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Tuning the Nucleophilicity in Cyclopropenylidenes

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Abstract

Cyclopropenylidenes are Hückel aromatic π -systems in which one of the ring atoms is a carbene center. Quantum chemical calculations at density functional level, supplemented by coupled-cluster calculations, indicate that these species have a sizeable energy separation between the lowest energy singlet and triplet states. Amino groups considerably increase the energy difference between these two states, while electron-withdrawing substituents decrease it. The 1,1-dimerization products of cyclopropenylidenes, namely triafulvalenes, are investigated. The calculations show that, without steric hindrance and considerable electronic stabilization, cyclopropenylidenes are kinetically not stable and dimerize. Different substituents (alkyl, silyl, terphenyl, amino, and phosphaneiminato) were probed to tune the energy levelling of the frontier orbitals in cyclopropenylidenes. Accordingly, it is predicted that by a suitable choice of substituents at the olefinic positions, cyclopropenylidenes can be more nucleophilic than their five-membered ring congeners, namely imidazol-2-ylidenes.

Keywords

cyclopropenylidenes; substituent effects; DFT calculations; S-T energy separation; dimerization energy; triafulvalenes

Introduction

Cyclopropenylidene **1** ($R = H$) is an archetypical ring carbene, which has been first detected in interstellar space,^[1] and in hydrocarbon flames;^[2] then, it was prepared in an acetylene-helium dc discharge.^[3] Under laboratory conditions, this very reactive species was first detected in matrices at very low temperature and detailed characterized by IR spectroscopy.^[4] A lifetime of a couple of hours at 35–40 K was established, and then polymerization occurred (Scheme 1).

Recently the bis(diisopropylamino) substituted cyclopropenylidene **1** ($R = N(iPr)_2$) was reported as a stable compound at room temperature.^[5] It has even been structurally characterized by a single crystal X-ray diffraction study. In addition a chiral diamino-substituted cyclopropenylidene has also been isolated by Holschumacher et al.^[6] The singlet diphenyl cyclopropenylidene **1** ($R = Ph$) has also been investigated lately by McMahon et al. by IR spectroscopy,^[7] albeit in an argon matrix at 10 K. Concomitant calculations predict that other structural isomers, such as propynylidene and propadienylidene, are higher in energy.

The fact that cyclopropenylidenes **1** are now isolable at room temperature, and thus are a novel type of stable nucleophilic carbenes, prompted us to investigate in detail their electronic properties with a variety of substituents [$R = \text{CH}_3$, SiH_3 , NH_2 , $t\text{Bu}$, TMS (trimethylsilyl), NMe_2 , $\text{N}(i\text{Pr})_2$ and $\text{N}(t\text{Bu})_2$]. The silyl groups exemplify π -electron withdrawing substituents, while the amino groups are representatives for π -donors. We also included in our repertoire another type of donor substituent, the phosphorane-iminato ligand, which so far has not been utilized for the stabilization of any carbenes.

A wealth of quantum chemical calculations on parent **1** and its valence isomers has already been reported.[8–30] Most of these investigations are concerned with a detailed spectroscopic analysis of parent **1** or its various valence isomers (e.g.[24,29]), and only a few studies deal with the singlet-triplet (S-T) energy gap.[8,14] Based on MCSCF calculations[8] the S-T gap for the parent compound was estimated to approximately 52 kcal/mol.

In the present publication we report quantum chemical calculations, which deal with some chemical aspects, hitherto not analyzed, but which are of essential importance for the experimental verification of other cyclopropenylidenes, and their assignment of reactivity. In more detail the following points will be considered. a) The S-T energy separation in **1** and the substituent effects; this gives a first understanding of the kinetic stability of cyclopropenylidenes. b) The nucleophilicity and electrophilicity of these new stable carbenes will be compared with the well known cyclic diaminocarbenes (NHCs) **2**. [31] Our investigations predict that cyclopropylidenes with a suitable substitution pattern can be more nucleophilic than any other stable carbenes experimentally reported so far. c) The possible products, which result from 1,1-dimerization[32] will be studied; it will be shown that the easiness of this process depends on the S-T energy separation of the carbene, as well as the steric demand of the substituents.

