

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © Copyright, 1978, by the American Chemical Society

VOLUME 100, NUMBER 5

MARCH 1, 1978

## Multiplicity of the Ground State and Magnitude of the $T_1$ - $S_0$ Gap in Substituted Carbenes<sup>1</sup>

N. Colin Baird\* and Kathleen F. Taylor<sup>2</sup>

Department of Chemistry, University of Western Ontario,  
London, Ontario, Canada N6A 5B7. Received May 31, 1977

**Abstract:** Ab initio molecular orbital calculations are reported for methylene and for a variety of carbenes of formula HCX (where X = F, OH, OCH<sub>3</sub>, NH<sub>2</sub>, CH<sub>3</sub>, CH<sub>2</sub><sup>-</sup>, CH<sub>2</sub><sup>+</sup>, CN, CHO, CHCH<sub>2</sub>), for C(CH<sub>3</sub>)<sub>2</sub>, C(CN)<sub>2</sub>, C(NH<sub>2</sub>)(CN), and for C<sub>3</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>4</sub>, and C<sub>4</sub>H<sub>4</sub> ring systems containing a divalent carbon. Using the STO-3G basis and 2 × 2 configuration interaction for S<sub>0</sub> and restricted open-shell theory for the lowest triplet T<sub>1</sub>, optimum geometries were determined for the simple systems. Calculation of the T<sub>1</sub>-S<sub>0</sub> energy gap for the systems was accomplished with five 3d orbitals included in the basis set for the carbene carbon in most instances.

### Introduction

The electronic structure of methylene, CH<sub>2</sub>, has been the subject of a large number of ab initio quantum-mechanical calculations (for summaries of these results, see ref 3-5). This system has attracted wide interest not only because its small size allows the use of sophisticated methods, but also because of the controversy surrounding many of its properties. Of particular interest in recent years has been the magnitude of the energy gap between the triplet ground state T<sub>1</sub> (or <sup>3</sup>B<sub>1</sub> in spectroscopic notation) and the lowest excited singlet state S<sub>0</sub> (or <sup>1</sup>A<sub>1</sub>).

The fact that some substituted methylenes such as dicyanomethylene<sup>6</sup> have triplet ground states whereas others such as fluoromethylene,<sup>7</sup> difluoromethylene,<sup>8</sup> and chloromethylene<sup>7</sup> have singlet ground states has also attracted some interest. Using extended Hückel theory, Hoffmann and co-workers deduced the conditions in carbenes under which the singlet state would be stabilized differentially relative to the triplet.<sup>9,10</sup> Although reports of calculations for a few substituted methylenes have appeared,<sup>11</sup> there seems to have been no systematic attempt using ab initio calculations to test Hoffmann's predictions. In this report we present such a study of the effect both of substitution and of changes in bond angle in determining the T<sub>1</sub>-S<sub>0</sub> energy gap and the multiplicity of the ground state in a variety of carbenes.

### Details of the Method and Test Calculations

All results contained herein are obtained from ab initio SCF molecular orbital calculations. The basis orbitals are least-squares expansions of Slater-type orbitals (STOs) in terms of three Gaussian-type orbitals. For 1s, 2s, and 2p STOs, the contraction coefficients and Gaussian exponents of Pople and co-workers were used,<sup>12</sup> whereas for the 3d STOs the parameters of Stewart were employed.<sup>13</sup> All integrals over Gaussian orbitals were generated using the IBMOL subroutines.

The angular dependencies for 3d orbitals available in this package are  $xy$ ,  $xz$ ,  $yz$ ,  $x^2$ ,  $y^2$ , and  $z^2$ . Our use of the latter trio as independent functions is equivalent to using the real 3d orbital pair  $3d_{x^2-y^2}$  and  $3d_{3z^2-r^2}$  plus an additional function of s character. In the choice of a suitable Slater exponent for the 3d polarization functions, some guidance is available from the extensive STO calculations for the linear molecules HCCH, HCCF, CO<sub>2</sub>, and CO.<sup>14</sup> The optimum 3d STO exponents for carbon found in these calculations range from 1.5 to 2.7 and cluster about the average of 2.0. Prototype calculations in this laboratory yielded similar results for CH<sub>2</sub> itself; the optimum exponents for the singlet and triplet states were found to be 1.7 and 2.0, respectively. On this basis, a "standard" value of 2.0 for the carbon 3d STO exponent was chosen and is used in all calculations herein. The standard molecular STO exponents recommended by Pople and co-workers<sup>12</sup> are used for the 1s, 2s, and 2p orbitals, except in the "double-zeta" calculations in which those of Huzinaga and Arnau<sup>15</sup> are employed for carbon and assumed values of 1.2 and 1.5 are used for hydrogen.

The wave functions for the lowest triplet states T<sub>1</sub> are obtained using Roothaan's restricted open-shell method.<sup>16</sup> For the closed-shell singlets S<sub>0</sub> the molecular orbitals are obtained for a single-determinant representation of the  $-\sigma^2\pi^0$  configuration by the standard Hartree-Fock-Roothaan procedure. Interaction between this configuration and the doubly excited  $-\sigma^0\pi^2$  configuration is included in the calculation of the total energy of the singlet state. By incorporating this limited amount of configuration interaction (CI), the correlation of motion of the two nonbonding electrons between the  $\sigma$  and the  $\pi$  orbital is allowed for in the singlet state; of course, such correlation is included automatically for the triplet state.

