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Critical Compilation of Physical Properties
of Short-lived Intermediates

CARBENES AND CARBENE ANALOGUES

(Technical Report)

Prepared for publication by

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Critical compilation of physical properties of short-lived intermediates: Carbenes and carbene analogues (Technical Report)

Abstract - A critical compilation is presented of physicochemical parameters of carbenes (unstable derivatives of two-coordinated carbon) and their analogues, such as silylenes, germylenes, and stannylenes. Experimental data evaluated is from the following methods: pulsed methods of generation and spectral registration; low-temperature matrix spectra IR, UV, ESR etc; gas phase methods of molecular studies, such as mass-, microwave- and photo-electron spectroscopy and gas electronography; and high level computational techniques.

CONTENTS

INTRODUCTION

Reactive intermediates - free radicals, ions, ion-radicals, carbenes, etc. are always the subject of special interest in determining reaction mechanism and pathways, as well as the structure of final products. Some aspects of reactive intermediate chemistry have been described in many reviews and monographs including the excellent serial publication **"Reactive Intermediates"** (*Wiley & Sons*, Vol.1, 1978; Vol.2, 1981; Vol.3, 1985). However, experimentally obtained structural and energetic parameters of these species were not systematically surveyed in these publications. At the same time the development of modern physical organic chemistry is characterized by the wide application of quantitative data concerning structure and

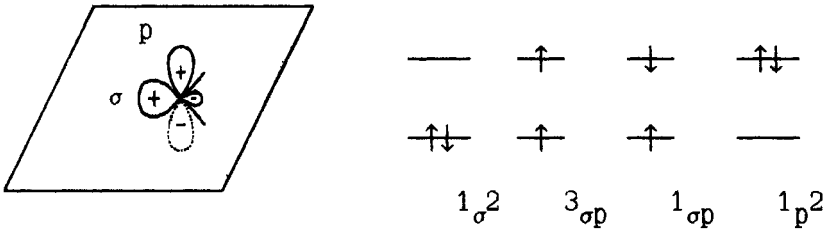
reactivity of the molecules including short-lived intermediates. In this connection the critical compilation of structural and energetic parameters of reactive intermediates becomes a vital task. It was the main purpose of the project, supported by **IUPAC** *Commission III.2* on Physical Organic Chemistry. This review has been prepared in the framework of the project. It concerns the critical compilation of physico- chemical parameters of carbenes - unstable derivatives of two-coordinated carbon, and their analogues - silylenes, germylenes, and stannylenes, obtained by experimental methods (pulsed methods of generation and spectral registration of short-lived molecules, low-temperature matrix IR-, UV-, ESR-, etc. spectra, gase phase methods of molecules studies - mass-, microwave-, photoelectron -spectroscopy, gas electronography, etc.) as well as the high level computitional techniques - another modern powerful tool of reactive intermediate studies.

The review deals with the data on the geometric and electronic structure parameters of carbenes, silylenes, germylenes, stannylenes in ground and excited states as well as their thermodynamic functions, ionization potentials, low-temperature matrix IR-, UV-, and ESR-spectral parameters. At the end of the review *ab initio* calculation of electron structure and geometry of these species are also presented.

The selection of experimental data was based on their reproducibility by different techniques. In the case, when there were several different values for a parameter, the value obtained by the most precise and reliable method was chosen. Footnotes are given when the value is not reliable according to the experts opinion.

At the beginning of the review we present in a general form the principal methods of carbenes and their analogues generation as well as the scope of the reactivity of these species.

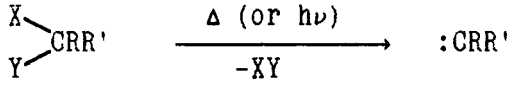
STRUCTURE, METHODS OF GENERATION AND PROPERTIES



Frontier MO of carbenes and their lowest configurations

I.1. Methods of carbene generation

I.1.1. *Reactions of α-elimination*



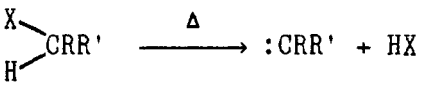
1) α-dehydrogenation (detachment of H_2 molecule)

$CH_2RR' \xrightarrow{\Delta} :CRR' + H_2$ R,R'=alkyl, Hal, etc.

$CH_4 \xrightarrow{\Delta \text{ or } h\nu} :CH_2 + H_2$

$CH_2X_2 \xrightarrow{h\nu} :CX_2 + H_2$ X=F, Cl, Br

2) α-dehydrohalogenation (detachment of HHal molecule)



$CHX_3 \xrightarrow{\Delta} :CX_2 + HX$

$CH_2X_2 \xrightarrow{\Delta} :CHX + HX$ X=F, Cl

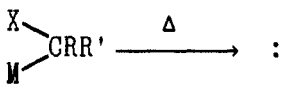
3) α-dehalogenation (detachment of Hal_2 molecule)

$CX_2RR' \xrightarrow{\Delta \text{ (or } h\nu)} :CRR' + X_2$

$CX_4 \xrightarrow{\Delta} :CX_2 + X_2$ X=F, Cl, Br

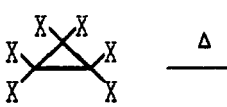
$CF_2X_2 \xrightarrow{h\nu} :CF_2 + X_2$ X=F, Cl

4) carbenes from halogen-organometallic precursors

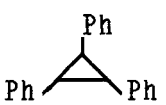


M=Li, MgX, ZnX, ER_2 (E=B, Al, Tl);
ER_3 (E=Si, Ge, Sn, Pb); HgX, etc.
X=F, Cl, Br, I

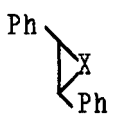
5) α-elimination of carbenes from cyclopropanes and three-membered heterocycles



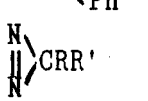
$\xrightarrow{\Delta} :CX_2 + X_2C{=}CX_2$ X=F, OMe



$\xrightarrow{h\nu} :CHPh + PhCH{=}CHPh$

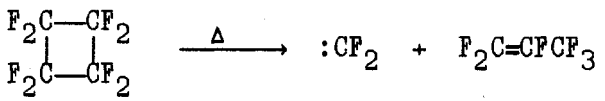


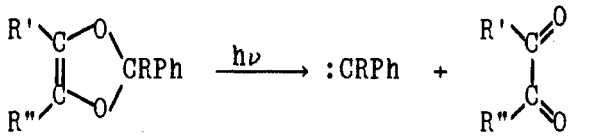
$\xrightarrow{h\nu} :CHPh + PhCH{=}X$ X = O, NPh

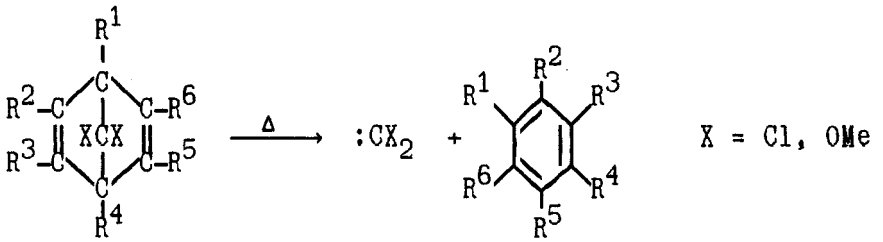


$\xrightarrow{\Delta \text{ (or } h\nu)} :CRR' + N_2$

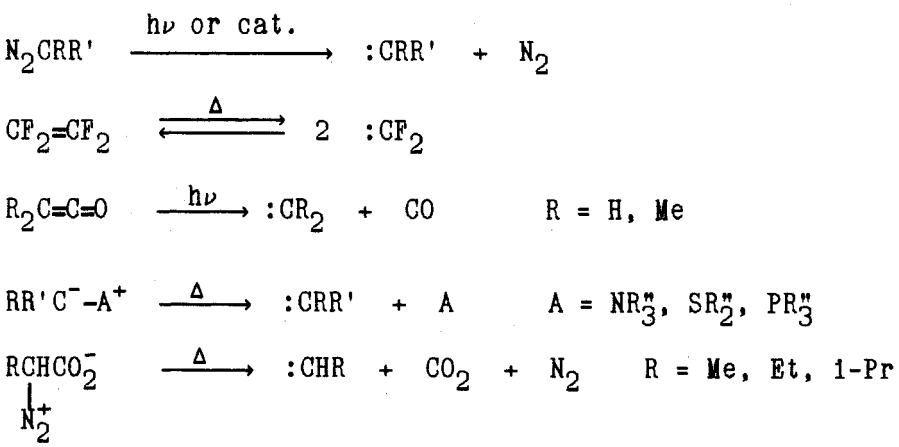
6) α-elimination of carbenes from other carbo- and heterocyclic compounds



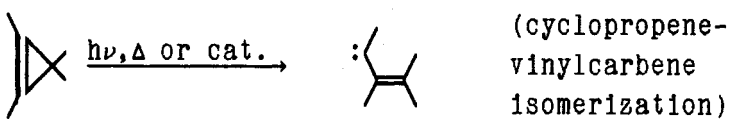




I.1.2. *Carbenes from diazocompounds, olefins, ketenes, ylides and related compounds*

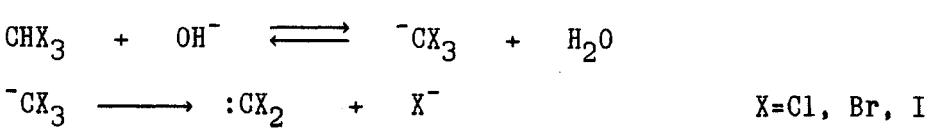


I.1.3. *Carbenes via intramolecular rearrangements*



I.1.4. *Solvolytic methods of carbene generation (based on the α-elimination reaction)*