Results and Discussion

a. Parent Cyclopropenylidene

It is informative to study first the molecular orbital system of the parent cyclopropenylidene **1** ($R = \text{H}$). It is constituted by a Hückel array of cyclic π -molecular orbitals plus the σ -orbital of the carbene function (Figure 1).

The electronic nature of **1** is dominated by cyclic π -conjugation; it follows the Hückel $4n+2$ rule and is similar to that in the cyclopropenyl cation.[33,34] According to EH calculations [35] the two orbitals π_2 and π_3 are alike in energy, the HOMO is the σ -orbital, and the π_1 is slightly below in energy. Consequently, for the energy lowest singlet state one expects a cyclic π -delocalization in the ring. In canonical structures it refers to contributions of **1a** and **1b** (Scheme 2).

In **1a** the lone pair acquires more s character than in **1b**. As will be shown later this argument plays an important role in determining the nucleophilicity of the carbene.

While the electronic configuration of the singlet ground state is defined readily by the configuration $|\pi_1^2\sigma^2\rangle$ [1A_1 , within C_{2v} -symmetry], it is more complicated for the lowest energy triplet state. The σ - and π_1 -orbital are fairly close in energy; hence, for the construction of a triplet state, one can promote one electron from either of the two orbitals into π_2 or π_3 . According to state averaged MCSCF calculations,[36] and in conformity with a previous analysis at a similar computational level,[8] excitations from the σ -orbital yield the lowest energy triplets. This gives rise to two possible triplet states for the cyclopropenylidene $|\pi_1^2\sigma^1\pi_3^1\rangle$ [3B_1] and $|\pi_1^2\sigma^1\pi_2^1\rangle$ [3A_2] sketched in the canonical structures **1c** and **1d** (Scheme 3).

These considerations derive from C_{2v} symmetry of the overall wave function, and **1c** and **1d** can be discussed in terms of Jahn-Teller distortion.[37] A third alternative must be considered, **1e**, which allows superimposition of **1c** and **1d**. The canonical structure **1d** implies a negative charge at the ring atoms and one expects overall a *nonplanar* equilibrium structure with pyramidalization of the substituents at the ring atoms, and different CC bond lengths. Such a conformation is preferable since it is known that cyclopropenyl radicals prefer a nonplanar conformation.[38] More details for the triplet energy hypersurface is given in the Appendix of this publication.

In order to reveal the S-T energy gap of the parent cyclopropenylidene **1**, we performed quantum chemical calculations at different levels of sophistication. This gives information about the validity of the different quantum chemical procedures for the evaluation of the various species. For all investigations a triplet-zeta basis set (TZVP, see Appendix) was employed, in order to obtain a reliable bonding description. The results are summarized in Table 1.

At all levels of sophistication the S-T energy separation appears fairly large. The largest has been found at the MP2 level and the smallest at the RI-BP86 level. For the singlet state the calculations reveal a delocalized π -system with CC-bonds shorter than a corresponding single bond, in comparison to for the triplet with two short and one long CC-bond. It is in accord with the canonical structure **1e**. Of further interest is the σ -orbital energy. For the given reference state (e.g. singlet), it varies considerably as a function of the method; it is larger for the B3LYP and MP2 procedures than for the RI-BP86 approximation. It has been shown, however, that a scale of orbital energies may well differ, but within a given method the relative ordering of orbitals is correctly reproduced.[39,40]

b. Cyclopropenylidene Derivatives

Next the effect of substituents on the S-T energy separation was studied. Since the essential bonding parameters are already well represented at RI-BP86/TZVP level, this procedure was used. Only symmetrical structures were considered (i.e. with identical substituents on both olefinic carbon atoms). The results, including the corresponding frontier orbital energies for the singlet states, are collected in Table 2.