To gain insight into the importance of CI, polarization functions, double- $\zeta$  basis sets, and geometry optimization in

**Table I.** Properties of CH<sub>2</sub> and HCF by Various Calculations

Molecule	Basis set		CI level	T <sub>1</sub> -S <sub>0</sub> gap <sup>a</sup>	Bond angle, deg	
	s,p	d			T <sub>1</sub>	S <sub>0</sub>
CH <sub>2</sub>	Minimal		None	37.3	124	100
	Minimal		2 × 2	28.7	124	101
	Double- $\zeta$		2 × 2	28.6	(124)	(101)
	Minimal	Minimal	2 × 2	18.4	123	99
	Double- $\zeta$	Minimal	2 × 2	21.3	128	102
	Exptl <sup>b</sup>			19.5	~138	102.4
				± 0.7		
HCF	Minimal		None	10.7	121	102
	Minimal		2 × 2	6.0	121	103
	Double- $\zeta$		2 × 2	7.2	(121)	(103)
	Minimal	Minimal <sup>c</sup>	2 × 2	-3.7	(121)	(103)
	Exptl <sup>d</sup>			<0		101.6

<sup>a</sup> T<sub>1</sub>-S<sub>0</sub> gap in kcal mol<sup>-1</sup>. A negative value means S<sub>0</sub> is the ground state. <sup>b</sup> P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3731 (1976). <sup>c</sup> Does not include 3d<sub>yz</sub> orbital; see text. <sup>d</sup> See ref 11b.

obtaining a realistic S<sub>0</sub>-T<sub>1</sub> energy gap, a number of calculations for CH<sub>2</sub> and CHF were performed and are summarized in Table I. The trends in the results are in agreement with the conclusions of Harrison.<sup>4</sup> In particular, the stability of the triplet relative to that of the singlet is exaggerated, and the bond angle in the CH<sub>2</sub> triplet is underestimated, in minimal basis set calculations with no CI. Inclusion of the interaction between  $\sigma^2\pi^0$  and  $\sigma^0\pi^2$  configurations lowers the singlet energy by 8.6 and 4.7 kcal mol<sup>-1</sup> in CH<sub>2</sub> and CHF, respectively, and increases the singlet state bond angle by 1° in both cases (Table I). Improving the basis set to the double- $\zeta$  level has virtually no effect on the S<sub>0</sub>-T<sub>1</sub> energy gap (Table I).

With the addition of 3d orbitals on carbon to the minimal basis set, the energetic advantage of T<sub>1</sub> over S<sub>0</sub> drops to 18.4 kcal mol<sup>-1</sup> for methylene, in excellent agreement with the latest experimental estimate (of 19.6 kcal). For CHF, the effect of polarization functions is to reverse the stability order, with the singlet now predicted to be the ground state of the system, in agreement with the interpretation of the UV spectrum of the molecule.<sup>7</sup> The use of a double- $\zeta$  basis of s and p orbitals (and a single- $\zeta$  basis for the d functions) improves the agreement between the calculated and the experimental bond angles in both states of CH<sub>2</sub>, and stabilizes the triplet slightly more than it does the singlet.

On the basis of the trends discussed above, we decided to incorporate the limited CI in the S<sub>0</sub> state and 3d polarization functions at divalent carbon atoms in all subsequent calculations for carbenes. A double- $\zeta$  basis set was not employed, however, given the small differential effect it had on the S<sub>0</sub>-T<sub>1</sub> gap relative to the computational cost involved. Furthermore, the 3d<sub>yz</sub> orbital was not included in the calculations<sup>17</sup> since it has a very small effect on the SCF energy, and actually worsens the CI-included energy of the singlets (since the " $\pi$ " virtual orbital becomes contaminated with 3d $\pi$  character).

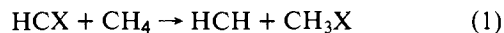
For the series of substituted methylenes HCH, HCF, FCF, HCOH, and HCCH<sub>3</sub> the lengths of the bonds to the carbene carbon, and the bond angle about this center, were optimized using the minimal s,p basis and CI but without polarization functions; the results are given in Table II. Given the lack of variation in the C-H distance found for these systems, "standard" values of 1.13 and 1.09 Å for S<sub>0</sub> and T<sub>1</sub> states, respectively, were assumed in the other derivatives. Similarly some of the bond distances and angles established for the mono-substituted methylenes HCX were used also for the disubstituted derivatives XCX; assumed values are listed in parentheses in Table II. The lengths of single bonds other than those involving the divalent carbon were also given assumed values, as were bond angles within the substituents (see Table II for details).

### Substituted Methylenes YCX

Calculated values for the energy difference  $\Delta E$  between the lowest singlet and triplet states of various substituted methylenes are given in Table III; a negative value for  $\Delta E$  implies the singlet S<sub>0</sub> is predicted to be the ground state rather than the triplet T<sub>1</sub>. Based upon experience with CH<sub>2</sub> and CHF, the  $\Delta E$  values calculated with the 3d orbitals included in the basis set should be quite realistic, and should be superior to the values calculated without the polarization functions. The differential stabilization of S<sub>0</sub> over T<sub>1</sub> due to substitution in HCF and CF<sub>2</sub> is computed to be 22.1 and 53.0 kcal mol<sup>-1</sup>, respectively (Table IV), in good agreement with the values of 21 and 57, respectively, reported in more extensive calculations by Staemmler<sup>11b</sup> and of 24 and 63, respectively, calculated by Harrison;<sup>11a</sup> the agreement in the predictions of the absolute energy gap is not as good, given the varying estimates of the gap in CH<sub>2</sub> itself (10 by Staemmler, 24 by Harrison). Interestingly, it appears that the magnitude of the substituent effect on the predicted T<sub>1</sub>-S<sub>0</sub> gap is almost independent of the inclusion of d orbitals in the basis set (Table IV). In particular, the addition of 3d orbitals stabilizes the singlet more than it does the triplet by 10 ± 2 kcal mol<sup>-1</sup> for the neutral molecules tested; indeed the "with 3d orbitals" values in Table III for C(CH<sub>3</sub>)<sub>2</sub>, HCC(H)=CH<sub>2</sub> and C(CN)<sub>2</sub> were estimated using this constancy. Lucchese and Schaefer<sup>11f</sup> have recently reported ab initio calculations for the latter system and find a differential lowering of S<sub>0</sub> by 10.8 kcal mol<sup>-1</sup> when d orbitals are included, in agreement with the constancy noted above.