1) alkali hydrolysis of haloforms



in phase-transfer conditions

$$CHCl_{3\,org} + NaOH_{aq} \xrightleftharpoons{\text{inter-phase}} Cl_3C^-Na^+$$

$$Cl_3C^-Na^+ + \rangle\overset{+}{N}\langle X^-_{org} \rightleftharpoons Cl_3C^-\overset{+}{N}\lessgtr_{org} + NaX_{aq}$$

$$Cl_3C^-\overset{+}{N}\lessgtr_{org} \rightleftharpoons :CCl_{2\,org} + \rangle\overset{+}{N}\langle Cl^-_{org}$$

$$:CCl_{2\,org} + reagent_{org} \longrightarrow product_{org}$$

2) other sources of halomethyl anions and halocarbenes

$$X_3CCOOM \rightleftharpoons M^+ + X_3CCOO^-$$

$$X_3CCOO^- \xrightarrow{\Delta} CO_2 + X_3C^- \qquad M = Li, Na, K$$
$$\downarrow \qquad X = Cl, Br$$
$$:CX_2 + X^-$$

$$ClXX'CCO_2R + R'O^- \longrightarrow :CXX' + Cl^- + R'OCO_2R$$
$$X = X' = Cl;\ X = Cl,\ X' = F$$

$$Cl_2XCCR \;(\overset{\|}{O}) + R'O^- \longrightarrow RCO_2R' + XCl_2C^-$$
$$\downarrow$$
$$:CXCl + Cl^-$$
$$R = H,\ Me;\ X = F,\ Cl$$

$$\left.\begin{matrix} Cl_3CSO_2X \\ Cl_3CPO(OEt)_2 \end{matrix}\right\} \xrightarrow{RO^-} Cl_3C^- \longrightarrow :CCl_2 + Cl^-$$
$$X = Cl,\ Me$$

$$PhCHXY \xrightarrow{RO^-} PhC^-XY \longrightarrow \begin{matrix} Ph \\ X \end{matrix}\!\!>\!C: + Y^-$$
$$X = F,\ Cl,\ Br;\ Y = Cl,\ Br$$

I.2. Reactivity of carbenes

An essential feature of carbene chemical behavior is their ability to transform into four-coordinated state with the formation of two single or one double (or coordination) bonds.

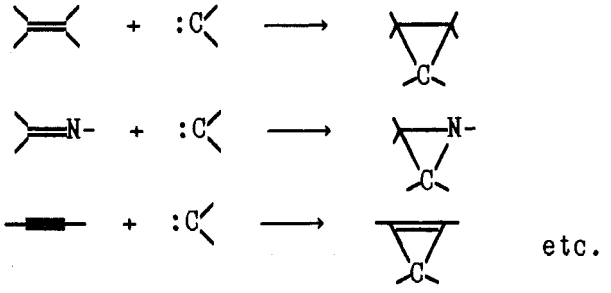
The main types of carbenes and their analogues reactions:

I.2.1. *Insertion into σ-bonds*

$$X\text{-}Y + :C\!\!<\!\!\!\!\diagup \longrightarrow X\text{-}\underset{|}{\overset{|}{C}}\text{-}Y$$

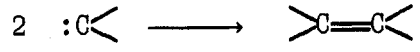
X-Y = C-H, C-Hal, O-H, N-H, S-H
M-H, M-Hal (M=Si, Ge, Sn etc.)

I.2.2. *Cycloaddition to multiple bonds*

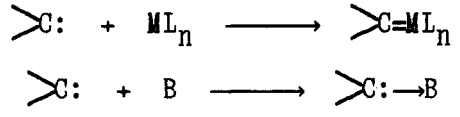


etc.

I.2.3. *Dimerization*

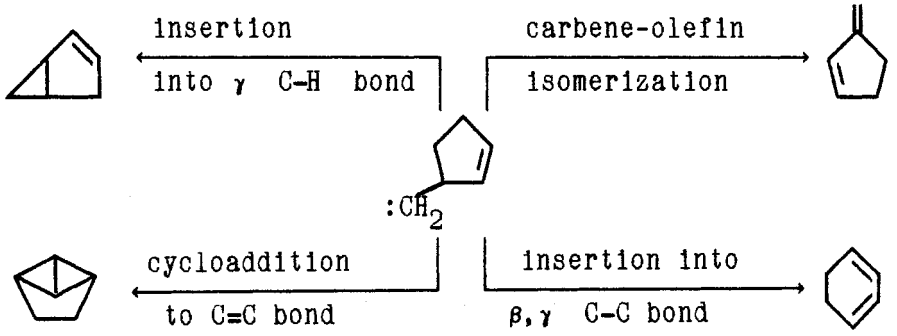


I.2.4. *Complex formation*



B= Lewis base

I.2.5. *Intramolecular reactions*



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CRITICALLY EVALUATED EXPERIMENTAL DATA

Table 1. The Ground state structure parameters of carbenes and their analogues

Molecule :MRR'	Ground state term	r_{M-R} ($r_{M-R'}$), Å	∠RMR', deg.	References
1	2	3	4	5
$:CH_2$	$^3B_1$	1.075-1.085	133.9-136	1-5
$:CF_2$	$^1A_1$	1.30	104.34-104.78	6-11
:CHF	$^1A'$	1.120 1.314	101.8	1,12-14
$:CCl_2$	$^1A_1$	1.70-1.758	108	6,15-19
:CHCl	$^1A'$	1.119-1.120 1.689-1.696	101-103	12,18,20,21
:CFCl	$^1A'$	1.30 1.70	105	22-25
$:CBr_2$	$^1A_1$	1.87-1.907	109-110	6,26-28
$:CI_2$	$^1A_1$	2.12*	110*	29-31
$:SiH_2$	$^1A_1$	1.516	92.1	32-35
$:SiF_2$	$^1A_1$	1.590-1.595	100.88	6,36-52
:SiHF	$^1A'$	1.52* 1.60*	100*	29,30,53
$:SiCl_2$	$^1A_1$	2.044-2.083	102.8-105	6,54-57
:SiHCl	$^1A'$	1.561 2.064	102.8	58
:SiFCl	$^1A'$	1.60* 2.05	100*	29,30,53
$:SiBr_2$	$^1A_1$	2.194-2.243	102.7-109	6,54,56
:SiHBr	$^1A'$	1.56 2.231	102.9	58, 59
$:SiI_2$	$^1A_1$	2.44*	110*	29, 30
:SiHI	$^1A'$	1.56 2.451	102.7	53, 60
:SiHOH	$^1A_1$	-	113-114.5	61
$:GeH_2$	$^1A_1$	1.60*	90*	62
$:GeF_2$	$^1A_1$	1.732	97.2	63-67
$:GeCl_2$	$^1A_1$	2.186	100.4	6,68,69
$:GeBr_2$	$^1A_1$	2.337	101.2	6,70
$:GeI_2$	$^1A_1$	2.540	102.1	30

Table 1 (end)

1	2	3	4	5
:GeHBr	$^1A'$	1.53 2.30	100	71
:Ge(OCBu$_3$-*t*)$_2$	$^1A_1$	1.83-1.86	85.9	233
:M(OAr)$_2$ M=Ge	$^1A_1$	1.802-1.812	92.0	234
M=Sn	$^1A_1$	2.005	88.8	235
M=Pb	$^1A_1$	-	86.2	235
Ar=C$_6$H$_2$Me-4-Bu$_2$-*t*-2,6				
:Sn(XAr')$_2$ X=NH	$^1A_1$	2.03	89.6	235
X=S	$^1A_1$	2.435	85.4	236
Ar'=C$_6$H$_2$Bu$_3$-*t*-2,4,6				
:M[N(SiMe$_3$)$_2$]$_2$ M=Ge	$^1A_1$	1.89	101	237
M=Sn	$^1A_1$	2.09	104.7	77,237
:M[CH(SiMe$_3$)$_2$]$_2$ M=Ge	$^1A_1$	2.04	107	238
M=Sn	$^1A_1$	2.24	96	238
:SnF$_2$	$^1A_1$	1.893-1.96	94-96	6,72
:SnCl$_2$	$^1A_1$	2.342-2.346	98.5-99	6,73
:SnBr$_2$	$^1A_1$	2.497-2.64	100.0-100.5	6,74,75
:SnI$_2$	$^1A_1$	2.706-2.78	103.8	75,76
:M[N(CMe$_2$)(CH$_2$)$_3$(CMe$_2$)]$_2$ M=Ge		1.88	111.4	239
M=Sn		2.09	96	77
:PbF$_2$	$^1A_1$	1.989-2.03	90-95	6,72,78
:PbCl$_2$	$^1A_1$	2.444-2.445	98.3-98.5	6,72,75,79
:PbBr$_2$	$^1A_1$	2.597	98.8	6,75
:PbI$_2$	$^1A_1$	2.804	99.7	75,80

* Estimated value.

Table 2. Ground state thermodynamic functions of carbenes and their analogues in vapour phase /81/

Molecule	ΔH_f(OK), kJ/mol	Function at 298.15K				
		C_p^o (T)	Φ^o(T)*	S^o(T)	H	ΔH_f^o
		(J/K)/•mol			kJ/mol	
1	2	3	4	5	6	7
$:CH_2$	390.0	33.8	161.5	194.8	9.9	390.4
$:CF_2$	-180.5	38.9	206.0	240.7	10.4	-180.0 -205 ± 12 /82/
:CHF	105.0	34.6	201.3	234.8	10.0	105.3 109 ± 12 /82/
$:CCl_2$	225.0	46.5	226.5	264.9	11.5	226.2 163 ± 12 /82/ 230 ± 8 /83/
:CHCl	308.0	36.7	200.7	234.8	10.2	308.3 298 ± 21 /82/
:CFCl	-	-	-	-	-	25 ± 20 /84,85/ -8 ± 29 /82/
$:CBr_2$	350.0	49.3	247.4	288.4	12.2	336.6
$:CI_2$	470.0	50.9	261.8	304.2	12.6	468.4
$:SiH_2$	275.0	35.0	173.8	207.4	10.0	273.3 289 ± 12 /86/ 286 /87/ 269.0 ± 1.3 /88
$:SiMe_2$	-	-	-	-	-	122 /89/ 109 /90/
:SiHMe	-	-	-	-	-	214 /91/
$:SiHSiMe_3$	-	-	-	-	-	271 /92/
$:SiF_2$	-592.0	44.5	218.9	256.5	11.2	-592.8
:SiHF	-161.0	37.8	204.3	238.6	10.2	-162.7
$:SiCl_2$	-163.2	51.3	239.5	281.5	12.5	-163.1
:SiHCl	56.3	41.0	215.4	251.2	10.7	54.9 71 /87/
:SiFCl	-	-	-	-	-	-377 ± 20 /29,30/

Table 2 (end)