For all of the investigated compounds, the S-T energy separation results again sizeable. For the parent cyclopropenylidene, it is comparable in magnitude to the acyclic diaminocarbene, [42,43] but essentially smaller than for NHCs **2**. [44] Silyl groups ($R = SiH_3$, TMS) and phenyl groups ($R = Ph$, Terphen) decrease the S-T energy separation. These substituents can be considered as π -acceptors, and thus lower the LUMO of the parent system. However this argument assumes that substituent effects on the LUMO are stronger than on the HOMO. Importantly, the S-T energy gap and the energy of the σ -orbital are significantly larger with amino substituents. Pyrrolidino groups which are known to activate considerably an aromatic system,[45] act here similar to dimethylamino groups. With respect to the alkyl- and aryl-substituted derivatives the change in the HOMO energy is approximately 0.5 eV. The influence of an amino group on the S-T energy separation of **1** can be readily understood by consideration of canonical resonance structures **1f** and **1g** depicted in Scheme 4.

In **1f** the endocyclic double bond is located distal to the carbene function while it is lateral in **1g**. In other words the amino group induces a shortening of C(1)C(2) and a lengthening of C(2)C(2') bonds. This view is confirmed by the results of the calculations (see Table 1 and Table 2). It is also in accordance with the results of a population analysis.[36] The induction of a negative charge at the carbene center increases the nucleophilicity of the σ -orbital (Table 2). As compared with parent **1** ($R = H$) the p-character of the σ -orbital is increased. It is the consequence of a rehybridization of the ring orbitals. In **1g** the lateral bonds (to the carbene

function) are shortened when compared with **1f**. Hence these bonds acquire more s-character while leaving the p-electrons to the nonbonding σ -orbital.

A special case is provided by the per-alkyl substituted bulky amino-derivatives. While in **1** [$R = \text{NH}_2$, $\text{N}(\text{CH}_3)_2$, $\text{N}(\text{pyr})_2$] the amino groups are in plane with the ring moiety, such as to maximize π -bonding, in the sterically overloaded systems ($R = \text{N}(t\text{Bu})_2$, $\text{N}(\text{TMS})_2$) the amino groups tend to rotate out of plane formed by the three-membered ring. Corresponding plots of the equilibrium geometries of the singlet states of **1** with $R = \text{N}(t\text{Bu})_2$ and $\text{N}(\text{TMS})_2$ are presented in Figure 2. The twist angle between both groups results for $R = t\text{Bu}$ 55.2 degrees and for $R = \text{TMS}$ 43.2 degrees. Interestingly, the corresponding triplet equilibrium geometry could not be determined by calculations for $R = \text{N}(t\text{Bu})_2$. The corresponding triplet state is not a stable entity on the electronic hypersurface. The steric strain exerted by the $\text{N}(t\text{Bu})_2$ groups is so large that it opens without activation energy barrier to the corresponding propadienylidene biradical.

Some considerations regarding the steric effects of these large substituents compared to diisopropylamino groups (the substituents used for the experimentally characterized derivative) must be discussed here on the basis of the Tolman's concept.[46] For the tert-butyl group, the substituents at the tetrahedral carbon atom are similar in size, and can be inscribed into a *right circular cone*. For iso-propyl groups, the three substituents at the central carbon are different in size leading to an *oblique cone* (Scheme 5).[47]

Hence it is obvious that with di(*iso*-propyl)amino substituents, various conformations are possible, and they differ only slightly in energy (Figure 3). All of the conformers are energy minima on the corresponding electronic hypersurface, and **1A** is the least stable conformer. This is due to the mutual steric hindrance of the methyl groups, which is rather strong and induces a slight distortion of the amino groups out of plane with the three-membered ring system; the corresponding twisting angle results to 34.2 degrees. For **1B** and **1C**, the methyl groups can minimize eclipsing of the hydrogens, and it is optimum for **1C**.