Substitution of one or both hydrogens in methylene by groups which have a lone pair of p $\pi$  electrons on the atom bonded to the carbene carbon is predicted to stabilize preferentially the singlet to such a degree that it becomes the ground state of the system. Experimentally it is known that HCF, FCF, and probably NCCNH<sub>2</sub> have singlet ground states<sup>7,8,18</sup> in agreement with the calculations, although the T<sub>1</sub>-S<sub>0</sub> gaps are not known.




An estimate of the stabilization of the carbene (by a substituent X) over and above that obtained in a paraffinic system can be deduced by computing the energy change in the following "isodesmic" reaction:<sup>19</sup>



Values computed for both the triplet and the singlet states by this method are listed in Table IV. The S<sub>0</sub> stabilization energies are in excellent agreement with the magnitude of the dative  $\pi$ -bonding between the p $\pi$  lone pair on X and the empty p $\pi$  orbital on Ċ as measured by the energy change in S<sub>0</sub> which occurs upon removal of the latter orbital from the basis set (Table IV). The differential stabilization of S<sub>0</sub> in the substituted carbenes is not as large as is the strength of the two-electron  $\pi$  bond since the T<sub>1</sub> state also experiences some stabilization upon substitution. Presumably, the triplet stabilization is due primarily to the three-electron interaction(s) between singly-occupied orbitals on Ċ and the lone pair(s) on X (Figure 1). Interestingly there appears to be a preference for conjugation of the singly-occupied  $\sigma$  (rather than the singly-occupied  $\pi$ ) with a single lone pair on X, since the optimum geometry (by a margin of 49 and 17 kcal mol<sup>-1</sup>) for both HCNH<sub>2</sub> and HCCH<sub>2</sub><sup>-</sup> is twisted about the central bond and flapped at the lone pair atom. There is a small preference (0.6 kcal mol<sup>-1</sup>) for a twisted geometry in HCOH even though rotation about the C-O bond here simply interchanges the orbital types on Ċ which interact with the two (nonequivalent) oxygen lone pairs.

To confirm our suspicion that no significant portion of the differential stabilization of S<sub>0</sub> states in  $\pi$ -donor substituted carbenes is due to inductive effects, prototype calculations were executed on the species HCCH<sub>2</sub><sup>+</sup>. To ensure the -CH<sub>2</sub><sup>+</sup> would