1	2	3	4	5	6	7
$:SiBr_2$	-36.6	53.6	259.9	304.6	13.3	-51.0
$:SiI_2$	95.3	55.5	276.6	324.1	14.2	93.0
$:GeF_2$	-572.3	47.8	231.1	270.7	11.8	-574.0
$:GeCl_2$	-170.5	53.8	251.2	295.7	13.3	-171.0
$:GeBr_2$	-46.0	55.8	271.5	319.1	14.2	-61.0
$:GeI_2$	53.5	56.4	285.4	334.5	14.6	50.3
$:SnF_2$	-508.1	49.7	241.0	282.0	12.2	-511.0
$:SnCl_2$	-200.8	54.6	259.9	305.8	13.7	-202.6
$:SnBr_2$	-102.7	56.4	280.0	328.9	14.6	-119.0
$:SnI_2$	-3.4	56.7	292.7	342.6	14.9	-8.1 -451.4 ± 9.2 /92/
$:PbF_2$	-440.3	51.0	249.2	291.4	12.6	-443.4
$:PbCl_2$	-173.5	55.3	268.5	315.5	14.0	-175.5
$:PbBr_2$	-87.6	57.0	289.2	339.6	15.0	-104.0
$:PbI_2$	-5.4	57.2	301.4	352.5	15.2	-10.3

* $\Phi^{O}(T) = S^{O}(T) - (H^{O}(T)-H^{O}(0))/T$ (reduced Gibbs energy)

Table 3. Ionization potentials of carbenes and their analogues in ground state*

Molecule		*IP*, eV	References
$:CH_2$		10.40	1,93-102
$:CF_2$		11.8	84,96-98,103
:CHF		10.49	82
:CFCl		10.6-10.8	82,84,104
$:CCl_2$		9.10-10.36	82,83,105
:CHCl		9.84	82
$:CBr_2$		9.8-10.2	30,106,107
:CHBr		11.3-12.1	107,108
$:SiF_2$		10.8-11.3	109-112
$:SiCl_2$		10.0-10.6	113,114
$:GeF_2$		11.6-11.8	67,109,115
$:GeCl_2$		10.2-10.4	68,116,117
$:GeBr_2$		9.5	116
$:SnF_2$		11.5	117
$:SnCl_2$		10.2	118
$:SnBr_2$		10.0	118
$:PbF_2$		11.6	117
$:PbCl_2$		10.3-11.2	119,120
$:PbBr_2$		10.2	119
$:M\left[N\begin{matrix}CMe_2\\CMe_2\end{matrix}(CH_2)_3\right]_2$	M=Ge	6.90	77
	M=Sn	6.80	77
$:M[N(SiMe_3)_2]_2$	M=Ge	8.68	240
	M=Sn	8.38	240
	M=Pb	8.16	240
$:M[N(SiMe_3)Bu\text{-}t]_2$	M=Ge	8.27	240
	M=Sn	7.90	240
	M=Pb	7.69	240
$:M[CH(SiMe_3)_2]_2$	M=Ge	7.75	240
	M=Sn	7.42	240
	M=Pb	7.25	240

*For leading review on ionization potentials of transient molecules see: R.D.Levin, S.G Lias. "*Ionization potential and appearance measurements, 1971-1981*", Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand. (U.S.), No 71 (1982).

Table 4. The excited states energies of three-atom carbenes and their analogues*

Molecule and ground state term	Excited state term	Excitation energy from the ground state, eV	References
1	2	3	4
$:CH_2$, $^3B_1$	$^1A_1$	0.39	121-125
	$^1B_1$	1.27-1.31	1,35,125,126
$:CF_2$, $^1A_1$	$^3B_1$	1.86-2.46	29,30,127-130
	$^1B_1$	4.62-5.0	7,19,131
:CHF, $^1A'$	$^3A''$	0.0-0.6	132
	$^1A''$	2.14	12,13,21,133,134
$:CCl_2$, $^1A_1$	$^3B_1$	1.49	29,30,135
	$^1B_1$	2.10-2.5	135-141
:CHCl, $^1A'$	$^3A''$	0.99	29,30
	$^1A''$	1.52	12,20,21,133
:CFCl, $^1A'$	$^3A''$	1.61	29,30
	$^1A''$	3.11-3.13	22,24,25,142
$:CBr_2$, $^1A_1$	$^3B_1$	1.24	29,30
	$^1B_1$	1.85-1.86	28,143
:CFBr, $^1A'$	$^1A''$	<2.76	144
:CClBr, $^1A'$	$^1A''$	1.99	28,143
$:CI_2$, $^1A_1$	$^3B_1$	1.7**	29,30
	$^1B_1$	1.7**	29,30
$:SiH_2$, $^1A_1$	$^3B_1$	0.2-0.9	145,146
	$^1B_1$	1.93	32,34
	$^3B_2$	3.0**	147
$:SiMe_2$, $^1A_1$	$^1B_1$	2.33	148
$:SiF_2$, $^1A_1$	$^3B_1$	3.26	37,41,43,50,149
	$^1B_1$	5.47	40,150
	$^3B_2$	7.71	29,30
:SiHF, $^1A'$	$^3A''$	0.62**	29,30
	$^1A''$	2.88	151,152

Table 4 (end)

1	2	3	4
$:SiCl_2$, $^1A_1$	$^3B_1$	2.84	17,74
	$^1B_1$	3.61-3.94	17,153-159
:SiHCl, $^1A'$	$^1A''$	2.57	58
:SiFCl, $^1A'$	$^3A''$	>2.5	29,30
$:SiBr_2$, $^1A_1$	$^3B_1$ and $^1B_1$	>2.5	29,30
	$^1B_1$	~3.42	155
:SiHBr, $^1A'$	$^1A''$	2.47	58
$:SiI_2$, $^1A_1$	$^3B_1$ and $^1B_1$	>2.5	29,30
:SiHI, $^1A'$	$^1A''$	2.26	60
$:GeF_2$, $^1A_1$	$^3B_1$	3.72	160
	$^1B_1$	5.44	161
	$^3B_2$	8.43	40,111
$:GeCl_2$, $^1A_1$	$^3B_1$	2.78	17,162
	$^1B_1$	3.84	17,162
	$^3B_1$ (?)	2.16	163
:GeHCl, $^1A'$	$^1A''$	2.67	164
$:SnF_2$, ^1A	^3B	3.47**	29,30
	$^1B_1$	5.05	165
$:SnCl_2$, $^1A_1$	$^3B_1$	2.76	153,166
	$^1B_1$	3.85-4.00	17,154
$:PbF_2$, $^1A_1$	$^3B_1$	3.47**	29,30
	$^1B_1$	5.03	165
$:PbCl_2$, $^1A_1$	$^3B_1$	2.73**	29,30
	$^1B_1$	3.84	17,154
$:PbBr_2$, $^1A_1$	$^3B_1$	3.04**	167
	$^1B_1$	4.03**	167
$:PbI_2$, $^1A_1$	$^3B_1$	2.41**	167
	$^1B_1$	4.22**	167

* For leading review on electronic energy levels of transient molecules see: M.E.Jacox. *J. Phys. Chem. Ref. Data.* **17**, 269 (1988)

** Estimated value

Table 5. Excited states structure parameters of three-atom carbenes and their analogues

Molecule :MRR'	Excited state term	r_{M-R} ($r_{M-R'}$), Å	∠RMR', deg.	References
$:CH_2$	$^1A_1$	1.11	102-104	1,3,35
	$^1B_1$	1.06	140	1,35
$:CF_2$	$^3B_1$	1.305	134.3	68,116
:CHF	$^1A''$	1.12	127.2	12,117
		1.297		
	$^3A''$	1.077	120.4[a]	132,137
		1.321		
$:CCl_2$	$^3B_1$	1.730	125.5	137
:CHCl	$^3A''$	1.075	123.3	137
		1.735		
$:CBr_2$	$^3B_1$	1.74[b]	150[b]	27
$:SiH_2$	$^3B_1$	1.55[c]	123.5[c]	145,147
	$^1B_1$	1.49	122-123	32-34
$:SiF_2$	$^3B_1$	1.71[c]	114.9[c]	39,168
	$^1B_1$	1.60	115.9	32,41,42,169
:SiHCl	$^1A''$	1.48	116.1	58
		2.05		
:SiHBr	$^1A''$	1.50	116.6	58
		2.21		
:SiHI	$^1A''$	1.50	116.2	60
		2.43		
$:GeF_2$	$^3B_1$	-	111.6	160

[a] ab initio calculations

[b] unreliable data (see /170/)

[c] estimated value

Table 6. Zero field parameters (according to ESR) and bond angles at the central atom of carbenes in triplet ground state

Molecule :CRR'			D^*, cm^{-1}	E^*, cm^{-1}	∠CRR', deg.	Ref.
1			2	3	4	5
$:CH_2$			0.60-0.79	0.052-0.069	136±8	171-177
:CHC≡CR	R=H		0.628	0	180	178
	R=Me		0.626	0	180	178
	R=Ph		0.541	0.0035	-	178
:CHC≡CC≡CR	R=Me		0.609	0	180	178
	R=t-Bu		0.606	0	180	178
	R=Ph		0.553	0	180	178
:CHCN			0.863	0	180	178
$:C(CN)_2$			1.002	0.0033	165-170	179
$:CHCF_3$			0.712	0.021	~160	179
$:CH(CF_2)_nCF_3$	n=2		0.723	0.027	~160	179
	n=3		0.720	0.024	~160	179
$:C(CF_3)_2$			0.744	0.0437	~140	179
$:C(CMe_3)_2$			0.689	0.039	~143	180
$:CAd_2$	(Ad=adamantyl)		-	-	~152	181
$:CHC_6H_4R$	R=H		0.515	0.0251	~155	182,183
	$R=3-NO_2$		0.523	0.0243	-	184
	$R=4-NO_2$		0.486	0.022	-	184
	R=4-Ph		0.479	0.028	-	184
:CPhR	R=Me		0.496	0.0265	-	179
	R=cyclo-C_6H_{11}		0.492	0.025	-	179
	R=cyclo-C_5H_9		0.500	0.028	-	185
	R=cyclo-C_4H_7		0.488	0.026	-	185
	R=1-benzylcyclobutyl		0.488	0.026	-	185
	R=1-benzylcyclopropyl		0.473	0.026	-	185
	R=CN		0.648	0.014	-	184
:CHAr	Ar=1-naphthyl	cis	0.443	0.020	~140	186
		trans	0.463	0.021	~140	186
	Ar=2-naphthyl	cis	0.493	0.021	~140	186
		trans	0.471	0.024	~140	186
	Ar=9-phenanthryl	cis	0.436	-	-	189
		trans	0.470	-	-	189