We have calculated the chemical shifts for these conformations on the basis of the RI-BP86/TZVP approximation. For the reported amino-substituted cyclopropenylidene[5] the ^{13}C -NMR signal are at 184 (C(1)) and 158 (C(2)) ppm, in reference to tetramethylsilane. This is in perfect agreement with the results of the calculations, which predict 189 (C(1)) and 157 (C(2)) ppm, for conformation **C**, in contrast to **A** [C(1) 195, C(2) 157 ppm] and **B** [C(1) 187, C(2) 157, C(2') 151 ppm].

c. Nucleophilicity of Cyclopropenylidenes compared to other Carbenes

The philicity of is one of the most important aspects of a singlet carbene and has been scrutinized for the cyclopropanation reaction in terms of Hamett type substituents[48]. frontier orbital considerations[51,52,53,54] and on the basis of electron affinities and ionization potentials of singlet carbenes[49]. Hence, the orbitals depicted in Figure 4 (orbital energies are in eV)[50] give a good rational for the philicity of carbenes, which is determined by the frontier orbital model of carbene reactivity.[51–54] Kohn-Sham energies were for this purpose taken, since it has been shown that these parallel Hartree-Fock type calculations.[39,40]

CF_2 has an energetically low-lying LUMO, and accordingly it is a typical electrophilic carbene. On the other hand NHC **2** ($R = \text{H}$ was chosen) has been so far considered as one of the most nucleophilic carbenes. It has a very high lying HOMO and exerts also an extremely large S-T energy separation.[44] With respect to these extremes the cyclopropenylidenes are of very much interest. The cyclopropylidenes have frontier orbital characteristics of the NHC and thus are nucleophilic carbenes. The amino-substituted derivative **1** ($R = \text{NH}_2$) has a HOMO, even higher than that of **2**, and should therefore be even more nucleophilic.

Can the nucleophilicity of cyclopropenylidenes further be enhanced? The cyclopropenylidene is π -aromatic; however, since cyclopropanes are known to feature σ -aromaticity,[55–60] cyclopropenylidenes are also σ -aromatic. Consequently, it should be possible to polarize the σ -system of the three-membered ring, and accordingly to further lower the ionization potential of the HOMO. An amino group lowers the HOMO energy by approximately 0.5 eV compared to H (see Table 2). Imino-[61] or even better iminato-type substituents should be even more effective, since they possess a lone pair within the ring plane, which could transmit electron density to the HOMO of the carbene. We have evaluated two different phosphaneiminato-substituted cyclopropenylidenes **3** (Figure 5).

In Figure 5, the structures have been described within a ylid formalism, i.e. with no valence extension at the phosphorus atoms. There is now a common understanding that d-orbitals which are required for valence extension to ylene-structures do rarely participate in these structures. [62] The phosphaneiminato substituents with the phosphorane group *cis* to the carbene center is more stable than all other possible conformations. It is due to the attraction of the positively charged phosphonium groups by the negatively charged carbene center, as revealed by corresponding population analysis.[36] Two representatives of **3** have been investigated with PMe_3 (**a**) and $\text{P(NMe}_2)_3$ (**b**) substituents. The energy of the σ -orbital (HOMO) of **3a** and **3b** is similar, but 1.9 and 1.0 eV higher (i.e. a lower ionization potential) than **1** and the diamino substituted cyclopropenylidene, respectively! Thus one predicts that these compounds should be extremely nucleophilic. Importantly, at the same time they are predicted to feature a large S-T separation, which should make them very stable towards dimerization (vide infra).

d. Dimerization of Cyclopropenylidenes: Triafulvalenes

The fate of a carbene, whether or not it remains a stable species under laboratory condition, is essentially depending on the possibility to undergo 1,1-dimerization.[32] In the case of cyclopropenylidenes **1**, this process leads to the corresponding triafulvalenes, which are highly reactive compounds, and were hitherto structurally not characterized (Scheme 6).[63–65]

