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Quantum-chemical studies of the structure and reactivity of carbenes

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ABSTRACT. **The results of quantum-chemical studies on the electronic and geometrical structures and of the singlet–triplet splitting of carbenes (methylene and its derivatives, including unsaturated and cyclic carbenes) are examined and surveyed. The factors regulating the geometrical characteristics and the multiplicity of the electronic ground state of carbenes are discussed. The features of the reaction pathways leading to the addition of electrophilic and nucleophilic carbenes to single and double bonds and the structures of the transition states are analysed.**

Contents

I. Introduction 622
II. Methylene 622
III. Derivatives and isoelectronic analogues of methylene 626
IV. Unsaturated and cyclic carbenes 627
V. Reactions of carbenes 629

I. Introduction

The improvement of the methods of modern quantum chemistry and especially the colossal progress in the development of high speed computers have created during the last decade a new situation in chemical science. In many fields, theory has become an equal partner of experiment not only in the formulation of general rules and the development of a conceptual language but also in direct quantitative estimation of particular physical and structural characteristics as well as reactivity. The important role of quantum-chemical analysis, which has assumed a parallel or even a leading position, is manifested particularly strikingly in the study of kinetically unstable intermediate compounds whose experimental detection frequently requires the overcoming of considerable difficulties. Carbenes and their analogues are precisely compounds of this kind. An enormous number of original and review communications have been devoted to the theoretical study of carbenes. The fact that carbenes are non-classical organic structures—derivatives of divalent carbon (more precisely dicoordinate carbon), characterised by a very narrow energy gap between the lowest electronic states with different multiplicities—is of special interest for theory. This leads to unique features in the structure and reactions of carbenes which do not fit within the framework of standard classical ideas.

The main task of this review is to demonstrate the role and possibilities of quantum-chemical research in individual principal aspects of the chemistry of carbenes. We shall consider initially a key carbene–methylene. This is a polyatomic molecule which has been subjected to what has probably been the most detailed theoretical study. The structural and energetic parameters of methylene have been calculated in recent years with unprecedented accuracy. The data obtained constitute the basis of the analysis of the geometrical and electronic structures of substituted carbenes and their analogues. Equal attention will be devoted to both quantitative calculations and to qualitative theories which make it possible to treat in general terms the available results and to predict new ones. The description of reactivity will be limited to the consideration of two most representative types of carbene reactions—addition (insertion) to σ and π-bonds.

Although the review deals almost exclusively with studies of the last decade only, it by no means represents an exhaustive treatment even of this period. Nevertheless we hope that the data presented will make it possible to deduce the leading trends in theoretical research into carbenes—the field of chemical knowledge in which the interaction of theory and experiment is especially effective.

II. Methylene

Although the rigorous spectroscopic identification of methylene, obtained in the flash photolysis of gaseous diazomethane, was not achieved until the beginning of the 1960's,[1,2] this simplest divalent carbon compound has been at the centre of attention of chemists—both experimenters and theoreticians—for almost a century since Nef's first "general theory of methylene" (see the relevant reviews[3–5]). The explanation is, firstly, that methylene is the prototype of all carbenes and without due understanding of the nature of its electronic states, structural features, and reactivity, it is impossible to proceed to the formulation of general ideas about the corresponding characteristics of more complex carbenes and their analogues. Secondly, the study of methylene has created a situation, rare as regards its fruitfulness, of a true partnership and mutual enrichment between theory and experiment in chemical science.

In view of the small size of the methylene molecule, in the 1970's it already became possible to calculate all its characteristics using the most powerful arsenal of non-empirical (*ab initio*) quantum-chemical methods, which are comparable to or even superior to modern experimental methods as regards accuracy. Even in the qualitative aspect, the rigorous theoretical conclusions proved to be more accurate than the conclusions drawn from earlier or current experiments. Thus theoretical predictions have stimulated the formulation of more refined experiments and promoted their more accurate interpretation. The need to test and improve quantum-chemical methods, induced by the observed incomplete agreement between the theoretical predictions and experimental data, stimulated in its turn the development of a methodology for the selection of computational models adequate for the problem formulated. The triumphal history, as regards quantum chemistry, of the establishment of the existing views of the electronic and steric structures and

Table 1. The electronic structure, geometry, and energy characteristics of the angular structure of methylene in different electronic states.

Electronic state	Electron shell	Designation adopted*1	HCH angle, deg		R_{CH}, nm		Relative energy, kJ mol^{-1}*3	
			calc.*2	expt.	calc.*2	expt.	calc.	expt.
$^3B_1$	$(1a_1)^2(1b_2)^2(2a_1)^1(1b_1)^1$	$^3(\sigma p)$	134±2 [16]	133.84±0.05 [17]	0.1088 [16]	0.108 [17]	0	0
1^1A_1	$(1a_1)^2(1b_2)^2[(2a_1)^2-\lambda_1(1b_1)^2]$ $(0<\lambda_1<1)$	$^1(\sigma^2)$	102.4 [18]	102.4 [19]	0.112 [18]	0.11 [19]	41.00*4	37.75±0.058 [20]
$^1B_1$	$(1a_1)^2(1b_2)^2(2a_1)^1(1b_1)^1$	$^1(\sigma p)$	141.2 [21]	140 [19]	0.1065 [21]	0.106 [19]	139.7 [22]	—
2^1A_1	$(1a_1)^2(1b_2)^2[\lambda(2a_1)^2+(1b_1)^2]$ $(0<\lambda<1)$	$^1(p^2)$	180 [23]	—	0.107 [23]	—	279.8 [23]	—

*1According to the σ,p designations, introduced by Hoffmann et al.,[24] the $2a_1$ MO belong to the σ type and the $1b_1$ MO belong to the p type; only the principal components of the two-determinant function are indicated for the 1^1A_1 and 2^1A_1 electronic states.[25] *2The basis set $(5s3p1d/3s1p)$ was used by McLaughlin et al.[16] and 617 configurations were examined taking into account the configuration interaction (CI); the DZP basis set was used by Bauschlicher and Shavitt[18] and in the calculation for the $^1A_1$ state, account was taken of all the singly and doubly excited configurations constructed both relative to the $(2a_1)^2$ configuration and relative to the $(1b_1)^2$ configuration (2R-CI, see Table 2); Meadows and Schaefer[21] used the $(9s6p3d/4s2p)$ basis set; Bauschlicher and Yarkony[23] used the Dunning–Husinaga basis set, supplemented by d and p functions, and the MC SCF method; in the calculation for the 2^1A_1 state, they took into account all the singly and doubly excited configurations (SD-CI, see Table 2). *3A detailed compilation of the singlet-triplet ($^3B_1$–$^1A_1$) CH_2 splittings is given in Table 2. *4The estimate is based on the calculated ($^1B_1$–$^3B_1$) energy difference[22] and the experimental ($^1B_1$–$^1A_1$) difference equal to 98.74 kJ mol^{-1}.[26]
Note. Here and henceforth the numerals in square brackets denote references (Editor of Translation).

energetics of the electronic state of methylene has been described in detail in numerous reviews[5–10] and here we shall trace only concisely the principal stages in the solution of the problems involved, emphasising the final results.

1. Electronic configuration

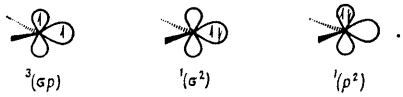
Methylene belongs to the class of molecules with a triplet electronic ground state, which has been unambiguously demonstrated by the observation of the EPR spectrum of CH_2 in a xenon matrix at 4.2 K.[11,12] The results of almost all sufficiently rigorous computations, both semiempirical (INDO,[13] MINDO,[3,14] MNDO[15]) and non-empirical, agree with the idea that the triplet electronic state of CH_2 is energetically preferred, and this conclusion remains valid for all the geometrical forms of methylene possible in principle: linear ($D_{\infty h}$) and angular (C_{2v}) (Table 1). Fig. 1 presents Walsh's diagram illustrating the dependence of the positions of the energy levels of the valence MO of methylene on the HCH valence angle.

For the electronic valence shell $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2$, the electronic states of the linear molecule are arranged in the following energy sequence:

$$^3\Sigma_g^- < {}^1\Delta_g < {}^1\Sigma_g^+.$$

The angular deformation of the linear structure of methylene induces the splitting of the $^1\Delta_g$ state into the $^1A_1$ and $^1B_1$ states.