Table 6 (continuation)

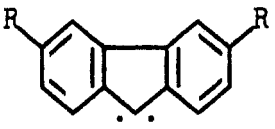
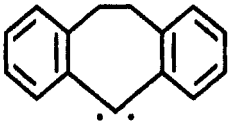
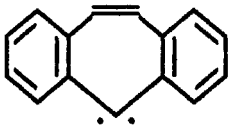
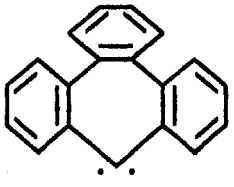
1			2	3	4	5
:CHAr	Ar=2-biphenyl		0.510	0.020	-	190
	Ar=1-anthryl	cis	0.390	-	-	189
		trans	0.420	-	-	189
	Ar=9-anthryl		0.301	-	-	189
	Ar=2-quinolyl	cis	0.531	-	-	189,191
		trans	0.504	-	-	189,191
	Ar=3-quinolyl	cis	0.497	-	-	189,191
		trans	0.470	-	-	189,191
	Ar=4-quinolyl	cis	0.467	-	-	189,191
		trans	0.487	-	-	189,191
	Ar=8-quinolyl	cis	0.433	-	-	189,191
		trans	0.464	-	-	189,191
	Ar=1-pyrenyl		0.40	-	-	192
:$CPhCH_2Ph$			0.493	0.029	-	184
:$CPhC_6H_4R$-4	R=H		0.408	0.021	$147.6^{\pm}1.8$	186-188
	R=Me		0.407	0.019	-	184
	R=MeO		0.404	0.019	-	184
	R=Cl		0.403	0.019	-	184
	R=Br		0.392	0.019	-	184
	$R=NO_2$		0.377	0.018	-	184
:$C(C_6H_4OMe\text{-}4)_2$			0.407	0.019	-	184
:CAr_2	(Ar=9-phenanthrolyl)		0.301	0	180	184
	R=H		0.408	0.028	135	193-196
	R=Br		0.399	0.028	-	197
			0.393	0.017	150	198
			0.379	0.016	-	198
			0.422	0.019	-	198

Table 6 (continuation)

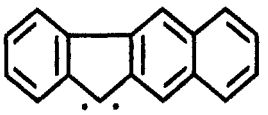
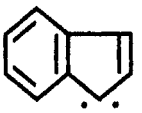
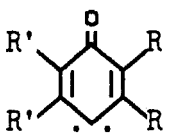
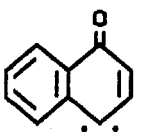
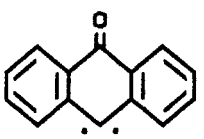
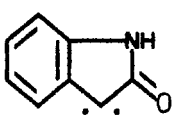
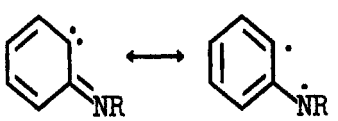
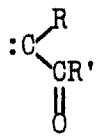
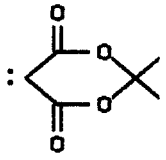
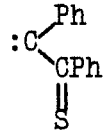
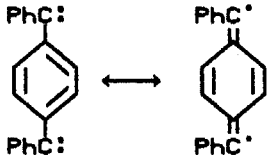
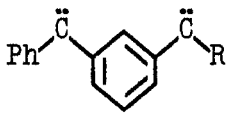
1			2	3	4	5
			0.39	0.030	-	199
			0.378	0.016	-	194
			0.409	0.012	-	194
			0.317	0.009	-	200
	R=R'=H		0.318	0.006	-	201
	R=Cl, R'=H		0.328	0.009	-	201
	R=H, R'=Cl		0.347	0.001	-	201
	R=t-Bu, R'=H		0.314	0.005	-	201
			0.333	0.011	-	201
			0.364	0.018	-	202
			0.38	0.03	-	184
	R=H		0.170	0.003	-	203
	R=Me		0.146	-	-	203
	R=Ph		0.105	0.003	-	203
	R=n-$C_{10}H_{21}$		0.13	0.004	-	203
$R=R^1=R^2=R^3=H$		cis	0.458	0.020	-	189,204
$:C(R)C(R^1)=CR^2R^3$		trans	0.408	0.023	-	189,204
$R=R^1=R^2=H$,		cis	0.457	0.021	-	189
R^3=Me		trans	0.409	0.024	-	189
$R=R^1=H$,		cis	0.454	0.020	-	189
$R^2=R^3$=Me		trans	0.412	0.024	-	189

Table 6 (end)

1		2	3	4	5
	$R=R^2=R^3=H$, $R^1=Me$ cis	0.431	0.025	-	189
	trans	0.401	0.025	-	189
	$R^1=R^2=R^3=H$, R=Me cis	0.453	0.020	-	189
	trans	0.399	0.022	-	189
	$R=R^2=R^3=Me$, $R^1=H$ cis	0.442	0.023	-	189
	trans	0.400	0.022	-	189
	$R=Ph, R^1=H, R^2=R^3=Me$ cis	0.357	0.019	-	189
	R=H, R'=Me cis	0.663	0.030	-	189,205,206
	trans	0.617	0.053	-	189,205,206
	R=H, R'=Et cis	0.661	0.031	-	189,205,206
	trans	0.616	0.053	-	189,205,206
	R=H, R'=H, CF_3 cis	0.605	0.034	-	189,205,206
	trans	0.572	0.079	-	189,205,206
	R=R'=Ph cis	0.392	0.052	-	184,189
	trans	0.312	0.052	-	184,189
	R=MeOCO, R'=Me trans,trans	0.604	0.031	-	189
	cis,trans	0.606	0.051	-	189
		0.578	0.035	-	189
		0.032	0.011	-	207
		0.052	0.002	-	207
	R=H	0.084	0.023	-	208
	R=Ph	0.070-0.071	0.019-0.020	-	209,210

* For definition of these values see: E.Wasserman, L.C.Snyder, W.A.Yager. *J. Chem. Phys.* **41**, 1736 (1964)

Table 7. Geometric and electronic structure parameters of carbenes and their analogues MX_2 in the $^1A_1$ state /211/

M	X	∠XMX, deg.	*IP*, eV	Energy of transition $^1A_1 \longrightarrow {}^1B_1$, eV
C	H	102	10.4	0.9
Si	H	92	-	1.9
Ge	H	90	-	-
C	F	105	11.4-11.8	4.6
Si	F	101	11.0-11.3	5.5
Ge	F	97	11.6-11.8	5.4
Sn	F	95	11.5	5.1
Pb	F	95	11.6	5.0
C	Cl	108	9.1-10.4	2.1
Si	Cl	105	10.0-10.6	3.7
Ge	Cl	100	10.4	3.8
Sn	Cl	99	10.2	3.9
Pb	Cl	98	10.3	3.8
C	Br	110	10.1	1.9
Si	Br	105	-	3.4
Ge	Br	101	9.5	-
Sn	Br	100	10.0	-
Pb	Br	99	10.2	-

Table 8. Bond lengths and force constants of MX_2 and MX_4 molecules in ground state

M	X	MX_2 molecules			MX_4 molecules		
		r_{M-X}, Å	f_{M-X}, N/m·10^2	References	r_{M-X}, Å	f_{M-X}, N/m·10^2	References
C	H	1.08	5.2	2,29,30	1.093	5.4	29,30,215
C	F	1.30	6.0-6.2	6-8,22	1.32	5.6-7.0	6,15,215
C	Cl	1.70-1.76	3.0	212	1.77	3.1-3.6	6.212,215
C	Br	1.87-1.91	2.4	26	1.942	2.4	29.30,215
Si	H	1.52	2.4-2.8	32	1.46-1.48	2.8	216-218
Si	F	1.59	5.0-5.4	213	1.55	6.2-6.6	6,219,220
Si	Cl	2.04-2.08	2.2-2.4	55,56,214	2.02	2.8-3.4	6,72,221-22
Ge	H	1.60	2.1	62	1.53	2.6	218
Ge	F	1.73	4.1	63,65	1.67	5.6	6,222-224
Ge	Cl	2.19	2.1	214	2.11	2.4-2.9	6,214,221, 225
Sn	Cl	2.34	1.9-2.1	6,75,76,214	2.28-2.30	2.5-2.6	6,214,222, 223,226-230
Sn	Br	2.34-2.35	1.6	70	2.27-2.44	1.9-2.4	6,225,231
Pb	Cl	2.45	1.7	6,214	2.43	2.1	214,226-228 232

REFERENCES TO TABLES 1–8

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Table 9. Low-temperature matrix IR- and UV-spectra of carbenes*

Carbene Multiplicity	Precusor and conditions of generation	Spectra	Reference
1	2	3	4
$:CH_2$ triplet	UV-photolysis of H_2CN_2 in Ar-matrix, 6K	**IR:** 1116 cm^{-1}	1
$:CD_2$ triplet	UV-photolysis of D_2CN_2 in Ar-matrix, 6K	**IR:** 819 cm^{-1}	1
$:CF_2$ singlet	UV-photolysis of CF_4 (λ>300nm) in Ar-matrix, 4-20K	**IR:** 1222vs,1102v 668w cm^{-1}; **UV:**210-270 nm	2
:CHF singlet	Vacuum UV-photolysis of CH_3F in Ar(N_2)-matrix,14K	**IR:** 1406vw,1181.5m, 1178m cm^{-1}	3
:CDF singlet	Vacuum UV-photolysis of CDF_3 in Ar(N_2)-matrix,14K	**IR:** 1183m,1180m, 1046m,1043m cm^{-1}	3
$:^{13}CHF$ singlet	Vacuum UV-photolysis of $^3CH_3F$ in Ar(N_2)-matrix,14K	**IR:** 1401w, 1154m cm^{-1}	3
$:CCl_2$ singlet	Reaction of Cl_2 with atomic C in N_2-matrix,14K	**IR:** 748vs,721wm cm^{-1}	4
	Pyrolysis of $C_6H_5HgCCl_3$ at 350°C,Ar-matrix,10K		5
	UV-photolysis of $Cl_2C{=}C{=}O$ (λ>200nm) in Ar-matrix,12K		6
	Pyrolysis of $Cl_2C{=}C{=}O$ at 930°C ($5{\cdot}10^{-3}$Torr), Ar-matrix, 12K		6
	Pyrolysis of $C_6H_5HgCCl_2Br$ at 250-450°C,Ar-matrix,15K		7
	Resonance photoionization of CCl_4 in Ar-matrix,15K		8
:CHCl singlet	Reaction of HCL with atomic C in Ar(N_2)-matrix,14K	**IR:** 1201wm, 815s cm^{-1}	9
:CFCl singlet	Vacuum UV-photolysis of CH_2FCl and CD_2FCl in Ar-matrix,14K	**IR:** 1146vs, 742s cm^{-1}	10
	$CHFCl_2$ and CH_2FCl,Ar-discharge,Ar-matrix,15K	**UV:** 340-390nm	11, 12