Table II. Calculated Geometries for Carbenes<sup>a</sup>

Molecule	Y- $\ddot{C}$ -X angle, deg		H- $\ddot{C}$ length, Å		$\ddot{C}$ -X length, Å		Additional information <sup>b</sup>
	T <sub>1</sub>	S <sub>0</sub>	T <sub>1</sub>	S <sub>0</sub>	T <sub>1</sub>	S <sub>0</sub>	
H $\ddot{C}$ H	124	101	1.09	1.13			
H $\ddot{C}$ F	121	103	1.10	1.14	1.34	1.32	
F $\ddot{C}$ F	119	103			1.34	1.32	
H $\ddot{C}$ OH	123	102	1.10	1.13	1.38	1.34	(R <sub>OH</sub> = 0.97 Å; $\angle$ COH = 105°)
H $\ddot{C}$ OCH <sub>3</sub>	(123)	(102)	(1.10)	(1.13)	(1.38)	(1.34)	Twisted (90°) about CO bond in T <sub>1</sub> (R <sub>OC</sub> = 1.36 Å; $\angle$ COC = 105°; $\angle$ OCH = 109.5°)
H $\ddot{C}$ NH <sub>2</sub>	124	103	(1.09)	(1.13)	1.44	1.35	(Twisted 90° about CO bond in T <sub>1</sub> ) (R <sub>NH</sub> = 1.00 Å; $\angle$ CNH = $\angle$ HNH = 120° in S <sub>0</sub> , = 109.5° in T <sub>1</sub> )
H $\ddot{C}$ CH <sub>3</sub>	124	104	1.09	1.12	1.52	1.54	Twisted (90°), flapped in T <sub>1</sub> ( $\angle$ CCH = $\angle$ HCH = 109.5°)
H <sub>3</sub> C $\ddot{C}$ CH <sub>3</sub>	(124)	(104)			(1.52)	(1.54)	( $\angle$ CCH = $\angle$ HCH = 109.5°)
H $\ddot{C}$ CN	126	104	(1.09)	(1.13)	1.45	1.46	( $\angle$ C $\ddot{C}$ N = 180°) <sup>c</sup> R <sub>CN</sub> = 1.16 Å in T <sub>1</sub> , = 1.17 Å in S <sub>0</sub>
N $\ddot{C}$ CCN	(126)	(104)			(1.45)	(1.46)	Same as HCCN
H $\ddot{C}$ CHO	126	106	(1.09)	(1.13)	1.50	1.53	( $\angle$ OCH = $\angle$ OCC = 120°) R <sub>CO</sub> = 1.23 Å in both T <sub>1</sub> and S <sub>0</sub>
H $\ddot{C}$ CHCH <sub>2</sub>	124	103	(1.09)	(1.13)	1.48	1.51	Twisted (90°) about $\ddot{C}$ C in S <sub>0</sub> R <sub>CC</sub> = 1.32 Å in both T <sub>1</sub> and S <sub>0</sub>
H <sub>2</sub> N $\ddot{C}$ CN	(124)	(103)			(1.45)	(1.46)	$\angle$ C $\ddot{C}$ C = 125° in T <sub>1</sub> , = 122° in S <sub>0</sub> (R <sub>amino N-C</sub> = 1.44 Å in T <sub>1</sub> , = 1.35 Å in S <sub>0</sub> ) (H <sub>2</sub> N $\ddot{C}$ geometry as per H $\ddot{C}$ NH <sub>2</sub> ) ( $\ddot{C}$ CN geometry as per H $\ddot{C}$ CN)
H $\ddot{C}$ CH <sub>2</sub> <sup>-</sup>	123	105	(1.09)	(1.13)	1.46	1.35	( $\angle$ CCH = $\angle$ HCH = 109.5° in T <sub>1</sub> , = 120° in S <sub>0</sub> )
H $\ddot{C}$ CH <sub>2</sub> <sup>+</sup> (no p $_{\pi}$ on $\ddot{C}$ )	(130)	102	(1.09)	(1.13)	(1.43)	1.67	Twisted (90°), flapped in T <sub>1</sub> ( $\angle$ HCH = $\angle$ HCC = 120°)
(p $_{\pi}$ on $\ddot{C}$ )	130	180	(1.09)	(1.13)	1.43	1.29	( $\angle$ HCH = $\angle$ HCC = 120°)
III 	63.6	58.7			1.48	1.53	R <sub>CC</sub> = 1.56 in T <sub>1</sub> , = 1.50 in S <sub>0</sub> ( $\angle$ HCH = 120°)
IV 	52.9	54.1			1.47	1.44	R <sub>CC</sub> = 1.31 Å in both T <sub>1</sub> and S <sub>0</sub> $\angle$ HCC = 147° in T <sub>1</sub> , = 148° in S <sub>0</sub>
V 	(87.4)	(87.4)			(1.46) <sup>d</sup> (1.52) <sup>e</sup>	(1.46) <sup>d</sup> (1.52) <sup>e</sup>	(R <sub>C=C</sub> = 1.32 Å in both T <sub>1</sub> and S <sub>0</sub> ) (R <sub>CC</sub> = 1.52 Å in both T <sub>1</sub> and S <sub>0</sub> ) ( $\angle$ HCH = 109° in both T <sub>1</sub> and S <sub>0</sub> ) ( $\angle$ C = CH = 133.7° in both T <sub>1</sub> and S <sub>0</sub> )

<sup>a</sup> Values in parentheses were assumed, not optimized. <sup>b</sup> All R<sub>CH</sub> = 1.09 Å assumed for noncarbene carbons. <sup>c</sup> Optimum  $\ddot{C}$ CN angles found in ref 11f are  $\sim$ 177° and  $\sim$ 174° for T<sub>1</sub> and S<sub>0</sub>. <sup>d</sup> R( $\ddot{C}$ -CH<sub>2</sub>). <sup>e</sup> R( $\ddot{C}$ -CH).

act only as a  $\sigma$ -electron acceptor and not as a  $\pi$ -electron acceptor (vide infra), no p $_{\pi}$  orbital on the substituent carbon was included in the basis set here. The inductive effect of the highly electronegative -CH<sub>2</sub><sup>+</sup> group is found to favor the triplet state slightly more than the singlet, and thus it increases slightly the T<sub>1</sub>-S<sub>0</sub> gap (Tables III and IV).

The effect of alkyl substitution in methylene is rather mild, with the singlet experiencing a slightly greater stabilization than the triplet; thus the T<sub>1</sub>-S<sub>0</sub> gap is reduced by about 2 kcal mol<sup>-1</sup> for each methyl group substituted (see Tables III and IV). Staemmler's calculations<sup>11b</sup> predicted a 4-kcal drop in the gap upon substitution of a methyl group for hydrogen in CH<sub>2</sub>. Methyl substitution for the hydroxy hydrogen in HCOH alters the T<sub>1</sub>-S<sub>0</sub> gap by only 0.1 kcal mol<sup>-1</sup> (Table III).

The relative energies of the S<sub>0</sub> and T<sub>1</sub> states of several HCX species with  $\pi$  bonds in the substituents X are also listed in Table III. In none of the cases considered is the singlet predicted to be the ground state of the system. Indeed, the triplets of HCCN, HCCHO, and HCCHCH<sub>2</sub> are more stable than are the singlets to a degree which exceeds slightly that for methylene (Table III). The fact that the optimum  $\ddot{C}$ -X bond lengths in T<sub>1</sub> are shorter than those in S<sub>0</sub> (see Table II)