The structure of the electronic shells of different electronic states of the angular (C_{2v}) form of methylene is characteristic of biradical systems having virtually degenerate highest partly occupied MO.[7] Table 1 illustrates the types of occupation of the MO of methylene and the corresponding electronic states and also presents data obtained by the most rigorous non-empirical calculations in which account has been taken of the electronic correlation and the experimental data for the geometrical characteristics of these states. On the other hand, the $^3(\sigma p)$ and $^1(\sigma p)$ states are described satisfactorily by the usual one-determinant functions:



The states $^1(\sigma^2)$ and $^1(p^2)$, having the same symmetry, require the application of two-determinant functions taking into account the contributions of doubly excited configurations.

2. The geometry of the electronic ground state

The first non-empirical calculation, carried out in 1960[27] using a minimal basis set of Slater type orbitals with allowance for the introduction of a fairly large number (at that time) of electronic configurations (128), already led to the conclusion that the angular structure of the triplet state $^3B_1$ with a HCH angle of 129° is preferred. However, this conclusion was regarded as one not meriting particular confidence, because the interpretation of the electronic spectrum of methylene, current at the time, although not excluding its assignment to a bent structure,[2,19,28] nevertheless favoured the alternative linear $D_{\infty h}$ form.

The conclusion drawn from subsequent quantum-chemical calculations for the methylene molecule (see Schaefer's detailed review[29]) that the triplet state has a linear structure was regarded as "being in excellent agreement with the observed electronic states of CH_2",[28] whereas predictions of the angular structure were regarded

as a consequence of an unsuccessful selection of the computational method.

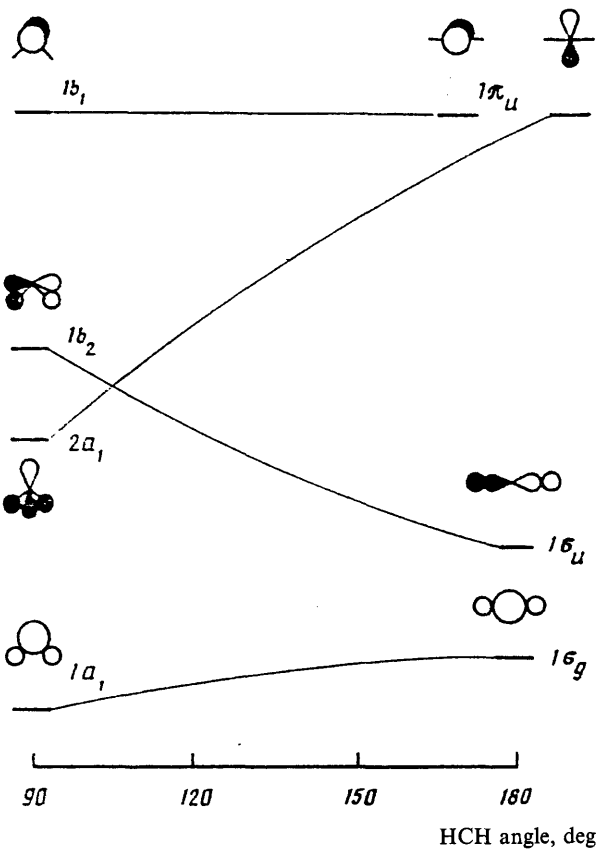


Figure 1. The correlation diagram for the lowest valence MO of the linear and angular structures of methylene illustrating the dependence of the energy levels of the orbitals on the HCH angle.

The situation changed radically after non-empirical calculations,[30] performed with an extremely high degree of accuracy (basis set of Gaussian orbitals of the *DZ* type, allowance for 408 configurations including all single and double excitations) and predicting a HCH angle of 135.1° for the angular C_{2v} form of the ground state of methylene. This value proved to be in good agreement with the value 135 ± 8° obtained soon afterwards from the analysis of the EPR spectrum of triplet methylene,[11] which induced a return to the interpretation of the spectroscopic parameters of CH_2 on the basis of the bent structure.[31] According to the best experimental estimate, it is currently believed that the HCH angle for methylene in the $^3B_1$ state is 133.84 ± 0.05° [17] (Table 1). The energy barrier to the planar inversion of the triplet ($^3B_1$) methylene, i.e.

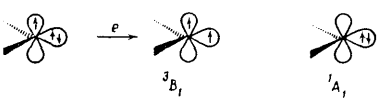


is only 22.32 ± 0.96 kJ mol^{-1} [17] and only two vibrational levels lie below the barrier. This means that the methylene molecule in the ground state should be regarded as essentially quasi-linear, like BaX_2 (X = Cl, Br).[32]

3. Singlet–triplet splitting

The most exact energy difference (ΔE_{S-T}) between the ground triplet ($^3B_1$) and first excited singlet ($^1A_1$) states is 37–38 kJ mol^{-1}. Before proceeding to the discussion of the experimental and calculated data, we may note the difference between the values of ΔE_{S-T} determined experimentally and obtained as a result of the primary quantum-chemical calculation. In the former case, ΔE_{S-T} corresponds to the energy difference between the ground vibrational states (which were designated by T_0) and in the second to the difference (T_e) between the energies of the minima on the potential energy surfaces for the electronic states $^3B_1$ and $^1A_1$. Since in the ground electronic state $^3B_1$ the C–H bonds are shorter and stronger than in the state $^1A_1$ (see Table 1; the experimental energies of the C–H bonds and the theoretical values close to them are 441 kJ mol^{-1} for $^3B_1$ and 410 kJ mol^{-1} for $^1A_1$ [33]), the extension of these bonds in the state $^3B_1$ requires more energy. As a result, the energy of the zero-point vibrations is greater for the triplet state than for the excited singlet state. According to Petek et al.[34] and Bunker and Jensen,[35] $T_e - T_0$ = 0.12 ± 0.71 kJ mol^{-1}. Although allowance for the relativistic correction (about 0.17 kJ mol^{-1} [5,36]) increases this difference to 0.3 kJ mol^{-1}, it is clear that the effects considered are comparatively small.

Up to the middle of the 1970's, ΔE_{S-T} = 33 ± 4 kJ mol^{-1} was adopted as an experimental estimate based on different indirect determinations,[29,37,38] which was in acceptable agreement with the results of most accurate non-empirical quantum-chemical calculations.[6,29,39] However, a direct determination of ΔE_{S-T} in the laser photoionisation of the CH_2^- anion was reported in 1976. This yielded 81.6 ± 2.9 kJ mol^{-1}.[40]



The subsequent series of calculations, in which an increasingly higher accuracy was employed (see the relevant reviews[9,10]) did not bring the theoretical value ΔE_{S-T} and that found by Zittel et al.[40] closer together. This induced theoreticians to reinterpret the experimental data.[41] According to Zittel et al.[40] and Engelking et al.,[41] the beam of CH_2^- anions contains no vibrationally excited ions which could lead to the appearance of additional "hot bands" in the photoelectron spectrum. However, calculation of the energy of the vibrational levels using wave functions obtained with the aid of the generalised valence bond method showed that the fourth vibrational level of CH_2^- lies above the ground vibrational level of the triplet $^3B_1$ state of CH_2,[42] which means that three "hot" bands might have been observed in the photoelectron spectrum of CH_2^- and this band assignment would in fact lead to T_0 = 37.6 kJ mol^{-1} [43,44] in agreement with previous theoretical and experimental data. Modification of the photoionisation experimental method in order to exclude the appearance of "hot bands" made it possible to obtain experimentally T_0 = 37.6 kJ mol^{-1}.[45] Very similar values of T_0 (35.6 ± 2.9 kJ mol^{-1} [46] and 37.86 ± 0.025 kJ mol^{-1} [47]) were found almost simultaneously in other studies whose aim was a direct experimental determination of the energy of the singlet–triplet

splitting in methylene (see also a detailed compilation in other reviews[5,8,9]). At the present time the most accurate experimental estimate of ΔE_{S-T} is believed to be $T_0 = 37.75 \pm 0.058$ kJ mol^{-1}.[20] When account is taken of the corrections for the relativistic effects and the zero-point vibration energy, $T_e = 38.03 \pm 0.84$ kJ mol^{-1} (the diagonal correction to the Born–Oppenheimer approximation is 0.46 kJ mol^{-1} [48]).

4. Methylene as a test structure in quantum chemistry

The theoretical results examined above have generally been achieved with methods giving the highest degrees of accuracy whose employment in the study of more complex carbenes involves considerable computational difficulties. The questions to what extent particular properties of methylene are described by simpler methods, including semiempirical ones and also whether qualitative theoretical ideas adopted in chemistry are applicable to the description of the properties of methylene have therefore acquired extremely great importance. Although the answers to these questions do not guarantee an unambiguous selection of an adequate method for the calculation of the characteristics of more complex carbenes, nevertheless they could be regarded as a very important basis for such a selection and for the estimation of the reliability of a particular calculation.