Table 9 (continuation)

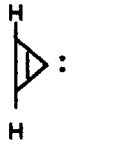
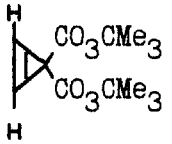
1	2	3	4
:CBr_2 singlet	Reaction of CBr_4 with atomic Li in Ar-matrix,15K	**IR:** 641s, 595w cm^{-1}	13
	Vacuum UV-photolysis of $HCBr_3$ in Ar-matrix,20K		14
	Proton radiolysis of $HCBr_3$ in Ar-matrix,15K		15
:CClBr	Pyrolysis of $C_6H_5HgCClBr_2$ at 250-450 C,Ar-matrix,15K	**IR:** 744,611 cm^{-1}	7
:CFBr singlet	$CHFBr_2$ and CH_2FBr,Ar-discharge,Ar-matrix,15K	**IR:** 1157vs,659w, 656w,647w cm^{-1}	11, 12
:CI_2 singlet	Reaction of CI_4 with atomic Li in Ar matrix,15K	**IR:** 525w cm^{-1}	16
	Pyrolysis of CI_4 at 400°C,Ar-matrix,15K	**IR:** 535w cm^{-1}	16
:CFI singlet singlet	CH_2FI,Ar-discharge, Ar-matrix,15K mic C in Ar(N_2)-matrix,14K	**IR:** 1133vs,1121, 583,576,573s cm^{-1}	11, 12
 triplet	Pyrolysis of  at 480°C,Ar-matrix,12K	**IR:** 1278.6,1277.7, 1063.6,887.1, 787.8 cm^{-1}	17, 18
:CHC≡CH triplet	UV-photolysis of (λ=313,254nm) in Ar-matrix,12K 	**IR:** 3293.0,3266.0, 582.4,547.2,408.8, 402.6,259.9,245.9 cm^{-1}	17
:C=C=CH_2 triplet	UV-photolysis of :CHC≡CH, (λ=313nm) in Ar-matrix,12K	**IR:** 3059.6,3049, 1963.2,1952.2, 1449.3,1446.9,1025.0, 1004.8,999.5 cm^{-1}	17
:CHCN triplet	UV-photolysis of N_2CHCN (λ>350nm) in Ar-matrix,12K	**IR:** 3229s,1735s, 1178.5m,458m cm^{-1} **UV:** 320-340 nm	19
:CDCN triplet	UV-photolysis of N_2CDCN (λ>350nm) in Ar-matrix,12K	**IR:** 2424ms,1729.5s, 1127w,405wm, 317.5m cm^{-1}	19

Table 9 (continuation)

1	2	3	4
:^{13}CHCN triplet	UV-photolysis of $N_2{}^{13}$CHCN (λ>350nm) in Ar-matrix,12K	**IR:** 3229.0,1698.0, 1176.5,458.0 cm^{-1}	19
:CHC^{15}N triplet	UV-photolysis of N_2CHC^{15}N (λ>350nm) in Ar-matrix,12K	**IR:** 3229.0,1718.0, 1168.0,458.0 cm^{-1}	19
:$C(CN)_2$ triplet	UV-photolysis of $(NC)_2CN_2$ (λ>350nm) in Ar-matrix,4K	**IR:** 1756m,1158w, 392w cm^{-1}	20
:$C(CF_3)_2$ triplet	UV-photolysis of $(CF_3)_2C$=N-N (λ>200nm) in Ar-matrix,12K	**IR:** 1380m,1344s, 1197s,1157m, 671m cm^{-1}	21
:$C(CF_3)C(O)CF_3$ triplet	UV-photolysis of $CF_3C(O)(CF_3)CN_2$ (λ>335nm) in Ar-matrix,12K	**IR:** 1763m,1751w, 1748w,1235m,1226s, 1209s,1199s,1167m, 1014w,1011w,905w, 860m,720w,692m, 545w,410w cm^{-1}	22
:$C(CF_3)C(O)C_2F_5$ triplet	UV-photolysis of $C_2F_5C(O)(CF_3)CN_2$ (λ>335nm) in Ar-matrix,12K	**IR:** 1752 cm^{-1}	22
:$C(C_2F_5)C(O)CF_3$ triplet	UV-photolysis of $CF_3C(O)(C_2F_5)CN_2$ (λ>335nm) in Ar-matrix,12K	**IR:** 1762 cm^{-1}	22
:$C(CH_3)OCH_3$ triplet	UV-photolysis of $CH_3O(CH_3)C$=N-N (λ=312nm) in N_2-matrix,10K	**IR**(trans): 1330,1288, 1160,1100,550 cm^{-1} **UV**(trans): 376 nm **IR**(cis): 1320,1275 cm^{-1} **UV**(cis): 385 nm	23
:$C(Cl)OCH_3$ singlet	UV-photolysis of $CH_3O(Cl)C$=N-N (λ=370nm) in N_2-matrix,12K	**IR:** 2975w,1475m, 1465m,1445m,1439m, 1309w,1299m,1140s, 947s,840m,810w,773w, 690m,451m,400m,394m cm^{-1} **UV:** 360 nm(ε 65 l/mol·cm)	24

Table 9 (continuation)

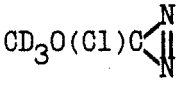
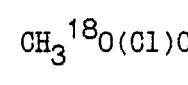
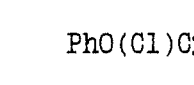
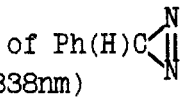
1	2	3	4
:C(Cl)OCD$_3$ singlet	UV-photolysis of  (λ=370nm) in N -matrix,12K	**IR:** 2180w,1362m, 1329w,1305w,1071m, 1050m,950s,925w,805m, 794w,777w,769w,749s, 669m,434m,383m,377w cm^{-1}	**24**
:C(Cl)^{18}OCD$_3$ singlet	UV-photolysis of  (λ=370nm) in N_2-matrix,12K	**IR:** 1446m,1435w, 1277s,1267m,1135m, 920m,820m,793w, 770s,683m,441m, 394m,389w cm^{-1}	**24**
:C(Cl)OPh singlet	UV-photolysis of  (λ=366 and 304 nm) in N_2-matrix,10K	**IR**(cis): 1623w,1597m, 1485s,1464w,1309w,1288w, 1273w,1121m,1069w,1000w, 967w,909m,808m,800w, 744s,678m,550m,415w cm^{-1} **IR**(trans): 1623w,1597w, 1252w,1174w,1148w,1140w, 1021m,1000w,967w,849s, 774m,744s,678m,550m,429w cm^{-1} **UV:** 320 nm(ε 100 l/mol cm)	**25**
:CHPh triplet	UV-photolysis of $PhHCN_2$ (λ>478nm) and of  (λ>338nm) in Ar-matrix,10-15K	**IR:** 3065m,1500m,1460m, 1455w,1432,1390w,1210w, 1090w,1060w,1020w,940w, 885w,760w,740s, 670s,550w,447s cm^{-1} **UV:** 245, 370-434 nm (λ_{max} 430 nm)	**26, 27**
:C(Cl)Ph singlet	UV-photolysis of  (λ>340nm) in Ar-matrix,12K and (λ>300nm) in solid benzene,77K	**IR:** 1593m,1480w,1445m, 1320w,1304m,1284w,1245m, 1226w,1206w,1169s,1023w, 998w,847w,764s,738s,718w, 686w,667m,609w,567m cm^{-1} **UV:** 307,310 nm	**27, 28** **29**
:C(Br)Ph singlet	UV-photolysis of  (λ>340nm) in Ar-matrix,12K and (λ>300nm) in solid i-octane,77K	**IR:** 1588s,1473w,1443m, 1319w,1303m,1281w,1240m, 1224s,1172s,1162w,1023w, 998w,844w,833s,763s,755m, 734w,686m,672s,658s,604m, 553m,544w,500w cm^{-1} **UV:** 328,330 nm	**30** **29**

Table 9 (continuation)

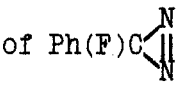
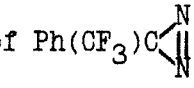
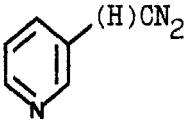
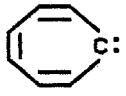
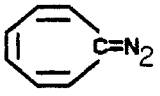
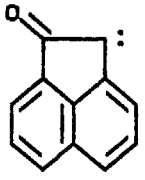
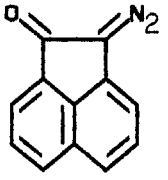
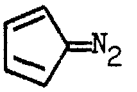
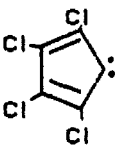
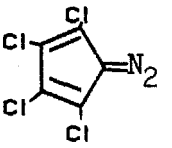
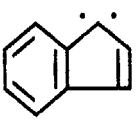
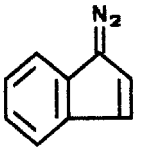
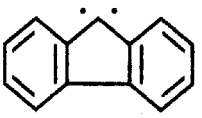
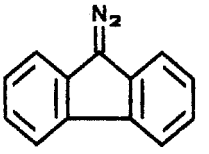
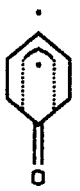
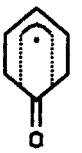
1	2	3	4
:C(F)Ph singlet	UV-photolysis of  (λ>338nm) in Ar-matrix,15K and (λ>300nm) in solid i-octane,77K	**IR:** 1595s,1450m, 1311m,1222s,1164s, 1107s,1082s,1061s, 1020m,834m,758s, 690m,678m,623m cm^{-1} **UV:** 270-300 nm	27 29
:C(CF_3)Ph triplet	UV-photolysis of  (λ>340nm) and of Ph(CF_3)CN_2 (λ>300nm) in Ar-matrix,12K	**IR:** 1599s,1460w,1403m, 1394w,1210s,1163m,1140s, 1129w,1100s,1090w,979w, 913m,751w,743m,671w, 665m,608w,602w cm^{-1}	30
:CPh_2 triplet	UV-photolysis of Ph_2CN_2 (λ>543nm)in Ar-matrix,10K	**IR:** 3072m,1539w,1479m, 1465w,1432w,1282w,1089w, 1060w,1020m,891w,759m, 743s,733w,700m,673s,662w, 565w,496m,456w cm^{-1} **UV:** 454 nm	31
:$^{13}CPh_2$ triplet	UV-photolysis of $Ph_2{}^{13}C{=}N_2$ (λ=543nm) in Ar-matrix,10K	**IR:** 3072m,1538w,1472m, 1467w,1432w,1258w,1089w, 1059w,1019m,887w,755m, 742s,699m,676s,672s,650w, 561m,491m,457w cm^{-1}	31
 triplet	UV-photolysis of  (λ>474nm) in Ar-matrix,10K	**IR:** 1595,1520,1379, 1325,1233,1221,1110, 1015,990,983,943,788, 688,628,600,550,505, 441, 430 cm^{-1}	32
 triplet	UV-photolysis of  (λ>574nm) in Ar-matrix,10K	**IR:** 638 cm^{-1} **UV:** 220,282,294,307, 460,469,491,530 nm	33
 triplet	UV-photolysis of  (λ=365±8nm) in Ar-matrix,10K	**IR:** 1665,1015,767 cm^{-1} **UV:** 563.2,573.4,590.3, 597.1,621.3 nm	34