suggests that conjugation of the single carbene carbon  $\pi$  electron to the two  $\pi$  electrons of the group X is more important than is the delocalization of the latter into the empty p $_{\pi}$  orbital on  $\ddot{C}$  in the singlet state. The calculated H $\ddot{C}$ X bond angles in both states of these derivatives are very similar to those for methylene itself (Table II). In contrast, substitution of hydrogen in the methylene singlet by the very strong  $\pi$ -acceptor group -CH<sub>2</sub><sup>+</sup> (with p $_{\pi}$  orbital included in the basis set now) results in a *linear* geometry about  $\ddot{C}$ . In this case the gain in bonding energy obtained by formation of a dative two-electron  $\pi$  bond using the  $\sigma^0\pi^2$  configuration offsets the loss in stability associated with the  $\sigma^2$  to  $\pi^2$  promotion. The lesser gain in  $\pi$  bond energy which would be obtained by this process in HCCN and in HCCHO apparently is insufficient to overcome the energy requirement for two-electron promotion. Note, however, that the  $\ddot{C}$ -C bond in the formylcarbene S<sub>0</sub> state does twist 90°, and the H- $\ddot{C}$ -C angle then opens up slightly, to allow some delocalization of the carbon lone pair into the carbonyl  $\pi$  system.<sup>20</sup> Vinylmethylene, on the other hand, prefers to remain in a coplanar geometry in S<sub>0</sub>. The geometries about  $\ddot{C}$  in the ground T<sub>1</sub> states of the methylenes substituted by -CN, -CHO, -CHCH<sub>2</sub>, and -CH<sub>2</sub><sup>+</sup> are all planar. Previ-

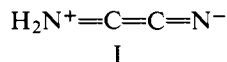
**Table III.** Calculated  $T_1$ - $S_0$  Gap (in kcal mol<sup>-1</sup>) for Carbenes

Molecule	Gap calculated <sup>a</sup>	
	Without 3d orbitals	With 3d orbitals
HCH	28.7	18.4
HCF	6.0	-3.7
FCF	-26.3	-34.6
HCOH	-4.5	-14.5
HCOCH <sub>3</sub>	-4.4	(-14 ± 2)
HCNH <sub>2</sub>	-8.2	-20.0
HCCH <sub>3</sub>	25.9	16.6
H <sub>3</sub> CCCH <sub>3</sub>	23.8	(14 ± 2)
HCCN	30.1	19.2
NCCCN	27.6	(18 ± 2)
HCCHO	34.5	25.0
HCCHCH <sub>2</sub>	32.2	(22 ± 2)
H <sub>2</sub> NCCN	-10.7	(-21 ± 2)
HCCH <sub>2</sub> <sup>-</sup>	-37.8	-46.9
HCCH <sub>2</sub> <sup>+</sup> without p <sub>π</sub> on C̄	29.6	23.5
with p <sub>π</sub> on C̄	-11.0	-11.6
Structure III	1.8	-6.2
Structure IV	-59.0	-71.2
Structure V	15.9	(6 ± 2)

<sup>a</sup> Values in parentheses are estimated using an assumed 10 kcal mol<sup>-1</sup> drop from the "without 3d orbitals" result; see text for details. The geometries used in the calculations, and the extent of optimization done at the minimal s,p basis set level, are listed in Table II.

ous ab initio calculations for dicyanomethylene<sup>11f</sup> support these results, some of which are in disagreement with rather strong predictions by extended Hückel theory.<sup>9</sup> Note also that the ground states of C(CN)<sub>2</sub> and of HCCHCH<sub>2</sub> are known to be triplets<sup>6,21</sup> in agreement with the calculations (both ab initio and extended Hückel). The ground state of HCCH<sub>2</sub><sup>+</sup> is predicted to be the singlet. This singlet is not differentially stabilized by 10 kcal mol<sup>-1</sup> when d orbitals are added to the basis set, since the lone pair is purely 2p in character (with no s or d character allowed) in the linear geometry.

The "mixed substituent" case of aminocyanomethylene, H<sub>2</sub>N-C̄-CN, is of some interest since it is a tautomer of the HCN dimer.<sup>11e</sup> A previous STO-3G ab initio calculation<sup>11e</sup> for S<sub>0</sub> (with no CI included) gave, as optimum, a geometry linear about the carbene carbon and with a very short carbon-carbon bond and a relatively long carbon-nitrogen bond, all appropriate to structure I. Our approach for this system was

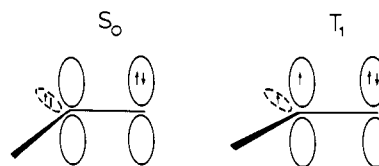
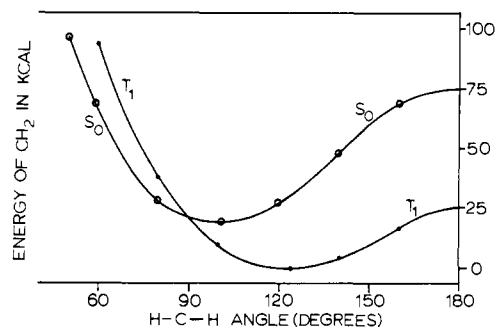


to employ bond lengths and angles found optimum for H<sub>2</sub>N-CH and HC-C≡N, and thus to determine the energy

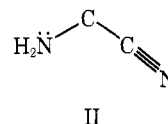
**Table IV.** Measures of Carbene Stabilization<sup>a</sup> (in kcal mol<sup>-1</sup>)

Molecule	Stabilization of state			Differential stabilization	
	From reaction in eq 1		From removal of carbene p <sub>π</sub> S <sub>0</sub>	From change in T <sub>1</sub> -S <sub>0</sub> gap	
	T <sub>1</sub>	S <sub>0</sub>		Without 3d orbitals	With 3d orbitals
HCF	15.8	38.5	42.1	22.7	22.1
FCF	21.4	76.5		55.0	53.0
HCOH	16.6	49.9	47.4	33.2	32.9
HCNH <sub>2</sub>	13.0	50.0	50.4	36.9	38.4
HCCH <sub>3</sub>	6.6	8.7	5.1	2.8	1.8
HCCN	10.1	8.8		-1.4	-0.8
HCCHO	8.9	3.2		-5.8	-6.6
HCCHCH <sub>2</sub>	12.2	9.4		-3.5	
HCCH <sub>2</sub> <sup>-</sup>	50.0	116.6	109.4	66.5	65.3
HCCH <sub>2</sub> <sup>+</sup>				-0.9 <sup>b</sup>	-5.1 <sup>b</sup>

<sup>a</sup> A positive value corresponds to a substituted carbene stabilized relative to CH<sub>2</sub>. <sup>b</sup> For the ion without a p<sub>π</sub> orbital on the carbene carbon.