We shall deal initially with non-empirical calculations (Table 2). The refinement of the results is achieved here both by expanding the set of basis functions and by improving the allowance for electron correlation. In order to obtain geometrical characteristics of methylene in the $^3B_1$ and $^1A_1$ states close to experimental values, it is sufficient to use even the minimal basis set (STO-3G) or the simplest split basis set (3-21G) of the orbitals and the transition from the approximation of the restricted Hartree–Fock method to the unrestricted method and allowance for the energy of electron correlation do not exert a significant influence on the results of the calculation of the CH bond length and the HCH angle.[58,59] On the other hand, Table 2 shows that the selection of the basis set and allowance for the correlation corrections are very important for the estimation of ΔE_{S-T}. When polarisation functions are included in the basis set, the state $^1A_1$ is stabilised to a greater extent because the description of the polarisation orbital of the unshared electron pair $2a_1$ is then improved more than that of the non-polar p orbital $^1b_1$ (Fig. 1). An especially significant improvement is attained when the two-determinant function (TCSCF) is resorted to for the state $^1A_1$. If account is taken of all the single and double excitations relative to both configurations used for the description of this state (2R-CI), it is possible to obtain $\Delta E_{S-T} = 41.0$ kJ mol^{-1}. According to the best estimate of ΔE_{S-T} obtained at the present time by the non-empirical calculation, this quantity is 37.78 kJ mol^{-1},[52] which virtually agrees with the experimental value.

In contrast to the non-empirical computational methods, for which there exists a definite hierarchy ensuring a gradual improvement of the results on going over to higher degrees of accuracy, the semiempirical methods have been parametrised in order to reproduce specific properties (see, for example, Minkin et al.[60]). As a result of this, not only individual properties of a compound but also the properties of all classes of compounds are described better by one of the methods than by others. Comparison of the results of calculations for methylene and its derivatives by the most widely used semiempirical CNDO, INDO,[61] MINDO/2,[62] MINDO/3,[63] and MNDO[15] methods shows quite definitely that preference should be given to the MINDO/3 method. The calculation by this method for the $^3B_1$ state yields the following values: HCH angle 134.1°, $R_{CH} = 0.1078$ nm, and $\Delta E_{S-T} = 36.4$ kJ mol^{-1},[14]† which agrees well with the most accurate experimental data (Table 1).

Table 2. The results of non-empirical calculations of the energy of the singlet–triplet splitting ΔE_{S-T} for methylene (in kJ mol^{-1}).

Basis set	Computational scheme*1					
	SCF	TCSCF	SD-CI	SD(Q)-CI	2R-CI	GVB-RCI
Minimal (2*s*1*p*) for C, (1*s*) for H	167.7 [49]	133.9 [50]				
DZ (4*s*2*p*/2*s*)	135.5 [18, 51]	95.4 [18, 51]	99.2 [18]	92.0 [18]	92.8 [18]	
DZP (4*s*2*p*1*d*/2*s*1*p*)	109.6 [18]	53.5 [18]	61.1 [18]	51.9 [18]	51.0*2 [18]	48.1 [52]
Extended basis set with polarisation functions (6*s*4*p*2*d*/3*s*2*p*)	104.6 [18]	46.4 [18]	55.2 [18]	45.6*3 [18]	44.3*4 [18]	
Very large basis sets [from (8*s*5*p*3*d*/4*s*1*p*) to (9*s*7*p*2*d*1*f*/5*s*2*p*)]	103.7 [18]	44.8 [53]	54.8 [54]	45.2 [54]	41.0 [53]	37.8 [52]

Note. Data presented in two reviews,[5,8] supplemented by the results of subsequent studies, were adopted as a basis; the experimental energy difference is $\Delta E_{S-T} = 37.75 \pm 0.058$ kJ mol^{-1}.[20]

*1For the readers convenience, the notation adopted in the original English language publications has been retained: TCSCF—two-configuration wave function for the state $^1A_1$ (see Table 1); SD-CI—configuration interactions (CI) with allowance for all the singly and doubly excited configurations; SD(Q)-CI—as for SD-CI but account is taken of the correction for fourfold excitations;[55] 2R-CI—allowance for single and double excitations both in the configuration $(2a_1)^2$ and in the configuration $(1b_1)^2$ for the state $^1A_1$; GVB-RCI—calculation by the generalised valence bond method taking into account the restricted CI.

*2With more complete allowance for the CI, $\Delta E_{S-T} = 50.1$ kJ mol^{-1} was obtained.[56]

*3Calculation in terms of the 6-31G basis set.

**Allowance for the electronic configuration in terms of the Meller–Plesset theory (MP4SDTQ) yields $\Delta E_{S-T} = 54.8$ kJ mol^{-1}; expansion of the basis set and extrapolation make it possible to obtain $\Delta E_{S-T} = 34.3$ kJ mol^{-1}.[33]

*4Calculation in terms of the (6*s* 4*p*2*d*; 4*s* 2*p*) basis set yields $\Delta E_{S-T} = 45.6$ kJ mol^{-1}.[57]

The question arises to what extent qualitative theories make it possible to account for the electronic and geometrical structure of methylene. The conclusion that the lowest singlet state of methylene $^1A_1$ or $^1(\sigma)^2$ has a bent structure follows quite definitely from simple orbital ideas and Walsh diagrams. This structure is preferred because of the significant decrease in the energy of the doubly

† However, one should note that the solution obtained by the MINDO/3 method for the state $^1A_1$ is triplet-unstable.[66] This means that the unrestricted Hartree–Fock (UHF) approximation must be resorted to, which makes it possible to obtain for the given state a solution with a lower energy (see, for example, Refs. 67–69). As a consequence of this, ΔE_{S-T} is reduced.

occupied $2a_1$ MO as the valence angle is reduced[64] (Fig. 1). When hybrid orbital ideas are used, i.e. on going over from canonical to localised orbitals, the valence state of the carbon atom of the angular form $^1(\sigma)^2$ of methylene can be described as $(sp^3)^2(sp)^2$, i.e. $s^{3/2}p^{5/2}$,[65] or as $(sp^2)^4$, i.e. $s^{4/3}p^{8/3}$,[8] whereas the valence state of carbon in the linear form is $(sp)^2(p)(p)$, i.e. sp^3. If the valence state of the carbon atom in methylene remained the same as in the ground state of the carbon atom $(1s)^2(2s)^2(2p)^2$, i.e. s^2p^2, singlet methylene would have an angular structure with a valence angle of 90°. In this structure, there is no need for energy expenditure on the $s \rightarrow p$ promotion of a whole electron, as in the transition to the linear form ($s^2p^2 \rightarrow sp^3$) or of "part" of an electron, as in the transition to forms with C–H sp^3-bonds (109.5°) or C–H sp^2-bonds (120°). However, with increase in the valence angle, the repulsion between the electron pairs of these bonds diminishes. The balance between the expenditure on the promotion of an electron from the s to the p orbital, which increases with increase in the valence angle, and the gain attained under these conditions in the repulsion energy of the electrons of the C–H bonds with a simultaneous increase in the strength of the latter as a result of the hybridisation of their constituent carbon orbitals determines the geometry of the singlet methylene.[6,65]

On the other hand, analysis of the Walsh diagram (Fig. 1) for the triplet state $^3B_1$ or $^3(\sigma p)$ does not make it possible to settle reliably on the angular structure. Indeed, the stabilisation attained with decrease in the valence angle of the singly occupied $2a_1$ MO is accompanied by an increase in the energy of the doubly occupied $1b_2$ MO and also by a slight destabilisation of the singly occupied $1b_1$ MO. In particular, Walsh himself was inclined towards the conclusion that the triplet state of methylene has a linear geometrical structure.[64] According to Dewar,[65] the angular structure of the triplet state of methylene can be accounted for within the framework of the idea of σ-conjugation if allowance is made for the fact that the transition, not requiring an energy expenditure on the promotion of s electrons, from the valence state $(sp)^2(p)(p)$, corresponding to the linear structure, to the state $(sp^2)^3(p)$ ensures additional stabilisation of the angular structure as a consequence of the σ-conjugation between the three-hybrid sp^2 orbitals.

