffuse 2s character. However, as the more electronegative halogen atoms replace hydrogen, the $3a_1$ orbital takes on a considerable measure of halogen 2p character. The $1b_1$ orbital (of CH$_2$), on the other hand, is relatively independent of substituent effects, to a large degree remaining a carbon 2p$_x$ orbital (x here parallel to the H-H axis). This in turn leads to the conclusion
that as electrons are withdrawn from carbon, the $a_1$ orbital will become more stable (with respect to the $b_1$ orbital) and give way to a ground state singlet.

Table IV indicates the qualitative correctness of the above interpretation. Both chemical intuition and the observed Mulliken populations suggest that fluorine is more electronegative than chlorine, and chlorine more so than bromine. Thus the singlet-triplet separation is greatest for CF$_2$, while CCl$_2$ is also predicted to have a ground state singlet. Although we did not perform comparable studies of CBr$_2$, it seems clear that the $^1A_1$ and $^3B_1$ states will be nearly degenerate, lying within one or two kcal of each other. In light of the greater reactivity$^{14,20,21}$ of singlet carbenes, it is not surprising that CBr$_2$ appears to have the characteristics of a ground state singlet.$^{23}$ The CHX species exhibit the same general trend, although here we are able to explicitly state that while there is a large difference between CHF and CHCl, a much smaller jump (both in terms of $\Delta E$ and Mulliken populations) occurs between CHCl and CHBr.

Finally, we note that all of the above halocarbenes (plus CBr$_2$) have been studied by Hoffman, Zeiss, and Van Dine$^{55}$ using extended Hückel theory. These authors emphasize that their results should be taken qualitatively rather than as precise quantum mechanical predictions. And in fact a number of the trends reported here are seen in this earlier semi-empirical study. For example the increase in triplet band angle from CHF to CHCl to CHBr is clearly apparent in the study of Hoffmann.$^{55}$ A similar relation between the CF$_2$, CCl$_2$ and CBr$_2$ bond angles (both singlet and triplet) is also observed. Furthermore their trends in singlet-triplet separation (e.g., that the CF$_2$ separation magnitude is much greater than that in CCl$_2$) are confirmed
here. Thus we see that semi-empirical methods, when used judiciously, can be of considerable qualitative predictive value.
References


52. T. H. Dunning, unpublished.


Table I. Dunning's contracted gaussian basis set for the bromine atom. The notation used follows reference 48.

<table>
<thead>
<tr>
<th>s-Exponents</th>
<th>Coefficients</th>
<th>p-Exponents</th>
<th>Coefficients</th>
<th>d-Exponents</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>439700.</td>
<td>0.000813</td>
<td>2957.</td>
<td>0.022262</td>
<td>134.8</td>
<td>0.018309</td>
</tr>
<tr>
<td>66030.</td>
<td>0.006285</td>
<td>700.3</td>
<td>0.180188</td>
<td>36.39</td>
<td>0.135002</td>
</tr>
<tr>
<td>15140.</td>
<td>0.031923</td>
<td>224.6</td>
<td>0.862405</td>
<td>12.16</td>
<td>0.426091</td>
</tr>
<tr>
<td>4317.</td>
<td>0.128793</td>
<td>82.59</td>
<td>0.343999</td>
<td>4.341</td>
<td>0.604271</td>
</tr>
<tr>
<td>1414.</td>
<td>0.394591</td>
<td>33.19</td>
<td>0.507099</td>
<td>1.535</td>
<td>1.000000</td>
</tr>
<tr>
<td>523.9</td>
<td>0.541292</td>
<td>14.20</td>
<td>0.258957</td>
<td></td>
<td></td>
</tr>
<tr>
<td>523.9</td>
<td>0.183066</td>
<td>14.20</td>
<td>0.079647</td>
<td></td>
<td></td>
</tr>
<tr>
<td>207.7</td>
<td>0.617646</td>
<td>7.438</td>
<td>0.373442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>86.54</td>
<td>0.253828</td>
<td>3.526</td>
<td>0.604912</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.52</td>
<td>1.000000</td>
<td>1.595</td>
<td>1.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.98</td>
<td>1.000000</td>
<td>0.4918</td>
<td>1.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.412</td>
<td>1.000000</td>
<td>0.1507</td>
<td>1.000000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.862</td>
<td>1.000000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5455</td>
<td>1.000000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1902</td>
<td>1.000000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table II. Singlet-triplet separations for a number of simple carbenes.