**Figure 1.**  $\pi$ -Bond interactions in the S<sub>0</sub> and T<sub>1</sub> states of substituted methylenes HCX.**Figure 2.** Calculated energy of S<sub>0</sub> and T<sub>1</sub> states of CH<sub>2</sub> vs. H-C-H angle.

for the structure II. The minimal STO-3G basis set energy (no CI) calculated by us for II is -183.3223 au, considerably more



negative than that of -183.2730 au obtained by us and by Moffat for I. Thus we conclude that although I may be a secondary minimum on the <sup>1</sup>A<sub>1</sub> state surface for H<sub>2</sub>NCCN, geometries of the structure II type are of significantly lower energy. The T<sub>1</sub>-S<sub>0</sub> gap in II is calculated to be 21 kcal mol<sup>-1</sup> (in favor of the singlet), very similar to the results for the amino-substituted methylene system itself (Table III).

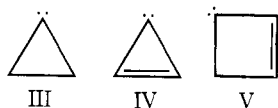
Finally, differential stabilization of the singlet carbenes relative to the triplets by reduction in the bond angle at -C̄- was explored. Calculation<sup>22</sup> of the energy of CH<sub>2</sub> as a function of H-C-H bond angle (see Figure 2) reveals that the S<sub>0</sub> and T<sub>1</sub> curves cross at 90° (in good agreement with the values from other ab initio calculations). The cyclic systems with small -C̄- angles explored in the present work were the saturated and unsaturated three-membered rings III and IV (both with assumed C<sub>2v</sub> symmetry) and the unsaturated four-membered ring V. In the case of III and IV the carbon-carbon bond

Table V. Absolute Energies (au) for Substituted Methylenes<sup>a</sup>

Molecule	T <sub>1</sub>		S <sub>0</sub>	
	Without 3d orbitals	With 3d orbitals	Without 3d orbitals	With 3d orbitals
HCH	-38.4317	-38.4496	-38.3858	-38.4204
HCF	-135.8979	-135.9632	-135.8883	-135.9691
FCF	-233.3650	-233.4654	-233.4070	-233.5206
HCOH	-112.2768	-112.3246	-112.2840	-112.3477
HCOCH <sub>3</sub>	-150.8417		-150.8486	
HCNH <sub>2</sub>	-92.7556	-92.7865	-92.7687	-92.8183
HCCH <sub>3</sub>	-77.0208	-77.0409	-76.9795	-77.0145
H <sub>3</sub> CCCH <sub>3</sub>	-115.6011		-115.5632	
HCCN	-128.9918	-129.0120	-128.9439	-128.9813
NCCCN	-219.5417		-219.4977	
HCCCHO	-149.6627	-149.6835	-149.6078	-149.6437
HCCCH <sub>2</sub>	-114.3809		-114.3296	
HCCH <sub>2</sub> <sup>-</sup>	-76.1708	-76.2059	-76.2311	-76.2806
HCCH <sub>2</sub> <sup>+</sup> with p <sub>π</sub> on C	-76.1481	-76.1740	-76.1656	-76.1925
HCCH <sub>2</sub> <sup>+</sup> without p <sub>π</sub> on C	-76.0753	-76.0999	-76.0281	-76.0624
Structure III	-114.3586	-114.3900	-114.3557	-114.3999
Structure IV	-113.0896	-113.1179	-113.1836	-113.2313
Structure V	-151.7485		-151.7232	

<sup>a</sup> Geometries are specified in Table II.

lengths (and thus the internal angles) were optimized, whereas those for V are assumed values (see Table II). (The optimized distances for IV agree very well with those reported independently by Hehre et al. and who optimized all geometric variables.)



Both three-membered ring systems III and IV are predicted to have singlet ground states according to calculations with d orbitals included. Although the  $\angle$  angles in these two rings do not differ greatly, the singlet differential stabilization of the cyclopropenylidene system IV is much larger, due to the aromatic  $2\pi$  electron network in the dominant configuration for S<sub>0</sub>. Large T<sub>1</sub>-S<sub>0</sub> gaps in favor of the singlet were also obtained for IV by Hehre et al. at both the STO-3G and the 4-31G basis set levels.<sup>11g</sup>

Although the  $\angle$  angle assumed in the cyclobutenylidene system V is less than 90°, the extrapolated T<sub>1</sub>-S<sub>0</sub> gap is  $6 \pm 2$  kcal mol<sup>-1</sup> in favor of the triplet. Presumably part of this advantage to T<sub>1</sub> is due to the presence of a double bond next to the carbene center (recall that the T<sub>1</sub>-S<sub>0</sub> gap in vinylmethylene is  $\sim 3.5$  kcal mol<sup>-1</sup> greater than in methylene). Although the size of this system and the number of independent geometrical variables precludes an economical geometry search, we anticipate that the resultant T<sub>1</sub>-S<sub>0</sub> gap would increase slightly as surely the T<sub>1</sub> state is more adversely affected by the arbitrary choice of a small  $\angle$  angle than is the singlet. Note, however, that if the actual T<sub>1</sub>-S<sub>0</sub> gap in CH<sub>2</sub> is appreciably less than is the most recent experimental value, then all our  $\Delta E$  values should probably be lowered by this amount to obtain realistic estimates (since the substituent effects are probably more reliable than are the absolute  $\Delta E$  magnitudes) and the "adjusted" value for V may become negative!