Table 9 (end)

1	2	3	4
 triplet	UV-photolysis of  (λ>300nm) in N_2-matrix,20K	**IR:** 1345w,1335m, 1101w,1074w,922w, 703s,577w cm^{-1} **UV:** 296 nm	**35**
 triplet	UV-photolysis of  (λ>312nm) in N_2-matrix,12K	**IR:** 1512,1508,1356, 1138,1127,892,882, 703,550,530 cm^{-1} **UV:** 304,310,316,320, 327,332,340,345 nm	**36**
 triplet	UV-photolysis of  (λ>330nm) in N_2-matrix,12K	**IR:** 1305,1302,1180, 766,751,744,741,690 cm^{-1} **UV:** 405,416,427,432, 435,440 nm	**36**
 triplet	UV-photolysis of  (λ>310nm) in N_2-matrix,12K	**IR:** 1599,1035,772,762, 755,743,729,713 cm^{-1} **UV:** 251,436,453,462 nm	36
 triplet	UV-photolysis of  (λ>495nm) in Ar-matrix,10K	**IR:** 1496s,1375m,1362w, 1260m,1076m,937w, 819s cm^{-1} **UV:** 290,297,338,351, 367,379,496,508,521, 535,550,566 nm	37, 38
 singlet	UV-photolysis of  (λ=543±10nm) in Ar-matrix, 10K	**IR:** 1720s,1713s,1679w, 1663w,1520w1305w,1105m, 896w,892w,843m,799m, 741m,583s cm^{-1} **UV:** 337,440 nm	37, 38

* For leading review on vibrational energy levels of transient molecules see: M.E.Jacox. *J. Phys. Chem. Ref. Data.* **13**, 945 (1984)

Table 10. Low-temperature matrix IR- and UV-spectra of carbene analogues

Carbene analog	Precusor and conditions of generation	Spectra	Reference
1	2	3	4
$:SiH_2$	Vacuum UV-photolysis of SiH_4, SiH_2D_2 and SiD_4 in Ar-matrix, 4-14K	IR: 2032vw,2022w,1008w cm^{-1}	39
:SiHD		IR: 879 cm^{-1}	
$:SiD_2$		IR: 1472w,1468m,729m cm^{-1}	
:SiHOH	Reaction of atomic Si with H_2O, D_2O, $H_2{}^{18}O$ and $D_2{}^{18}O$ at UV-photolysis (λ>400 nm) in Ar-matrix,15K	IR: 3650.0,1881.9,1847.1, 937.0,850.6,722.6,595.2 cm^{-1}	40
:SiHOD		IR: 1872.3,895.8,840.5, 563.2,489.8 cm^{-1}	
:SiDOD		IR: 1354.5,840.7,715.1, 521.2,447.3 cm^{-1}	
$:SiH(^{18}OH)$		IR: 1880.0,1841.8,932.1, 823.1,720.0,593.6 cm^{-1}	
$:SiH(^{18}OD)$		IR: 1872.0,892.3,812.1 560.5,486.9 cm^{-1}	
$:SiD(^{18}OD)$		IR: 1362.2,706.2,812.3, 444.0 cm^{-1}	
$:SiF_2$	Vacuum UV-photolysis of SiH_2F_2 and SiD_2F_2 in Ar-matrix,4-14K	IR: 855vs,843s,343 cm^{-1}	41
$:^{30}SiF_2$	Reaction of atomic Si with $^{30}SiF_4$,$^{29}SiF_4$ and $^{28}SiF_4$ at 1150°C, Ne(Ar)-matrix,15K	IR(Ne): 838.03,841.05, 847.3,851.3 cm^{-1}	42
		IR(Ar): 840.0,832.0 cm^{-1}	
$:^{29}SiF_2$		IR(Ne): 838.03,841.05, 845.6,843,11 cm^{-1}	
		IR(Ar): 840.0,832.0 cm^{-1}	
$:^{28}SiF_2$		IR(Ne): 864.6,861.58, 851.01,849.78 cm^{-1}	
:SiHF	Reaction of atomic Si with HF or DF at UV-photolysis in Ar-matrix,15K	IR: 1913.1,859.0,833.7 cm^{-1}	43
:SiDF		IR: 1387.4,833.3,638.4 cm^{-1}	

Table 10 (continuation)

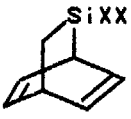
1	2	3	4
$:SiCl_2$	Vacuum UV-photolysis of SiH_2Cl_2 and SiD_2Cl_2 in Ar-matrix,14K	IR: 513s,502vs cm^{-1}	44
	Reaction of $SiCl_4$ with atomic Si (1000°C, 0.1-0.2 Torr), Ar(Ne,N_2)-matrix,15K	IR: multiplets of isotopic splitting 518.7--500.0 and 509.4-481.1 cm^{-1}	45
	Pyrolysis of Si_2Cl_6 (600-1000°C,10^{-2}-10^{-3} Torr),Ar-matrix,15K	IR: multiplets of isotopic splitting 512.0--506.8 and 501.2-487.6 cm^{-1}	46, 47
$:SiBr_2$	Reaction of $SiBr_4$ with atomic Si 1000°C,0.1-0.2 Torr) r(Ne,N_2)-matrix,15K	IR: multiplets of isotopic splitting 402.6--392.7 and 399.5-380.8 cm^{-1}	45
$:SiHCH_3$	Flash-photolysis of  (X,X'=H, D, Cl, CH_3, CH_2D)	IR(Ar): 2001 m,1935w cm^{-1} IR(N_2): 1986w,1978w cm^{-1} UV(Ar): 480 nm UV(N_2): 330 nm	48
$:SiDCH_3$		IR(Ar): 2008w,1937w, 1460w,1448w cm^{-1}	48
$:SiHCH_3$		IR(Ar): 2008w,1937w, 1454m,1409m cm^{-1} IR(N_2): 1990w,1982w, 1974w,1449m,1444m,1438m cm^{-1}	48
$:SiDCH_2D$		IR(Ar): 1223m,485m, 480w cm^{-1} IR(N_2): 1220m cm^{-1}	48
$:Si(Cl)CH_3$		IR(Ar): 840m cm^{-1} UV(Ar): 460 nm UV(N_2): 452 nm	48

Table 10 (continuation)

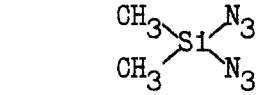
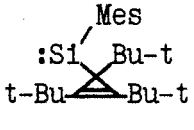
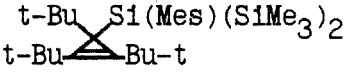
1	2	3	4
$:Si(CH_3)_2$	UV-Photolysis of $[(CH_3)_2Si]_6$ (λ=254nm) in solid 3-methyl-pentane(3-MP),77K and in Ar-matrix,10K	**IR**(Ar): 1438m,1220s cm^{-1} **UV**(Ar): 445 nm **UV**(3-MP): 655,453 nm	49, 50
	UV-photolysis of $[(CH_3)_2Si]_6$ (λ=254nm) in Ar-matrix, 28K	**IR**: 1435m,1220s, 1210m,850s,806vs, 735m,690m cm^{-1}	51
	UV-photolysis of  (λ=254nm) in Ar-matrix, 10-14K	**IR**: 2977s,2942m, 1435m,1222s,1212s, 844s,803w,690w cm^{-1}	52
$:Si(CH_2)_4$cyclo	UV-photolysis of the corresponding polysilane in hydrocarbon matrix, 77K	**UV**: 436 nm	53
$:Si(CH_2)_5$cyclo		**UV**: 449 nm	
$:Si(CH_3)C_6H_5$		**UV**: 490 nm	
$:Si(C_6H_5)_2$		**UV**: 495 nm	
$:Si(Mes)C(CH_3)_3$		**UV**: 505 nm	
:Si(Cl)Mes		**UV**: 487 nm	
$:Si(CH_3)$Mes		**UV**: 497 nm	
:Si(Mes)C≡CH		**UV**: 524 nm	
$:Si(Mes)C_6H_5$		**UV**: 530 nm	
$:Si(Mes)N(SiMe_3)_2$		**UV**: 404 nm	
$:Si(Mes)_2$	UV-photolysis of $(Me_3Si)_2Si(Mes)_2$ in 3-methylpentane matrix, 77K	**UV**: 577 nm	54
	UV-photolysis of  in 3-MP matrix, 77K	**UV**: 450 nm	55

Table 10 (continuation)