III. Derivatives and isoelectronic analogues of methylene

When the hydrogen atoms in the methylene molecule are replaced by the usual substituents (X, Y), the frontier character of the $^3(\sigma p)$ and $^1(\sigma^2)$ states is retained on passing to silylene and other isoelectronic analogues. However, the replacement of the hydrogen atom in CH_2 can induce changes in the XCY valence angle and in the singlet–triplet splitting extending to the stabilisation of the linear form and the reversal of the multiplicity of the ground electronic state. The latter effect is well known. For example, halogenomethylenes as well as silylene SiH_2 and germylene GeH_2 have singlet $^1(\sigma^2)$ ground electronic states.[5,25,70]

The question which substituents promote the stabilisation of the singlet or triplet electronic states is especially interesting, since the reactivity of the carbene depends significantly on the character of the electronic state. The triplet state is preferred if the energy difference between the frontier orbitals is less than the Coulombic repulsion integral J_{12} between the electrons in these orbitals, i.e. $\Delta\varepsilon_{12}-J_{12} < 0$. As a rule, this condition is fulfilled when the splitting of the level of the frontier orbitals $\Delta\varepsilon_{12} \leqslant 1.5$ eV (145 kJ mol^{-1}). With increase in the above energy gap, the ground state of the carbene corresponds to the singlet electronic configuration.[24] Thus the energy gap between the frontier orbitals a_1 and b_1 of methylene is 113 kJ mol^{-1} according to the extremely accurate MP4SDTQ/6-31G** calculations,[71] while for silylene the corresponding value is as much as 217 kJ mol^{-1}.

Hoffmann and co-workers[24,72] formulated qualitatively the general principles of the selection of substituents at the carbene centres which ensures an increase in the energy gap $\Delta\varepsilon_{12}$ and an increased stabilisation of the singlet (compared with the triplet) electronic state of the carbene.[24,72] The substituents must meet the following requirements: (1) they must tend to decrease the XCY valence angle, which leads, as can be seen from Fig. 1, to an appreciable increase in the distance between the σ and p levels; (2) it must have low-lying unoccupied π^* orbitals in one or both substituents; (3) it must have high-lying occupied π or n orbitals in these substituents. The orbital interaction diagrams illustrated in Fig. 2 explain the nature of the stabilisation of the states with closed electron shells.

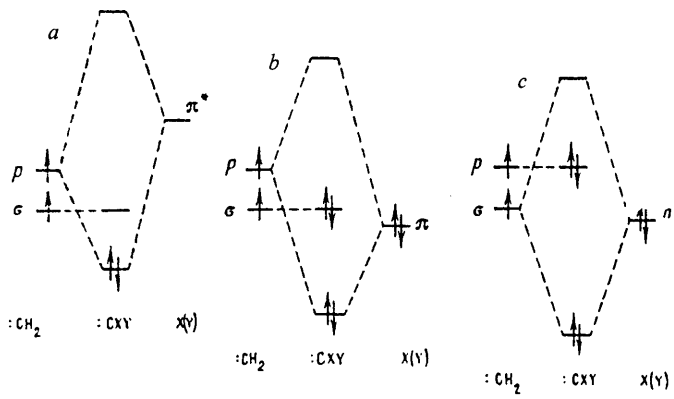


Figure 2. The interactions between the frontier orbitals of methylene (see Fig. 1) and the orbitals of the substituents X and Y in the carbene: CXY; *a*, acceptor substituents with a low-lying unoccupied π^* orbital; *b*, and *c*, donor substituents with high-lying occupied π and n (orbital of the unshared electron pair) orbitals.

Table 3. The singlet–triplet splitting energies ΔE_{S-T} for certain carbenes and their analogues obtained with the aid of non-empirical calculations taking into account the electronic correlation.

Molecule	ΔE_{S-T}, kJ mol^{-1}*1	Method of calculation*2	Refs.
CH_2	37.8 (37.75 [20])	See Table 2	[52]
CHF	−55.2 (~−63 [74]) [−94±28]	A	[74]
CHCl	−22.6 [−70±34]	A	[74]
CHBr	−17.2	A	[74]
CF_2	−240.5 (−236.8 [75])	B	[76]
CCl_2	−108.3 [−130±45]	B	[76]
CHLi	145.2	C	[77]
CLi_2	200.4	D	[78]
CHBeH	156.1	C	[77]
$CHBH_2$	−18.0	C	[77]
$CHNH_2$	−13.0	E	[79]
CHOH	−97.5	C	[77]
$C(OH)_2$	−110.0	F	[73]
FCCN	117.6	F	[73]
$HCCH_3$	69.4	E	[79]
$C(CH_3)_2$	58±8	E	[79]
HCCN	80.3	E	[79]
$C(CN)_2$	75±8	E	[79]
HCCOOH	31.8	G	[80]
$C(Bu\text{-}t)_2$	104.6	H	[81]
$C{=}CH_2$	−207.5	C	[77]
C=O	−682.8	C	[77]
SiH_2	−74.0 (~−58 [87])	I	[82]
	−77.8	K	[21]
	−68.6	C	[71]
	−73.6*3	L	[83]
SiHLi	40.6*4	C	[77]
$SiLi_2$	43.1	L	[83]
SiF_2	−309.6 (−314.6 [84])	L	[83]
GeH_2	−79.5	M	[85]
GeF_2	−309.6	M	[85]
NH_2^+	121.5	N	[86]
$NHLi^+$	175.7	D	[78]
NLi_2^+	166.1	D	[78]
	−25.9	E	[79]
	−298	E	[79]

Note. Compilations of data on the geometries of a number of substituted methylenes have been published.[7,73]

*1The experimental values are given in round brackets and the thermochemical estimates are given in square brackets.[74]

*2Here and below the designations indicated in Table 2 are used.

A) TCSCF, allowance for Davidson's correction;[55] basis set: *(5s4p2d)* for C, *(5s4p2d)* for F, *(3s2p)* for H, *(7s6p2d)* for Cl, and *(10s8p4d)* for Br.[74]

B) Generalised valence bond method (GVB); allowance for CI.

C) MP4SDTQ/6-31G*—calculation in terms of the 6-31G* basis set taking into account the electronic correlation on the basis of the Meller–Plesset perturbation theory (see the footnotes to Table 2).

D) *(9s5p/8s)* basis set for CLi_2 and the *(9s5p/4s/8s)*, 2R-CI basis set for CHLi.

E) STO-3G basis set for the triplet states; caculations in terms of the UHF approximation.

F) Basis set of the STO-3G type; CI 2 × 2 for the singlet state.

G) DZ basis set; SD-CI.

H) STO-3G basis set.

I) 6-31G** basis set; MCSCF.

K) *(9s6p3d)* basis set for silicon and *(4s2p)* basis set for hydrogen.

L) 6-31G* basis set; SD-CI.

M) DZ + P basis set; CI with allowance for not only single and double excitations but also triple excitations.

N) *(9s6p3d)* basis set for nitrogen and *(4s2p)* basis set for hydrogen; TCSCF.

*3When account is taken of the full CI, the quantity ΔE_{S-T} varies from −77 to −73 kJ mol^{-1} depending on the basis set.[88]

*4In calculations in terms of the DZ + P basis set, allowance for the CI (SD-CI) made it possible to observe two minima on the PES for HSiLi corresponding to different structures of the triplet state $^3A''$; ΔE_{S-T} = 29.3 kJ mol^{-1}.[89]

Table 3 presents a compilation of calculated data, which are currently most accurate, for the singlet–triplet splittings in certain simple derivatives and analogues of methylene (in conformity with the requirements imposed on the computational scheme which were discussed in the previous Section).

The results presented agree well with the predictions of the orbital model. In the presence of *n*,π-donor substituents (halogens, amino- and hydroxy-groups) as well as π-acceptor substituents with low-lying unoccupied π^* orbitals (BH_2, O=), the singlet electronic state of the carbene is highly stabilised. The decrease in the electronegativity of the central atom leads to the same result in the series of isoelectronic analogues of methylene: NH_2^+, CH_2, PH_2^+, SiH_2, GeH_2.

A convenient heuristic model, permitting an extremely reliable prediction of the trend towards the stabilisation or destabilisation of the singlet (triplet) state in carbenes and their analogues $AX_2(AXY)$ from the relation between the electronegativity of the central atom A and the substituents X, has been proposed.[78,90]

The increase in the electronegativity of the substituents X(Y) and in the electropositive character of the central atom A led ultimately to the ionic structure $X^-A^{2+}X^-$, in which A^{2+} has a valence electron shell similar to the shell of the beryllium atom with its singlet electronic state ^1S. Consequently, the above factors tend to stabilise the singlet forms of the carbenes and their analogues, as has been observed, for example, for dihalogenocarbenes, silylene, etc. On the other hand, a decrease in the electronegativity of the substituents X and an increase in the electronegativity of the central atom create conditions for the appearance of the limiting ionic structure $X^+A^{2-}X^+$, in which A^{2-} has the electron shell of the oxygen atom. It has a triplet (^3P) ground electronic term. Hence it follows that such substitutions should stabilise the triplet form of carbene and its analogues. This is confirmed by the preference for the triplet states of the cation $^+NH_2$ and the carbenes CHLi and CHBeH (Table 3).