For reference, the total energies calculated for the molecules discussed in this paper are listed in Table V.

## Conclusions

The nature of the ground state and the magnitude of the T<sub>1</sub>-S<sub>0</sub> energy gap in a series of substituted carbenes have been computed and appear to be in good agreement with experiment where the latter information is available. The changes in the

T<sub>1</sub>-S<sub>0</sub> gap relative to that for CH<sub>2</sub> are probably more reliable than are the absolute gap values themselves. In general the singlet S<sub>0</sub> appears to be the ground state of acyclic carbenes HCX and XCX whenever X has a lone-pair  $\pi$  donor atom bonded directly to C (i.e., when X = F, OR, NR<sub>2</sub>, CR<sub>2</sub><sup>-</sup>). In contrast, most  $\pi$ -electron acceptor groups (with the notable exception of CH<sub>2</sub><sup>+</sup> at least) do not alter the T<sub>1</sub>-S<sub>0</sub> gap sufficiently to alter the nature of the ground state from triplet to singlet. Angle reduction at the carbene center in three-membered rings is sufficient to make S<sub>0</sub> the ground state but the triplet is probably slightly more stable than is the singlet in four-membered rings, at least those possessing an internal double bond.

## References and Notes

- (1) (a) Research supported by the National Research Council of Canada. (b) Preliminary aspects of this work were reported at the VIII IUPAC Symposium on Photochemistry, Aix-en-Provence, France, in July 1976; *Pure Appl. Chem.*, **49**, 223 (1977).
- (2) Holder of NRCC Postgraduate Scholarships, 1975-77.
- (3) V. Staemmler, *Theor. Chim. Acta*, **31**, 49 (1973).
- (4) J. F. Harrison, *Acc. Chem. Res.*, **7**, 378 (1974).
- (5) J. H. Meadows and H. F. Schaefer, *J. Am. Chem. Soc.*, **98**, 4383 (1976).
- (6) E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 2075 (1965).
- (7) A. J. Merer and D. N. Travis, *Can. J. Phys.*, **44**, 525, 1541 (1966).
- (8) C. W. Mathews, *Can. J. Phys.*, **45**, 2355 (1967).
- (9) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).
- (10) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968).
- (11) Ab initio calculations for methylene derivatives include those (a) for CHF and CF<sub>2</sub> by J. F. Harrison, *J. Am. Chem. Soc.*, **93**, 4112 (1971); (b) for CHF, CF<sub>2</sub>, and CHCH<sub>3</sub> by V. Staemmler, *Theor. Chim. Acta*, **35**, 309 (1974); (c) for CHCH<sub>3</sub> by J. Altmann, I. G. Csizmadia, and K. Yates, *J. Am. Chem. Soc.*, **96**, 4196 (1974); (d) for formylmethylene by O. P. Strausz, R. K. Gosavi, A. S. Denes, and I. G. Csizmadia, *ibid.*, **98**, 4784 (1976); (e) for aminocyclopropane by J. B. Moffat, *J. Chem. Soc., Chem. Commun.*, 888 (1975); (f) for dicyanocarbene by R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **99**, 13 (1977); (g) for C<sub>3</sub>H<sub>2</sub> carbenes by W. J. Hehre, J. A. Pople, W. A. Lathan, L. Radom, E. Wasserman, and Z. R. Wasserman, *ibid.*, **98**, 4378 (1976); (h) for various carbenes with a total of two nonhydrogen atoms by W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
- (12) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (13) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).
- (14) A. D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions", IBM Corporation, San Jose, Calif., 1967.
- (15) S. Huzinaga and C. Arnau, *J. Chem. Phys.*, **53**, 451 (1970).
- (16) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
- (17) The coordinate system for HCX derivatives has C and X lying along the x axis and the H in the xy plane.
- (18) R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Matthews, *J. Am. Chem. Soc.*, **89**, 5673 (1967).

- (19) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).
- (20) Strausz et al. have previously reported a similar geometry for the singlet state of formylmethylene.<sup>11d</sup> Their prediction of a singlet ground state for this system, and similarly for methylmethylene in the calculations<sup>11c</sup> of Altmann, Csizmadia, and Yates, may well be due to the use of singlet state molecular orbitals to represent  $T_1$ , thereby biasing strongly the calculations in favor of the former.
- (21) (a) R. S. Hutton, M. L. Manion, H. D. Roth, and E. Wasserman, *J. Am. Chem. Soc.*, **96**, 4680 (1974). (b) At the suggestion of a referee, we have investigated the effect of including d orbitals on the oxygen atom in HCCHO. Adding  $d\sigma$  and  $d\pi$  orbitals to the minimal s,p basis set raises the  $T_1-S_0$  gap by 0.5 and 0.0 kcal mol<sup>-1</sup>, respectively; thus polarization functions on the oxygen are not important in determining the energy gap.
- (22) The C-H distances in the  $S_0$  and  $T_1$  states were held constant at 1.13 and 1.09 Å, respectively, in these calculations.