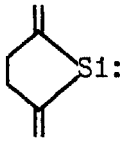
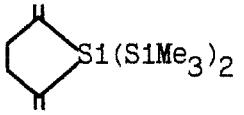
1	2	3	4
	UV-photolysis of  in 3-MP matrix, 77K	**UV:** 505 nm	69
$:GeH_2$	Vacuum UV-photolysis of GeH_4 or GeD_4 in Ar-matrix, 4-25K	**IR:** 1887wm, 1864wm,920wm cm^{-1}	56
$:GeD_2$		**IR:** 1338ms,1329vs, 1325vs,658 cm^{-1}	
$:GeF_2$	Evaporation of $(GeF_2)_n$ in Knudsen cell, Ar(Ne)-matrix, 5K	**IR:** 692,663 cm^{-1}	57
	Evaporation of GeF_4 in Knudsen cell over metallic Ge, Ar(N_2)-matrix, 4.2-10K	**IR**(Ar): 649 cm^{-1} **IR**(N_2): 653 cm^{-1}	58
$:GeCl_2$	Evaporation of $GeHCl_3$ or $(GeCl_2)_n$ in Knudsen cell,Ar(N_2)-matrix, 4.2-15K	**IR**(Ar): 399.7,396.6, 374.5,371.5 cm^{-1} **Raman spect.**(N_2): 390, 362,163 cm^{-1}	59 60
	Vacuum UV-photolysis of GeH_2Cl_2 in Ar-matrix, 4K	**IR:** 397m,372s cm^{-1}	61
:GeHCl	Vacuum UV-photolysis of GeH_3Cl or GeD_3Cl in Ar-matrix,4-25K	**IR:** 1862w cm^{-1}	62
:GeDCl		**IR:** 1343w cm^{-1}	
:GeHBr	UV-photolysis of GeH_3Br or GeD_3Br in Ar-matrix, 8-24K	**IR:** 1858,701,283 cm^{-1}	63
:GeDBr		**IR:** 1336,502,281 cm^{-1}	

Table 10 (continuation)

1	2	3	4
:GeO	Evaporation of Ge and GeO_2 mixture through Ta-tube (900 °C), Ar(Ne,Xe,Kr)-matrix, 5.5K	**UV:** 118-150,180-210, 240-270 nm	64
$:GeMe_2$	UV-photolysis of $(PhMe_2Ge)_2GeMe_2$, 3-MP matrix, 77K	**UV:** 422 nm	65
	UV-photolysis of $Me_2Ge(N_3)_2$, Ar matrix, 26K	**UV:** 405 nm	66
:GePhMe	UV-photolysis of $(Me_3Ge)_2GePhMe$, 3-MP matrix, 77K	**UV:** 456 nm	65
$:GePh_2$	UV-photolysis of $(Me_3Ge)_2GePh_2$, 3-MP matrix, 77K	**UV:** 462 nm	65
$:GeTol_2$	UV-photolysis of $Tol_2Ge(SiMe_3)_2$, 3-MP matrix, 77K	**UV:** 471 nm	67
:GeMes(t-Bu)	UV-photolysis of Mes(t-Bu)Ge(S $Me_3)_2$, 3-MP matrix, 77K	**UV:** 508 nm	67
$:GeMes_2$	UV-photolysis of $Mes_2Ge(SiMe_3)_2$, 3-MP matrix, 77K	**UV:** 550 nm	67
$:GeXy_2$	UV-photolysis of $Xy_2Ge(SiMe_3)_2$ 3-MP matrix, 77K Xy = 2,6-$Me_2C_6H_3$	**UV:** 543 nm	67

Table 10 (end)

1	2	3	4
$:GeAr_2$	UV-photolysis of $Ar_2Ge(SiMe_3)_2$, 3-MP matrix, 77K Ar = 2,6-$Et_2C_6H_3$	**UV:** 544 nm	67
$:GeAr'_2$	UV-photolysis of $Ar'_2Ge(SiMe_3)_2$, 3-MP matrix, 77K Ar'= 2,4,6-i-$Pr_3C_6H_2$	**UV:** 558 nm	67
$:SnCl_2$	Evaporation of $(SnCl_2)_n$ in Knudsen cell, $Ar(N_2)$-matrix, 4-15K	**IR**(Ar): 354.8,352.3, 334.6,330.7 cm^{-1}	60
		Raman spect.(N_2): 341,320,124 cm^{-1}	61
		Raman spect.(Ar): 353,332 cm^{-1}	
$:Sn(CH_3)_2$	Termolysis of $[Sn(CH_3)_2]_6$ or $[Sn(CD_3)_2]_6$ (130°C), Ar-matrix, 5K	**IR:** 2990,2924,1187, 1182w,774,745w, 739,518,504 cm^{-1}	68
$:Sn(CD_3)_2$		**IR:** 2240,2123,1032, 932,927w,596,569w 565,472,462 cm^{-1}	
$:PbCl_2$	Evaporation of $(PbCl_2)_n$ in Knudsen cell, $Ar(N_2)$-matrix, 4.2-15 K	**IR**(Ar): 322.3,319.5, 299.3,295.5 cm^{-1}	59
		Raman spect.(N_2): 305,281,104 cm^{-1}	60
		Raman spect.(Ar): 322,300,103 cm^{-1}	

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Table 11. Ab initio calculations of electron structure and geometry of carbenes and their analogues*

Molecule; the lowest singlet and triplet electron states		ΔE_{S-T}**, kJ/mol	Geometry (bond lengths in Å, angles in degs)	Method of calculation	References
1		2	3	4	5
$:CH_2$	$^1A_1$	37.8	CH 1.113 ∠HCH 101.8	A1	1
	$^3B_1$		1.084 133.2		
:CHF	$^1A'$	-55.2[a]	CH 1.104 CF 1.294 ∠HCF 103.3	A2	2
	$^3A''$		1.073 1.304 121.1		
:CHCl	$^1A'$	-22.6	CH 1.092 CCl 1.725 ∠HCCl 102.1	A2	2
	$^3A''$		1.070 1.699 124.4		
:CHBr	$^1A'$	-17.2	CH 1.091 CBr 1.884 ∠HCBr 102.0	A2	2
	$^3A''$		1.071 1.847 125.1		
$:CF_2$	$^1A_1$	-157.7	CF 1.369 ∠FCF 103.3	A3	4
	$^3B_2$		1.375 120.0		
$:CCl_2$	$^1A_1$	-108.3	∠ClCCl 102.6	A4	5
	$^3B_2$		124.5		
:CHLi	$^1\Delta$	145.2	CLi 1.875 ∠HCLi 180.0	A5	3
	$^3\Sigma$		1.893 180.0		
$:CLi_2$	$^1\Delta_g$	95.0	∠LiCLi 180.0	A6	6
	$^3\Sigma_g^-$		180.0		
:CHBeH	$^1\Delta$	156.1	CBe 1.631 ∠HCBe 180.0	A5	3
	$^3\Sigma^-$		1.642 180.0		
$:CHNH_2$	S	-132.6	CN 1.322 ∠HCN 107.4	A5	3
	T		1.385 126.8		
:CHOH	^1A	-97.6	CO 1.335 ∠HCO 103.1	A5	3
	^3A		1.370 124.7		
$:CHBH_2$	$^1A_1$	-18.0	CB 1.401 ∠HCB 180.0	A5	3
	^3A		1.523 141.1		

Table 11 (continuation)

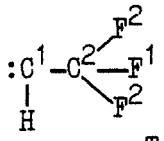
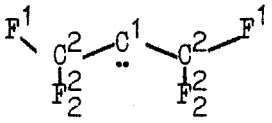
1		2	3	4	5
$:CHCH_3$	$^1A'$	44.8[b]	CC 1.508 ∢HCC 107.4	A5	3
	$^3A''$		1.495 130.9		
$:C(CH_3)_2$	S	58±8	CC 1.54 ∢HCC 104	A7	7
	T		1.52 124		
$:CHCF_3$	S	54.4	C^1H 1.091 C^1C^2 1.512 C^2F^1 1.362	A8	8
			C^2F^2 1.376 ∢HC^1C^2 103.1 ∢$C^1C^2F^1$ 114.4 ∢$C^1C^2F^2$ 110.3 ∢$F^1C^2F^2$ 106.6 ∢$F^2C^2F^2$ 108.4		
	T		C^1H 1.071 C^1C^2 1.474 C^2F^1 1.369 C^2F^2 1.377 ∢HC^1C^2 125.9 ∢$C^1C^2F^1$ 111.6 ∢$C^1C^2F^2$ 112.5 ∢$F^1C^2F^2$ 106.9 ∢$F^2C^2F^2$ 106.1		
$:C(CF_3)_2$	S	74.5	C^1C^2 1.525 C^2F^1 1.360 C^2F^2 1.366	A8	8
			∢$C^2C^1C^2$ 112.6 ∢$C^1C^2F^1$ 109.9 ∢$C^1C^2F^2$ 112.0 ∢$F^1C^2F^2$ 107.7 ∢$F^2C^2F^2$ 108.8		
	T		C^1C^2 1.485 C^2F^1 1.363 C^2F^2 1.367 ∢$C^2C^1C^2$ 128.3 ∢$C^1C^2F^1$ 109.4 ∢$C^1C^2F^2$ 112.3 ∢$F^1C^2F^2$ 107.7 ∢$F^2C^2F^2$ 107.1		
:CHCN	S	80.3	CC 1.46 CH 1.13 ∢HCC 104 ∢CCN 180	A7	7
	T		1.45 1.09 126 180		
:CHNC	S	52.8	∢HCN 103.3 ∢CNC 173.0 ∢HCNC 180	A9	9
	T		125.3 174.5 180		
$:C(CN)_2$	S	75±8	CC 1.46 ∢CCC 104	A7	7
	T		1.45 126		
:CHCHO	S	104.8	CH 1.13 CC 1.53 ∢HCC 106	A7	7
	T		1.09 1.50 126		
$:CHCH{=}CH_2$	S	92.8±8.4	CH 1.13 CC 1.51 ∢HCC 103 ∢CCC 122	A7	7
	T		1.09 1.48 124 125		
$:C(CN)NH_2$	S	-88.0	CC 1.46 ∢NCC 103	A7	7
	T		1.45 124		

Table 11 (continuation)