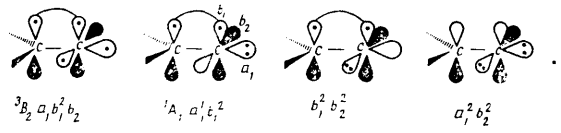
When substituents with a low electronegativity of the central atom, such as those of the Group I–III elements, are introduced at the carbon atom, an interesting stereoelectronic effect appears—the stabilisation of the linear $D_{\infty h}$ structure of the singlet state of the carbene CX_2. The linear form of these carbenes has been predicted qualitatively both within the framework of the delocalised three-centre two-electron bond model[91] and within the framework of the ideas of Pauling's resonance theory.[92] The Li, Be, and B atoms contain unoccupied *p* MO capable of forming common MO with the σ orbital of the singlet carbene, the best overlap conditions and hence the highest stabilisation being attained for the linear and not the angular configuration. The results of non-empirical calculations[59,71,77,78,93] (see also Table 3) agree with this model.

IV. Unsaturated and cyclic carbenes

The multiplicity and electronic structure of unsaturated and cyclic carbenes in their ground states and the reactivity associated with these features are determined by the following three factors: (1) the character of the hybridisation of the σ orbital of the carbene centre, which depends on its valence angle, (2) the aromaticity or anti-aromaticity of the π system which includes the π orbital of the carbene centre, and (3) the effects induced by the involvement of the σ orbital of the carbene centre in the formation of the cyclic σ-conjugation system. The importance of the first two factors was already noted in early theoretical investigations of the electronic structure of carbenes,[24,72,79] while the role of the σ-conjugation began to become clear comparatively recently.[65,94,95] We shall

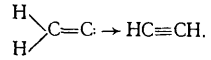
examine the manifestation of the above effects in relation to the most representative carbenes.

Vinylidene. Vinylidene is the prototype of unsaturated alkylidenecarbenes $R^1R^2C=(C)_n=C$: detected as intermediates in many reactions.[96] It can be regarded formally also as a cyclic carbene whose ring has contracted to the maximum extent, i.e. with the minimum (0°) valence angle at the carbene centre. As a result of this, the non-bonding σ orbital a_1 of the vinylidene has the greatest amount of *s* character[97] and therefore has a lower energy level than the σ orbital in methylene. As a result, the presence of the electron pair in the σ orbital (with the configurations $a_1^2b_1^2$ and $a_1^2b_2^2$) proves to be energetically more favourable than the occupation of the $a_1b_1^2b_2$ orbital corresponding to the triplet state. The largest additional contribution to the wave function of the ground singlet state $^1A_1$ of vinylidene also comes from the $b_1^2b_2^2$ valence configuration:[97]



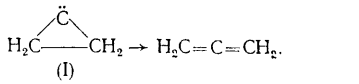
The results of numerous semiempirical[62,72,98] and non-empirical[97,99–101] calculations agree with experimental data[102] showing that the singlet electronic state of vinylidene is preferable. The calculated values of ΔE_{S-T} are as follows (in kJ mol^{-1}): –85.8 (MINDO/2 [62]), –192.0 [*ab initio*, generalised valence bond method, (4*s*2*p*1*d*, 4*s*2*p*1*d*/2*s*) basis set[99]], and –213.8 (*ab initio*, the same basis set, allowance for electron correlation on the basis of the many-particle perturbation theory[97]).

Structurally vinylidene is the prototropic tautomer of the thermodynamically more stable acetylene and the possibility of the experimental detection of vinylidene therefore depends on the energy barrier to the 1,2-shift of hydrogen:



According to the results of non-empirical calculations, the height of this barrier is (taking into account the zero-point vibration energies) 19.2 kJ mol^{-1} [103] or even 3.8 kJ mol^{-1} [104] and it has therefore been suggested that the structure of vinylidene corresponds to a very shallow minimum on the potential energy surface of C_2H_2 or in fact represents the transition state in a degenerate rearrangement of acetylene.[104] Calculations[105] have shown that the energy barrier to the 1,2-shift of hydrogen persists even when a very expanded basis set is used. The barrier has been estimated as 8–17 kJ mol^{-1} (the corresponding lifetimes range from 0.24×10^{-12} to 4.6×10^{-12} s). Experimental studies on the photoionisation of $H_2C=C^-$ have led to the conclusion that the vinylidene does indeed exist and has a lifetime of at least 10^{-14} s.[102] There exist fairly detailed reviews of the theoretical calculations of the 1,2-shift of hydrogen and other migrants in vinylidene and its derivatives.[104,106,107]

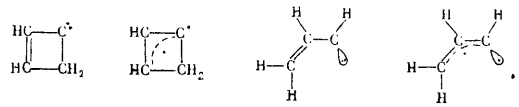
Cyclopropylidene (I). There are no experimental data for the multiplicity of the ground electronic state of cyclopropylidene, but, in view of the smallness of the valence angle at the carbene centre, one may expect in this instance the stability of the singlet electronic configuration $^1(\sigma^2)$. The σ-conjugation effect stabilising this configuration should also be manifested. Indeed, although the results of early non-empirical calculations using the orbital basis sets STO-3G [108] and 4-31G [109] indicated a triplet ground state, allowance for electron correlation and the inclusion in the basis set of polarisation functions led to a revision of this conclusion.[79,110,111] The calculated values of ΔE_{S-T} proved to be –52 kJ mol^{-1} [DZP basis set, SD(Q)-CI allowance for configuration interactions[110]] and –39 kJ mol^{-1} (MP3/6-31G** [111]). It is striking that the CH_2CCH_2 valence angle for the singlet state $^1A_1$ is smaller by 6–7° than for the triplet state. This creates an additional strain in the structure of the ground state of cyclopropylidene, which leads to a low-barrier valence isomerisation (of the "bond extension" type) to the more stable allene:



(I)

According to MP3/6-31G** calculations,[111] the barrier to this reaction is 48 kJ mol^{-1} (see also Klett and Johnson[112]).

Cyclobutenylidene (II). The role of the effect due to the fusion of the *p* orbital of the carbene centre with the π system of the remaining fragment of the molecule is clearly manifested in the case of cyclobutenylidene, although the CH_2CCH angle in this species is much smaller than the HCH angle in methylene. However, both semiempirical (MINDO/3 [113]) and non-empirical (STO-3G, 2 × 2 CI [79]) calculations make it necessary to give preference to the triplet ground state. The quantity ΔE_{S-T} has been estimated as 25 ± 8 kJ mol^{-1}.[79] The evident explanation is that the triplet cyclobutenylidene is in essence a stabilised σ,π-biradical of the allyl type (III):



(II) (III) (IV) (V)

The structure of the species (III) represents the cyclic analogue of the vinylmethylene (IV), which has been studied both experimentally[114] and theoretically[110,115] and for which a planar structure with a triplet ground electronic state of type (V) has been shown to be preferable.

Cyclopropenylidene (VI). When the *p* orbital of the carbene centre is included in the overall π system of the three-membered ring, the latter contains two π electrons, which means that the singlet $^1(\sigma^2)$ configuration is more favourable than the $^3(p\sigma)$ configuration. An important factor promoting the appearance of the $^1(\sigma^2)$ configuration is also the decrease in the energy of the σ orbital of the carbene atom as a consequence of the increased amount of *s* character as a result of the smaller bond angle as compared with methylene.[116,117] Thus the singlet state 1^1A_1 of the zwitter-ionic[25] π-aromatic type (VIa) is stabilised:

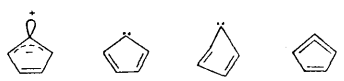


(VI) (VIa)

The stability of the singlet state of cyclopropenylidene has been predicted by both semiempirical[72,118–120] and non-empirical[79,93,121–124] calculations. According to the most accurate estimates, ΔE_{S-T} is –217 kJ mol^{-1} [MK SSP (MCSCF), (4*s*2*p*-C/2*s*-H) basis set[123]] and –294 kJ mol^{-1} (TCSCF, DZ + P basis set[124]). The calculated dipole moment (3.4 D)[124] is extremely high for a hydrocarbon, which agrees well with the prediction that cyclopropenylidene has the structure of the onium anion (VIa).