The dimers of **1** possess a conjugated π -system in which the two double bonds in the three-membered rings destabilize the central π -bond, and therefore it has a very low ionization potential. The extreme electron richness of triafulvenes have been discussed before by skilfully performed quantum chemical calculations.[66] At our quantum chemical level (RI-BP86/TZVP) of optimization we obtained the following orbital energies (in eV) for the HOMO's of the various olefinic systems: a) ethene –6.8, b) tetraaminoethene –4.2, c) parent triafulvalene –3.8 and d) its tetra-amino derivative –2.2. It is in conformity with the recent analysis.[66] If these orbital energies are assigned to Koopman energies, the tetra-amino triafulvalene is extremely electron rich and should be amenable for an easy oxidation reaction.

The energy gain for the dimerization reaction is rather large, since a σ - as well as a π -bond are formed simultaneously. It can only be encumbered by a large S-T energy separation and significant steric demand of the carbene. The former effect has been analyzed by Malrieu and Trinquier,[67] Carter and Goddard.[68,69] Another aspect is the proton induced dimerization of a carbene by a catalytic cycle;[70–73] in the present publication this aspect will not be deepened. Dimerization energies for a selected variety of differently substituted cyclopropenylidenes were calculated. In order to reveal the importance of entropy contributions for the reactions, we first performed vibration analyses (within the harmonic approximation), and secondly calculated free energy contributions by standard thermodynamic formula for the gas phase.[74] The overall results are summarized in Table 3.

As expected the dimerization energies are strongly mediated by the entropy contributions. In this respect an interesting study has been reported by Nyulaszi et al.[75] These authors relate the change in the Gibbs free energy to the overall stabilization energy given by an isodesmic

reaction. In general the entropy factor, in particular the contribution from the translational energy, should favor the monomer formation.[66,76] In the cases presented here only the amino-substituted cyclopropenylidenes reveal an endothermic reaction behaviour, largely driven by the entropy contributions. The differences in energy between the electronic and the entropy energy contributions for the dimerization reaction range from 12.7 kcal/mol ($R = H$) to 20.4 kcal/mol ($R = SiH_3$).

The most sterically overloaded carbene studied is the terphenyl derivatives. As a consequence of strain the $C(2)C(2')$ bonds slightly lengthen, while the $C(1)C(2)$ shortens as compared with the parent compound **1** ($R = H$). Despite the large steric shielding of the carbene center (see Figure 6, **1D**), an exothermic dimerization process is expected on the basis of the electronic energies (the calculation of the entropy contributions was not attempted due to the size of the molecular system). The corresponding triafulvalene is an energy minimum, in the corresponding equilibrium geometry the Terphen substituents are slipping away from each other, to minimize mutual steric hindrance (Figure 7). However, would **1D** dimerize? This remains an open question, since the necessary conformational changes might well cause a barrier towards dimerization. This aspect will be studied in further investigations.

Conclusions

The results of our investigations can be summarized as follows:

Cyclopropenylidenes are Hückel cyclic π -conjugated systems with two electrons in the cyclic moiety. Different states are a priori feasible for the triplet. Calculations show that the one lowest in energy involves the promotion of one electron from the σ to the π_3 orbital, and that the ring atoms are pyramidalized. The S-T energy separation is similar in magnitude to that of the acyclic bisaminocarbenes, but smaller than that of NHCs. Compared to the parent cyclopropenylidene, amino substituents increase the S-T energy difference by approximately 20 kcal/mol. At the same time the HOMO (σ -orbital) is higher in energy, and thus the cyclopropenylidenes become more nucleophilic than their five-membered ring analogues **2**. Even stronger donors are the phosphaneiminato-substituents. They lower the vertical ionization potential by almost 2 eV. Hence our investigations draw attention to a synthetic verification of differently substituted cyclopropenylidenes, which are predicted to be extremely nucleophilic.