## Electronic States of the NiO Molecule<sup>1,2</sup>

Stephen P. Walch and W. A. Goddard III\*

Contribution No. 5521 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

Received February 28, 1977

**Abstract:** Generalized valence bond and configuration interaction wave functions have been obtained as a function of  $R$  for numerous electronic states of NiO. All the lower states are found to involve the  $(4s)^1(3d)^9$  Ni atom configuration and O in the  $(2s)^2(2p)^4$  configuration. There are two groups of states. The lower group of states involves pairing singly occupied Ni(4s) and O( $2p\sigma$ ) orbitals into a (somewhat ionic)  $\sigma$  bond pair with various pairings of the Ni( $3d$ )<sup>9</sup> and O( $2p\pi$ )<sup>3</sup> configurations. This leads to a number of states, including the ground state, which we find to be  $X^3\Sigma^-$ . (The electronic structure is analogous to that of O<sub>2</sub>.) The calculated  $D_0$  and  $R_e$  for the  $X^3\Sigma^-$  state of NiO are 89.9 kcal/mol and 1.60 Å, respectively. The bond energy is in good agreement with the experimental value of  $86.5 \pm 5$  kcal/mol, while the  $R_e$  value is not known experimentally. The higher group of states involve a doubly occupied O( $2p\sigma$ ) orbital. The Ni(4s) orbital in this case is nonbonding and builds in 4p character to move away from the oxygen orbitals. The bonding mainly involves stabilization of the oxygen orbitals by the Ni( $3d$ )<sup>9</sup> core (somewhat analogously to the bonding in NiCO). Numerous allowed transitions between these states and the states of the lower group are calculated to be in the range 1.0–3.0 eV, where numerous bands are seen in emission.

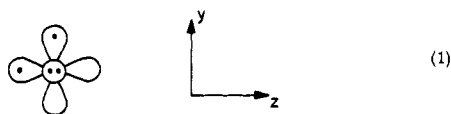
### I. Introduction

A great deal of attention is currently being directed toward the study of heterogeneous catalysis of various reactions by metal surfaces and homogeneous catalysis using transition metal complexes. A major difficulty in designing and interpreting experimental studies of such systems is that the electronic structure and bonding of unsaturated ligands to transition metals is poorly understood (even at a qualitative level) with very little in the way of quantitative thermochemical data. Indeed, there is currently only very sketchy experimental (or theoretical) information about such simple diatomic systems as transition metal oxides.<sup>3</sup> As part of a project aimed at providing both qualitative and quantitative information about chemisorption and reactions of atoms and molecules on metal surfaces, we carried out a rather extensive study of numerous electronic states of NiO as described herein.

In section II we present the qualitative description of the various states of NiO as obtained from the generalized valence bond (GVB)<sup>6</sup> calculations. Various calculational details are outlined in section III, while section IV describes the details of the configuration interaction (CI calculations). Finally, section V contains a summary of the main results obtained.

### II. Qualitative Description

The ground state of O( $3p$ ) has the configuration  $(1s)^2(2s)^2(2p)^4$  and can be visualized as in



where



indicates a  $2p_z$  orbital in the plane and  $\odot$  indicates a  $2p_x$  orbital pointing out of the plane.

Ni is a bit more complicated. Neglecting spin-orbit coupling, the ground state is  $^3D(4s^13d^9)$  while the  $^3F(4s^23d^8)$  state is at 0.03 eV.<sup>7</sup> Thus, both states could well play a role in the bonding. However, as shown in Figure 1, the 4s orbital of Ni is  $\sim 2.5$  times larger than the 3d orbitals, so that the bonding is dominated by the 4s orbital. In consequence, the lower bound states of NiO all have essentially  $(4s)^1(3d)^9$  character on the Ni.

Before examining the states of NiO we will consider NiH<sup>9</sup> since it illustrates the  $\sigma$  bonding without the complications of the  $\pi$  bonds.

Coupling the Ni( $s^1d^9$ ) state to the H leads to an attractive interaction much as in H<sub>2</sub>, whereas at large  $R$ , coupling the Ni( $s^2d^8$ ) state to the H leads to repulsive interactions (arising from the Pauli principle) somewhat analogous to the case of HeH or BeH. At small  $R$  the  $s^2d^8$  state can lead to bonding (the atomic state is promoted by splitting the 4s pair into two sp hybrids, one of which overlaps the H); however, the ground state of NiH has the  $s^1d^9$  configuration on the Ni. Allowing the orbitals to readjust, as in the GVB wave function, leads to mixing of small amounts of Ni  $4p\sigma$ , Ni  $3d\sigma$ , and H  $1s$  character into the Ni(4s) orbital; however, the qualitative description is as above.

Given that the ground state of NiH has  $4s^13d^9$  character on the Ni with the 4s orbital coupled to the H, we expect five low-lying states ( $^2\Delta$ ,  $^2\Pi$ , and  $^2\Sigma^+$ ) depending on which of the five d orbitals is singly occupied (i.e., which one has the hole). As discussed elsewhere<sup>9</sup> the best state has a  $\delta$  hole, the next best has a  $\pi$  hole, while the case with a  $\sigma$  hole is worst. The separations here are  $\delta \rightarrow \pi$  0.346 eV and  $\delta \rightarrow \sigma$  0.441 eV. (The effect leading to this ordering is referred to as the intraatomic coupling.<sup>10</sup>)

Now we consider NiO. Again we find the lower states to involve a Ni( $4s^13d^9$ ) configuration. Assuming this and pairing the Ni(4s) orbital with the singly occupied O( $2p\sigma$ ) orbital of (1) leads to five possible Ni  $3d^9$  configurations, each of which