Cyclopropenylidene has been identified in the matrix isolation of the products of the flash pyrolysis of a quadricyclane derivative[125] and the absence of the EPR signal confirmed the singlet character of its electronic state. Probably by virtue of its π-aromatic character, the species (VI) is distinguished by a fairly high stability towards isomerisation reactions. It is not fortuitous that cyclopropenylidene is one of the components of the molecular clouds in interstellar space.[126]

Cyclopentadienylidene (VII). The singlet π-aromatic six-electron configuration of cyclopentadienylidene arises under the conditions of the double occupation of the $^1(p^2)$ *p*-orbital of the carbene centre, so that the σ orbital remains unoccupied.[25] However, the 6π-electron structure (VIIa) with a carbanion–cation electron distribution (see, for example, the results of calculations by the MINDO/3 and MNDO methods[119,120]) is less stable according to non-empirical MCSCF calculations[127] than the π-antiaromatic 4π-electron structure of the type $^1(\sigma^2)$ (VIIb):

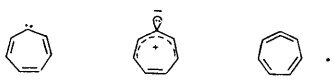


(VIIa) (VIIb) (VIII) (IX)

This unexpected result can be simply explained qualitatively within the framework of the idea of σ-aromaticity and σ-antiaromaticity.[94] In contrast to cyclopropenylidene, whose molecule is both π-aromatic and σ-aromatic, the simultaneous attainment of both π- and σ-aromaticity is impossible for cyclopentadienylidene. The structure (VIIa) is σ-antiaromatic, while the structure (VIIb) is π-antiaromatic. As a result, their energies may prove to be higher than the energy of the triplet state $^3B_1$. Accordingly the zwitterionic singlet state 2^1A_1 ($p^2\sigma^2$) and the singlet state $^1B_1$ of the biradical type ($p^1\sigma^1$) have similar energies for (VIIa), whereas the states 1^1A_1 ($p^0\sigma^2$) and $^1B_1(p^1\sigma^1)$ have similar energies for (VIIb). Consequently the "lumomeric"[128] forms (VIIa) and (VIIb) should be subject to a second-order Jahn–Teller effect and are unstable relative to the b_1-distortion ($a_1 \times b_1 = b_1$) with formation of the structure (VIII) having the C_s symmetry. As a result, the multiplicity of the ground electronic state is determined by the extent to which this distortion stabilises the singlet electronic configuration relative to the structure of the triplet state.

Indeed, according to semiempirical[94,120,129] and non-empirical[130] calculations, the planar structures (VIIa) and (VIIb) do not correspond to minima on the potential energy surface (PES) of the singlet state‡ in contrast to the C_s structure, which has a lower energy. According to the experimental data (see, for example, Wasserman et al.[132] and Baird et al.[133]), calculations by the MINDO/3,[94,120,129] MNDO,[120] and *ab initio*[94,130] methods indicate that cyclopentadienylidene has the $^3B_1$ triplet ground state.

Cycloheptadienylidene (X). With increase in ring size, the effects of σ-aromaticity and σ-antiaromaticity rapidly decay[65] and their role becomes insignificant. The degree of π-aromaticity [the tendency to form the 6π-electron onium anion (Xa)] proved insufficient for the stabilisation of the singlet $^1(\sigma^2)$ state as happens in the case of cyclopropenylidene:



(X) (Xa) (XI)

Indeed the EPR spectrum indicates the triplet character of cycloheptatrienylidene (X),[134,135] which agrees with the results of semiempirical calculations by the MINDO/3[120] and MNDO[120,136] methods. However, the results of non-empirical calculations[137,138] conflict with this conclusion. According to recent calculations (TCSCF, DZ + P basis set[138]), cycloheptatrienylidene nevertheless has a singlet ground state [the planar structure (X) with C_{2v} symmetry, ΔE_{S-T} = –18.8 kJ mol^{-1}]. At the same time, for the equilibrium geometry of the triplet state, the structure of the singlet state has an energy higher by 28.0 kJ mol^{-1}. This can be used to explain the experimental data[134,135] if it is assumed that the rate of the triplet–singlet transition is low and that the carbene (X), generated in the triplet form on photolysis of diazocycloheptatriene, does not have time to relax to the more stable singlet form during the measurement of the spectrum.

It has been shown by semiempirical[120,136,139] and non-empirical[139] calculations that the most stable valence-isomeric form of the carbene (X) is the less symmetrical chiral C_s structure of the singlet cycloheptatetraene (XI), whose energy is lower by 61–96 kJ mol^{-1} than that of the singlet cycloheptatrienylidene. The reactions and rearrangements of cycloheptatetraene (XI) then differ from the reactions of the carbene (X) and different pathways lead to their formation.[140,141]

The energy balance between the carbene and allene forms of cyclic carbenes is determined by the relative contributions of two opposed tendencies: the endeavour to retain the aromaticity in the carbene form and to undergo a transition to a structure with a tetravalent carbon atom. This balance depends primarily on the ring size. Thus, whereas the allene isomer of cyclopentadienylidene (VII) is too strained and does not correspond to a minimum on the PES for C_5H_4,[120] for both cyclononatetraenylidene C_9H_8 and the species (X), the stable cyclic isomer is cyclononapentaene.[120]

V. Reactions of carbenes

The experimental data concerning the influence of the multiplicity of the carbene on its reactivity enabled Skell and co-workers[4,142,143] to formulate definite rules. Firstly, carbenes react at much higher rates in the singlet electronic state than in the triplet state and the absolute rates of typical reactions involving addition to multiple bonds and insertion in C–H bonds normally exceed the rate of intersystem crossing. Secondly, single-stage stereospecific addition to double bonds is characteristic of singlet carbenes, while triplet carbenes react non-stereospecifically, forming initially an intermediate biradical on addition to one of the atoms of the double

‡ *Ab initio* calculations (3-21G basis set) have shown that the planar 6π-electron structures of aza-substituted (2,3-diaza- and 2,3,4- and 2,3,5-triaza) cyclopentadienylidenes also do not correspond to minima on the corresponding potential energy surfaces.[131]

bond. The formation of the trimethylene radical on addition of triplet methylene ($^3B_1$) to ethylene has been confirmed by semi-empirical[62,144] and non-empirical[145,146] quantum-chemical calculations.

Such specificity of the reactivity of carbenes as well as the fact that the majority of the experimentally investigated carbenes have a singlet state have been responsible for the special interest in the reactions of singlet carbenes. The vast majority of theoretical studies have been devoted to their analysis. We shall consider only the reactions involving addition to a carbon–carbon double bond and to single bonds in the study of which the conceptual basis of the theoretical chemistry of carbenes and their analogues has been created.

1. Addition to a C = C bond

From the electronic configuration $^1(\sigma^2)$ of singlet carbenes, one would expect that they should manifest both electrophilic (unoccupied p orbitals) and nucleophilic (the electron pair of the σ orbital) properties. In reactions involving addition to alkenes and other compounds with multiple bonds, the "philicity" of the carbene is determined by the energy gap (ε_{LUMO}–ε_{HOMO}) between the frontier orbitals of the reacting molecules. The stabilising two-electron interaction between these orbitals is greater the smaller the gap and the greater the overlap integral between the frontier orbitals in the region of the transition state of the reaction. The relative disposition of the frontier orbitals of the reactants most typical for carbenes is illustrated in Fig. 3*a*. It corresponds to the predominance of the electrophilic properties of the carbene. Fig. 3*b* illustrates the destabilisation of the p orbital of the carbene after the introduction of strong π-donor substituents X and Y, which has been predicted by non-empirical calculations[147] and which leads to the manifestation of nucleophilic properties ($\sigma \rightarrow \pi^*$ interaction). Finally there is a possibility of the approximate equality of the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow p$ interactions (Fig. 3*c*), which makes it possible to introduce the concept of ambiphilic carbenes.

The "philicity" of the carbene is directly related to the structure of the transition state of the addition reaction. It is well known that the orbital symmetry conservation rules forbid the symmetrical minimum movement pathway (C_{2v}).[144] For electrophilic carbenes with the predominant $\pi \rightarrow p$ interaction, the so called π-approach is preferable (Fig. 3). In the case of nucleophilic carbenes, the best conditions for the overlap of the σ_{CXY} and π^* orbitals are created by the asymmetric σ-approach (Fig. 3*b*). Using certain assumptions, the overlap integrals S between the corresponding frontier orbitals of the carbene and the alkene have been calculated[147,148] in terms of the versions based on the π- and σ-approaches and the energies of the above orbitals have been evaluated, which made it possible to find the stabilisation energies for the two types of interaction of the frontier orbitals:

$$\Delta E \simeq S^2_{HOMO\text{-}LUMO}/(\varepsilon_{LUMO} - \varepsilon_{HOMO} - Q),$$

where $Q \simeq 5$ eV is the correction for the change in the values of ε for the reactants when they approach one another.