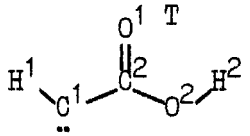
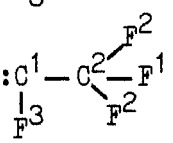
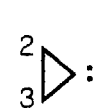
1		2	3	4	5
:CHCOOH	S	31.8	H^1C^1 1.093 C^1C^2 1.470 C^2O^1 1.243 C^2O^2 1.323 $\angle H^1C^1C^2$ 112.6	B1	10
	T		H^1C^1 1.072 C^1C^2 1.461 $\angle H^1C^1C^2$ 126.9 $\angle C^1C^2O^1$ 123.4 $\angle O^1C^2O^2$ 122.4 $\angle C^2O^2H^2$ 108.4		
$:C(CMe_3)_2$	S	104.6	CC 1.573 $\angle CCC$ 132.5	B2	11
	T		1.536 142.4		
:CFCN	S	121.9	$\angle FCC$ 105.2 $\angle CCN$ 180.0	B3	12
	T		134.4 180.0		
$:CFCF_3$	S	-38.1	C^1F^3 1.288 C^1C^2 1.548 C^2F^1 1.358 C^2F^2 1.368 $\angle F^3C^1C^2$ 104.1 $\angle C^1C^2F^1$ 110.4 $\angle C^1C^2F^2$ 111.1 $\angle F^1C^2F^2$ 107.8 $\angle F^2C^2F^2$ 108.5	A8	8
	T		C^1F^3 1.302 C^1C^2 1.485 C^2F^1 1.364 C^2F^2 1.370 $\angle F^3C^1C^2$ 120.0 $\angle C^1C^2F^1$ 109.5 $\angle C^1C^2F^2$ 112.5 $\angle F^1C^2F^3$ 107.8 $\angle F^2C^2F^2$ 106.6		
$:C{=}CH_2$	$^1A_1$	-207.5	CC 1.294 $\angle HCC$ 120.7	A5	3
	$^3B_2$		1.346 121.4		
$:C^1{=}C{=}CH_2$	$^1A_1$	-147.7	CC 1.333 CC^1 1.292 CH 1.084 $\angle HCH$ 116.6	B4	13
	$^3B_2$		CC 1.363 CC^1 1.216 CH 1.076 $\angle HCH$ 118.8		
	$^1A_1$	-277.8	CC^2 1.441 C^2C^3 1.317 C^2H 1.059 $\angle C^2CC^3$ 54.4 $\angle CC^2H$ 149.0	B5	14
	$^3A_2$		CC^2 1.343 C^2C^3 1.579 C^2H 1.053 $\angle C^2CC^3$ 72.1 $\angle CC^2H$ 157.9		
	S	-39.0	CC^2 1.531 C^2C^3 1.492 CH 1.074 $\angle C^2CC^3$ 58.3 $\angle HC^2C^3$ 154.9	B6	15
	T		CC^2 1.469 C^2C^3 1.582 CH 1.074 $\angle C^2CC^3$ 65.2 $\angle HC^2C^3$ 119.3		

Table 11 (continuation)

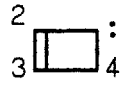
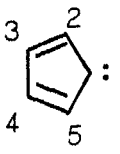
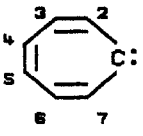
1		2	3	4	5
	S	25±8	CC^2 1.52 CC^4 1.52 C^2C^3 1.337 $\sphericalangle C^2CC^4$ 87 $\sphericalangle$HCH 109	A7	7
	T		CC^2 1.46 CC^4 1.52 C^2C^3 1.337 $\sphericalangle C^2CC^4$ 87 $\sphericalangle$HCH 109		
	$^1A_1$	110.4	CC^2 1.540 C^2C^3 1.323 C^3C^4 1.534 $\sphericalangle C^2CC^5$ 100.8	B5	16
	$^3B_1$		CC^2 1.458 C^2C^3 1.346 C^3C^4 1.486 $\sphericalangle C^2CC^5$ 109.1		
	S	-18.8	C^1C^2 1.446 C^2C^3 1.370 C^3C^4 1.421 C^4C^5 1.361 $\sphericalangle C^7C^1C^2$ 118.7 $\sphericalangle C^1C^2C^3$ 138.4 $\sphericalangle C^2C^3C^4$ 129.8 $\sphericalangle C^3C^4C^5$ 127.5	B7	17
	T		C^1C^2 1.427 C^2C^3 1.347 C^3C^4 1.466 C^4C^5 1.342 $\sphericalangle C^7C^1C^2$ 132.5 $\sphericalangle C^1C^2C^3$ 126.5 $\sphericalangle C^2C^3C^4$ 127.7 $\sphericalangle C^3C^4C^5$ 129.5		
$:SiH_2$	$^1A_1$	-68.6[c]	$\sphericalangle$HSiH 93.4	B8	18
	$^3B_2$		118.0		
:SiHLi	$^1A'$	40.6[d]	SiLi 2.635 $\sphericalangle$HSiLi 94.4	A5	3
	$^3A''$		2.406 140.5		
:SiHBeH	$^1A'$	37.6	SiBe 2.257 $\sphericalangle$HSiBe 94.2	A5	3
	$^3A''$		2.128 128.6		
$:SiHBH_2$	$^1A'$	-36.8	SiB 1.994 $\sphericalangle$HSiB 91.5	A5	3
	$^3A''$		1.961 123.1		
$:SiHCH_3$	$^1A'$	-82.8	SiC 1.907 $\sphericalangle$HSiC 95.8	A5	3
	$^3A''$		1.899 118.6		
$:SiHNH_2$	$^1A'$	-168.6	SiN 1.698 $\sphericalangle$HSiN 95.9	A5	3
	$^3A''$		1.710 120.7		
:SiHOH	$^1A'$	-159.0	SiO 1.638 $\sphericalangle$HSiO 97.1	A5	3
	$^3A''$		1.645 118.5		

Table 11 (end)

1		2	3		4	5
:SiHF	$^1A'$	-158.2	SiF 1.596	∠HSiF 98.3	A5	3
	$^3A''$		1.602	116.0		
$:SiLi_2$	$^1A_1$	43.1	SiLi 2.533	∠LiSiLi 92.0	B9	22
	$^3\Sigma_g^-$		2.429	180.0		
$:SiF_2$	$^1A_1$	-309.6	SiF 1.598	∠FSiF 99.6	B9	22
	$^3B_1$		1.598	113.6		
$:Si(CH_3)_2$	$^1A_1$	-96.0	SiC 1.926	∠CSiC 98.8	B9	22
	$^3B_1$		1.914	117.7		
$:SiHSiH_3$	$^1A'$	-43.1	SiSi 2.391	∠SiSiH 92.0	A5	3
	$^3A''$		2.322	121.6		
$:Si{=}SiH_2$	$^1A_1$	-42.7[e]	SiSi 2.175	∠SiSiH 123.5	A5	3
	$^3A_2$		2.280	163.3		
$:GeH_2$	$^1A_1$	-79.9	GeH 1.607	∠HGeH 92.6	B10	24
	$^3B_1$		1.566	123.7		
$:GeF_2$	$^1A_1$	-309.6	GeF 1.761	∠FGeF 97.5	B10	24
	$^3B_1$		1.749	112.1		
$:Ge(CH_3)_2$	$^1A_1$	-57.3	GeC 2.024	∠CGeC 97.8	B10	24
	$^3B_1$		1.999	117.5		

The data of the most precise calculations described in literature are presented.

**Positive value of ΔE_{S-T} shows that a triplet electron state has a lower energy than a singlet one.

[a] ΔE_{S-T} = -54.1 kJ/mol; MP4 SDTQ/6-31G* (Ref. 3)

[b] ΔE_{S-T} = 69.6 kJ/mol; STO-3G basis; for triplet state calculation at unrestricted HF-approach (Ref. 7)

[c] ΔE_{S-T} = -77.0 kJ/mol; obtained from MRCI+Q calculation at the geometry: SiH 1.502 Å, ∠HSiH 95° ($^1A_1$); SiH 1.465 Å, ∠HSiH 118° ($^3B_1$) (Ref. 19); UCISDQ(P)-calculation 6-31++G(2df,2p) leads to ΔE_{S-T} = -83.3 kJ/mol (Ref. 20)

[d] two minimums, corresponding to different structures of triplet state $^3A'$, on the potential surface of HSiLi were found at DZ+P with SD-CI-calculation; ΔE_{S-T} = 29.3 kJ/mol (Ref. 21)

[e] MC SCF CI-calculation (TZ+P basis) leads to the value of ΔE_{S-T} = -42.2 kJ/mol; SiSi 2.17, SiH 1.474 Å, ∠HSiH 112.6° ($^1A_1$); SiSi 2.269, SiH 1.479 Å, ∠HSiH 108.2° ($^3A_2$) (Ref. 23)

CALCULATION SCHEMES FOR ΔE_{S-T}

A1: basis TZ3p2fn/TZ2p, GVB-RCI

A2: basis for C (5s4p2d), for F (5s4p2d), for H (3s2p), for Cl (7s6p2d), for Br (10s8p4d), TCSCF, with Davidson's amendment (Ref. 26)

A3: MP3/6-31G*

A4: GVB-CI

A5: MP4 SDTQ/6-31G*-calculation in 6-31G* basis

A6: basis for :CLi_2 (9s5p/8s), for :CHLi (9s5p/4s/8s), 2R-CI

A7: STO-3G basis, for T_1-state - unrestricted HF calculations, for S_0 - 2x2 CI

A8: TCSCF for singlet state, DZP-type basis

A9: CI, 6-31G*//6-31G*

B1: DZP basis, SDCI, 19530 configurations for $^1A'$ state, 6635 for $^3A''$

B2: STO-3G basis

B3: STO-3G-type basis, for singlet state 2x2 CI, for triplet state - unrestricted HF calculations

B4: MP2/6-31G**

B5: CI-SD/6-31G*

B6: MP3/6-31G**//3-21G, including ZVPE

B7: DZ+d basis, CI-SD

B8: MP4 SD TQ/6-31G*

B9: 6-31G* basis, CI-SD

B10: DZ+P basis, CI-SDT, calculations of $Ge(CH_3)_2$ without CI

GLOSSARY OF ABBREVIATIONS AND TERMS USED IN TABLE 11

CI = configuration interaction

CI-SD = single and double excitations CI, single reference

CI-SDT = CI-SD plus triple excitations

2R-CI = two-reference CI-SD for singlet state (one for triplet)

TCSCF = two-configuration SCF for singlet (one for triplet); a special case of MCSCF

GVB = generalized valence bond. A restricted form of MCSCF that leads to orbitals localized on atoms (MCSCF = multiconfigurational SCF)

MP4SDTQ/6-31G//3-21G = full fourth-order Moller-Plesset calculations performed with the 6-31G basis set. "//" means "at the geometry from"

See the common basis set notations used in Ref. 25,26.

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