The orbital exponents given here are those of the d functions centered on carbon. A negative separation indicates a singlet ground state.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Polarization functions</th>
<th>Orbital Exponents</th>
<th>Separation (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Triplet</td>
<td>Singlet</td>
</tr>
<tr>
<td>CH₂</td>
<td>None</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>optimized d functions on C</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>d functions on C; p functions on H</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td>CHF</td>
<td>None</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>d functions on C</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>optimized d functions on C</td>
<td>0.66</td>
<td>0.61</td>
</tr>
<tr>
<td>CHCl₂</td>
<td>None</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>d functions on C</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>optimized d functions on C</td>
<td>0.49</td>
<td>0.46</td>
</tr>
<tr>
<td>CHBr</td>
<td>None</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>d functions on C</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>CF₂</td>
<td>None</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>d functions on C</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>optimized d functions on C</td>
<td>0.65</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>above plus d functions on F(α = 1.0)</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>same as above with reoptimized d functions on C</td>
<td>0.69</td>
<td>0.67</td>
</tr>
<tr>
<td>CCl₂</td>
<td>None</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>d functions on C</td>
<td>0.74</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>optimized d functions on C</td>
<td>0.45</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Table III. Summary of structural and energetic results for some simple carbenes. Bond distances are reported in Å, bond angles in degrees, and total energies in hartrees. The results in this table were obtained using double zeta basis sets, augmented by a set of d functions on the carbon atom. Experimental values are given in parentheses.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Triplet Carbene</th>
<th>Singlet Carbene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r(CH) r(CX) θ</td>
<td>r(CH) r(CX) θ</td>
</tr>
<tr>
<td>CH₂</td>
<td>1.075 128.8° -38.92374</td>
<td>1.106 (1.11^a)</td>
</tr>
<tr>
<td>CHF</td>
<td>1.077 1.321 120.4 -137.78813</td>
<td>1.111 (1.12^b,c) 1.325 (1.314^c)</td>
</tr>
<tr>
<td>CHCl</td>
<td>1.075 1.735 123.3° -497.83524</td>
<td>1.101 (1.12^d) 1.762 (1.689^d)</td>
</tr>
<tr>
<td>CHBr</td>
<td>1.075 1.891 125.6° -2610.67156</td>
<td>1.103 1.972</td>
</tr>
<tr>
<td>CF₂</td>
<td>1.311 117.8° -236.64961</td>
<td>1.306 (1.300^e)</td>
</tr>
<tr>
<td>CCl₂</td>
<td>1.730 125.5° -956.74187</td>
<td>1.756 109.4°</td>
</tr>
</tbody>
</table>


^b Assumed.

^c Reference 37.

^d Reference 41.

^e Reference 38.
Table IV. Mulliken populations and estimated singlet-triplet separations $\Delta E$ for several carbenes.

<table>
<thead>
<tr>
<th></th>
<th>Triplet C Population</th>
<th>Singlet C Population</th>
<th>Estimated $\Delta E$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$</td>
<td>6.36</td>
<td>6.25</td>
<td>$+19.5 \pm 0.7^a$</td>
</tr>
<tr>
<td>CHF</td>
<td>5.85</td>
<td>5.77</td>
<td>-2</td>
</tr>
<tr>
<td>CHCl</td>
<td>6.14</td>
<td>6.03</td>
<td>+6</td>
</tr>
<tr>
<td>CHBr</td>
<td>6.25</td>
<td>6.13</td>
<td>+8</td>
</tr>
<tr>
<td>CF$_2$</td>
<td>5.39</td>
<td>5.41</td>
<td>-36</td>
</tr>
<tr>
<td>CCl$_2$</td>
<td>5.99</td>
<td>5.89</td>
<td>-6</td>
</tr>
</tbody>
</table>

$^a$ Experimental result of W. C. Lineberger and co-workers, reference 36.
LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.