The ratio of the stabilisation energies in the nucleophilic (σ) and the electrophilic (π) approaches the theoretical value of the "philicity" $PI_{CXY} = \Delta E_n/\Delta E_e$, which is less than unity for electrophilic carbenes, more than unity for nucleophilic carbenes, and approximately unity for ambiphilic carbenes.

The values obtained are well correlated with the experimental quantities. The following experimentally known carbenes have been assigned to the electrophilic class: BrCCOOEt, MeCCl, CBr_2, PhCBr, PhCCl, PhCF, CCl_2, CFCl, and CF_2 (the electrophilicity diminishes from left to right); MeOCCl and MeOCF are ambiphilic and $(MeO)_2C$ and $MeOCNMe_2$ are nucleophilic. The "philicity" of the carbene can depend even on its conformation. Thus, according to a theoretical estimate,[149] the *cis*-conformer of methoxyphenylcarbene has nucleophilic properties, while its *trans*-conformer is ambiphilic. A review[148] presents calculated data also for the

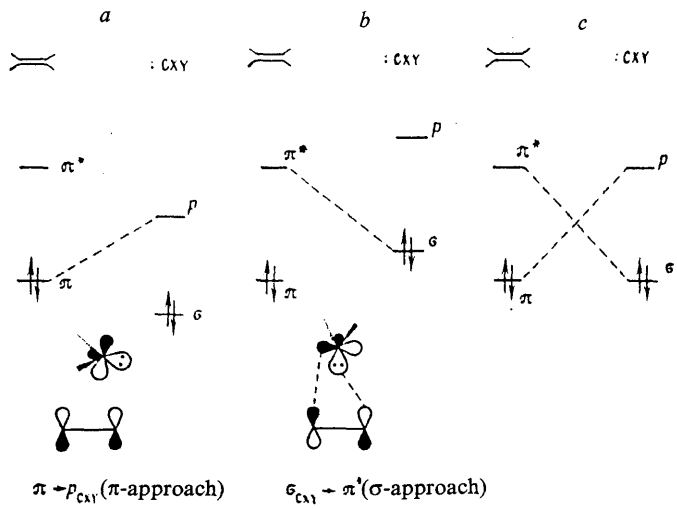


Figure 3. The principal versions of the relative positions of the energy levels of substituted carbenes: CXY and ethylene as a function of the substituents X and Y: *a*, electrophilic carbenes; *b*, nucleophilic carbenes; *c*, ambiphilic carbenes. The order of the energy levels for $:CCl_2$ (*a*) and $:C(NH_2)_2$ (*b*) is maintained.

differences between the orbital energies as a function of the nature of the substituents in the alkene (with the carbene unchanged). Electrophilic carbenes add more readily to alkenes with an electron excess, i.e. after the introduction of π-donors, while nucleophilic carbenes exhibit an increased reactivity following the weakening of the π-bond of the alkene, i.e. after the introduction of acceptor substituents.

Naturally, the "philicity" determined by the method indicated is associated with a specific alkene and on passing from one alkene to another the "philicity" series can be inverted.[148] The causes of this can be understood from Fig. 3: the stabilisation or destabilisation of the π,π^* levels of the alkene induced by the substituents can alter the relative contributions of the π–p and σ–π^* interactions. In practical correlations, the estimates of their extents are frequently restricted to the differences between the energies of the frontier orbitals and the calculation of the quantities ΔE is not resorted to. Thus the relative rate constants for the addition of dichlorocarbene to substituted styrenes are well correlated with the energy difference between the HOMO of styrene and the LUMO of the carbene.[150]

Direct calculations of the reaction pathway leading to the addition of carbenes to alkenes make it possible to discover important details of the internal reaction mechanism. At the level of non-empirical calculations, the reaction of singlet methylene with ethylene has been studied in greatest detail.[151] Like the addition of silylene,[152] this reaction proceeds without a barrier as the attacking species approaches under the plane of the alkene ("internal" approach). The "external" approach of methylene and other carbenes is energetically less favourable[153] and leads to their insertion in a C–H bond.[154] Calculations of reaction pathways of substituted carbenes with the location and identification of the structures of transition states are of greater theoretical interest. The "internal" pathway in the mutual approach of the reactants is a hybrid of the π- and σ-approaches and the transition states of all the reactions investigated have a common structure. In these states $r_1 \neq r_2$. The results of some of the calculations are presented in Table 4.

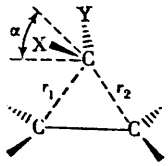


Table 4. Principal geometrical parameters of the structures of the transition states of the reactions involving the addition of carbenes to ethylene according to the results of non-empirical calculations.

Carbene CXY	r_1, nm	r_2, nm	α	Orbital basis set	Refs.
CCl_2	0.195	0.228	19.0	3-21G	[155]
CF_2	0.174	0.216	30.0	3-21G	[155]
FCOH	0.178	0.235	27.6	STO-3G	[147]
$C(OH)_2$	0.178	0.224	49.2	STO-3G	[156]
$C(NH_2)_2$	0.180	0.231	61.2	STO-3G	[156]

A characteristic of the transition states of the reaction involving addition to an alkene, which is especially sensitive to the "philicity" of the carbene, is the angle of inclination of the carbene plane relative to the plane of the double bond. According to Moss and co-workers,[147,148] one can assume that carbenes for which the angle α is less than 45° in the transition states of the reaction involving addition to alkenes are electrophilic. The angles $\alpha > 50°$ correspond to nucleophilic carbenes. The range $45° < \alpha < 50°$ corresponds to ambiphilic carbenes. Non-empirical[147,155,156] and semiempirical (MNDO)[157] calculations of the reaction pathways leading to the addition of various carbenes to ethylene confirmed this rule.

Calculations of the energy barriers and heats of the addition reaction showed that the selectivity of carbenes (at normal temperatures) is linearly related to their stability.[147] This conclusion, reached in the spirit of the usual activity–selectivity relation, does not, however, explain the experimental data about the entropic control of the addition of dichlorocarbene to alkenes,[158] the temperature dependence of the selectivity of dihalogenocarbenes,[159,160] and the zero and even negative activation energies for many cycloaddition reactions of carbenes.[161,162]

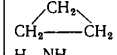
The last effect has come to be usually attributed to the presence on the reaction coordinate of an intermediate complex stable relative to the reactants. Such complexes, corresponding to the very early stages of the π-approach, do indeed appear in non-empirical calculations (basis sets up to the 6-21G level), but, when account is taken of the effects of electron correlation (MP 2/3-21G), they no longer correspond to minima on the PES and cannot therefore exist as kinetically isolatable species.[155,163] The vibration frequencies and entropies of the carbene–alkene reaction system have been calculated[155] at all its stages and the following hypothesis has been put forward. Since the entropy decreases monotonically as the reaction proceeds along the reaction coordinate and these changes are almost independent of the nature of the alkene and the carbene, when the enthalpy is rapidly reduced for reactive carbenes the quantity ΔG is controlled by the entropy term ($-T\Delta S$). Since ΔG reaches a maximum as a result of the increase in this term (with decrease of ΔH along the reaction coordinate), negative activation energies, characteristic of the reactions of the most electrophilic carbenes with electron-enriched alkenes, can also appear. Model potentials have been proposed[155] for the description of ΔH and $-T\Delta S$, which ensure a satisfactory reproduction of the experimental data for the reaction energetics without the inclusion of a stage involving the formation of intermediate complexes.

2. Insertion in single bonds

The reactions involving the addition of carbenes to single bonds, accompanied by the dissociation of the latter, have come to be designated as insertion in the bond. These reactions are extremely characteristic of carbenes and numerous theoretical studies have been devoted to them.[164–170] The calculations have established that the insertion in the H–H, C–H, halogen–halogen, and C–C bonds does not require the overcoming of an energy barrier and proceeds as a concerted reaction which does not follow the path of minimum motion. Two phases can be distinguished in the process involving insertion in a σ-bond: (1) electrophilic attack in which the unoccupied p orbital of the carbene interacts with the bonding orbital of the σ-bond attacked to form a three-centre bond; (2) the subsequent nucleophilic phase determined by the two-electron interaction of the σ orbital of the carbene with the antibonding σ^* orbital. In the second stage, the σ-bond is stretched and dissociates.

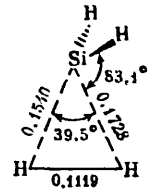
Insertion in the H–H bond. It followed from the early semiempirical (EHM) calculations[164] that the linear configuration >C...H–H, characteristic of a mechanism of the abstraction-recombination type, should occur in the reaction involving the insertion of methylene in the H_2 molecule up to the formation of the transition state. However, more rigorous non-empirical calculations[166,167] led to the observation of the extremely rapid formation of three-centre bonds in the initial stage of the reaction. In contrast to the singlet state, methylene in the ground triplet ($^3B_1$) state is inserted in the H–H bond, overcoming the activation barrier predicted by non-empirical calculations[171] (Table 5). The transition state has a linear configuration and the H–H...CH_2 distance is 0.140 nm. Triplet carbenes also tend to undergo hydrogen abstraction reactions ($^3CH_2 + H_2 \rightarrow CH_3 + H$) and the energy barriers in this and similar reactions are about 100 kJ mol^{-1}.[172]

Table 5. Results of non-empirical calculations of the activation barriers in reactions involving the insertion of carbenes and silylenes in σ-bonds.

Carbene (silylene)	σ-Bond	Reaction product	Method of calculation	Activation barriers*, kJ mol^{-1}	Refs.
$CH_2(^1A_1)$	H—H	—	DZ, CI	0	[167]
$CH_2(^3B_1)$	H—H	CH_4	DZ, CI	45.2	[171]
SiH_2	H—H	SiH_4	DZ+P, CI	26.3	[173]
CHF	H—H	CH_3F	MP4/6-31G*	64.0 (2.7)	[174]
CF_2	H—H	CH_3F_2	MP4/6-31G*	197.0	[174]
SiHF	H—H	SiH_3F	MP4/6-31G*	130.0	[174]
SiF_2	H—H	SiH_2F_2	MP4/6-31G*	273.0	[174]
	H—H		DZ, CEPA	171.2	[168]
$CH_2(^1A_1)$	H—CH_3	C_2H_6	MP3/6-31G*	0	[175]
$CH_2(^1A_1)$	H—CH_2CH_3	CH_3—CH_2—CH_3	MP3/6-31G	0.9	[169]
SiH_2	H—CH_3	SiH_3CH_3	MP3/6-31G*	115.1	[175]
$CH_2(^1A_1)$	H—SiH_3	SiH_3CH_3	MP3/6-31G*	0	[175]
SiH_2	H—SiH_3	Si_2H_6	MP3/6-31G*	0	[175]
$CH_2(^1A_1)$	CH_3—CH_3	$CH_3CH_2CH_3$	MP3/6-31G	192.5	[169]
$CH_2(^1A_1)$		H_2C—CH_2 | | H_2C—CH_2	MP3/6-31G	9.2	[169]
$CH_2(^1A_1)$	H—NH_2	CH_3NH_2	MP4/6-31G*	52.3 (118.0)	[176]
SiH_2	H—NH_2	SiH_3NH_2	MP4/6-31G*	159.1 (104.6)	[177]
SiH_2	H—PH_2	SiH_3PH_2	MP4/6-31G*	83.7 (75.3)	[177]
$CH_2(^1A_1)$	H—OH	CH_3OH	MP4/6-31G*	0	[176]
SiH_2	H—OH	H_3OH	MP4/6-31G*	92.1 (54.4)	[177]
SiH_2	H—SH	SiH_3SH	MP4/6-31G*	58.6 (37.7)	[177]
$CH_2(^1A_1)$	H—F	CH_3F	MP4/6-31G*	0	[176]
SiH_2	H—F	SiH_3F	MP4/6-31G*	41.8 (29.3)	[177]
SiH_2	H—Cl	SiH_3Cl	MP4/6-31G*	33.5 (8.4)	[177]

*The stabilisation energy (E_{st}) of the intermolecular complex relative to the separated reactants is indicated in brackets. The activation barrier differs in such cases from the energy of the complex. For $E_{st} > E_a$, the reaction proceeds without a barrier.

Experimental data for the insertion of silylene in the H_2 molecule are still not available, but according to estimates[178] the lower limit of the activation barrier is 23 kJ mol^{-1}. Theoretical estimates[173,179] (Table 5) agree with this value. Analysis of the structural changes during the reaction $^1SiH_2 + H_2 \rightarrow SiH_4$ led to the conclusion that they are almost identical with those found for the reaction of methylene with hydrogen. The main cause of the appearance of the activation barrier is the different order of the singlet and triplet states of silylene and the appreciable *S–T* splitting.[180,181] The structure of the transition state in the reaction involving the insertion of silylene in the H_2 molecule is shown below [the distances are expressed in nanometers and the calculation was carried out by the MCSCF (4,4)/6-31G* method]:[178]



The influence of the substitution of the hydrogen atoms in silylene on the exothermicity and activation barrier of the reaction involving insertion in H–H bonds has been investigated in relation to its fluoro- and difluoro-derivatives.[174] The activation barrier increases by ~80 kJ mol^{-1} when one fluorine atom is introduced and by 130 kJ mol^{-1} when two fluorine atoms are introduced. This result is almost independent of the size of the basis set and the allowance for the correlation energy. Analysis of the structures of the transition states made it possible to conclude that they become of a "later" type and that there is a simultaneous decrease in the exothermicity of the insertion reaction, in agreement with Hammond's postulates.

A very high activation barier (171 kJ mol^{-1}) has been predicted in non-empirical calculations[168] for the insertion of the cyclic carbene cyclopropenylidene in the H–H bond. This is apparently caused by the marked destabilisation of the "electrophilic" π^* orbital of the carbene and the associated difficulties in the initial stage of the reaction.

Insertion in C–H and Si–H bonds. The insertion of singlet methylene in a C–H bond proceeds without a barrier or with very low activation barriers (0.9 kJ mol^{-1} for ethane) according to experimental[182] and theoretical[169,175,183] data, while an appreciable barrier (115 kJ mol^{-1}) has been predicted for silylene, which agrees with the experimental observations (70–80 kJ mol^{-1} [184,185]). The transition states of the reactions have angular structures with three-centre bonds.

The insertion of methylene and silylene in a Si–H bond does not require the overcoming of an activation barrier. This experimental conclusion has been reproduced theoretically only after careful allowance for correlation corrections.[175]

Insertion in a C–C bond. According to non-empirical calculations taking into account the correlation energy and using an extended basis set of the type 6-31G,[169] the energy profile of the reaction involving the insertion of methylene in a C–C single bond is mainly determined by steric factors. Thus the activation barrier to the insertion in a C–C bond is very high (192.5 kJ mol^{-1}). On the other hand, the similar reaction with cyclopropane should proceed without activation (the barrier is only 9.2 kJ mol^{-1}). After insertion in a C–C bond of a strained ring, whose electron density has a maximum outside the bond axis, strong electronic interactions become possible over longer internuclear distances and the insertion in strained C–C bonds should therefore proceed without an activation barrier according to Gordon et al.[169] Table 5 presents calculated data also for reactions involving the insertion of carbenes in other bonds of the type X–H.

Naturally, the carbene cycloaddition and insertion reactions examined by no means exhaust the entire wide variety of their reactivity. On the other hand, it is these reactions that determine the fundamental stages in the main types of intramolecular rearrangements of carbenes, including the 1,2-shift, ring expansion, and other reactions.[186–188]

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During the preparation of the review for the press, a number of studies on the electronic structure and reactivity of carbenes were published. In particular, semiempirical (MNDO) and non-empirical (3-21G basis set, TCSCF, SD-CI) calculations for low-energy electronic states of cyclopropenylidene (VI) and cyclopentadienylidene (VII) were carried out.[189,190] The lowest biradical type singlet state $^1A_2$ (structure with the C_{2v} symmetry) of cyclopentadienylidene has a lower energy than the singlet states $1^1A_1(p^0\sigma^2)$ (VIIb) and $^1B_1$. The structure (VIIa) of the state $2^1A_1(p^2\sigma^0)$ does not correspond to a minimum on the PES. Non-empirical calculations[190] did not confirm the existence of the allene-type structure (IX), detected in calculations by the MNDO method.[120]

In order to explain the experimentally observed findings concerning the influence of electron-donating solvents on the reactivity of carbenes, non-empirical calculations (3-21G basis set) were carried out[191] for the addition of methylene to ethylene in the presence of a single water molecule. A complex between water and methylene molecules, whose formation makes it possible to account for the decrease in the electrophilicity of methylene, has been found on the PES.

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