On the basis of electronic energies the dimerization of cyclopropenylidenes are exothermic, albeit to much less extent for the amino derivatives. The inclusion of entropy contributions mediates the exothermic energy balance. The dimeric triafulvalenes are sizeable electron rich at the central π -bond, and therefore are predicted to undergo easy oxidation.

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Appendix

a. Computational Details

For all calculations the TZVP basis set of Ahlrichs et al. was employed.[77] It is of triple-zeta quality and augmented by polarization functions at all atoms. All triplet states were investigated within unrestricted wave functions. For the singlet state the UMP2-procedure spin contamination was fairly small ($\langle S^2 \rangle \approx 0$), and needed no correction with the spin projection procedure of Schlegel.[78] The coupled-cluster calculations included triple corrections to the overall correlation energy.[79] The single-point calculations rely on the MP2 (UMP2) energy

optimized geometries. All structures were identified as energy minima with a vibration analysis within the harmonic approximation. The entropies were calculated with a scaling factor of 0.9 for the vibrational contributions, $T = 298.15$ K and $P = 0.1$ MPa. The calculations were performed with the Turbomole 5.7.1[80] and the G03[81] suits of program systems.

b. Triplet States

For the construction of the triplet states one electron can be promoted from the σ -orbital at the carbene site into the π_2 or π_3 molecular orbital of the cyclic π -system. The overall wave function for a planar C_{2v} -symmetrical triplet can thus be described by eq. (1), with $c = 1$ for the 3A_2 and $c = 0$ for the 3B_1 component.

$$\psi = c\phi(^3A_2) + \sqrt{1 - c^2}\phi(^3B_1) \quad (1)$$

It refers to the canonical structures **1c** and **1d**. Since the 3A_2 component bears a negative charge at one of the ring carbon atoms the energy lowest geometry is expected to obey pyramidalization at the ring atoms. This is taken in account by adopting a C_1 -symmetrical structure lowest in energy of the triplet. It is ramificated in the following data, as obtained from UMP2/TZVP calculations (Table 4).

Table 4

UMP2/TZVP calculations at triplet states, $\langle S^2 \rangle$ values are calculated according to ref. [78].

State	symmetry	-E (au)	ΔE (kcal/mol)	ZPE ^a	NIMAG ^b	$\langle S^2 \rangle^c$
3A_2	C_{2v}	114.9344	0.0	0.0265	2	2.125
3B_1	C_{2v}	114.9201	9.0	0.0357	0	2.020
$^3A''$	C_s	114.9344	0.0	0.0265	2	2.124
3A	C_1	114.9483	-8.7	0.0369	0	2.026

^a ZPE = zero point energy (in atomic units (au))

^b NIMAG = number of imaginary frequencies

^c $\langle S^2 \rangle$ = value for spin projection.

Accordingly the 3B_1 component of the wave function is an energy minimum, but the least stable structure. In the most stable one the carbon atoms adopt a pyramidal conformation, albeit the energy difference between energy lowest planar and pyramidal conformation results to less than 10 kcal per mole.

References and Notes

1. Kaiser RI. Chem. Rev 2002;102:1309. [PubMed: 11996539]
2. Taatjes CA, Klippenstein SJ, Hansen N, Miller JA, Cool TA, Wang J, Law ME, Westmoreland PR. Phys. Chem. Chem. Phys 2005;7:806.
3. Thaddeus P, Vritileh JM, Gottlieb C-A. Astrophys. J 1985;299:L63.
4. a) Reisenauer HP, Maier G, Riemann A, Hoffmann RW. Angew. Chem 1984;96:596. Angew. Chem., Int. Ed. Engl 1984;23:641. b) Maier G, Reisenauer HP, Preiss T, et al. Pure Appl. Chem 1997;69:113.
5. a) Lavallo V, Canac Y, Donnadiou B, Schoeller WW, Bertrand G. Science 2006;312:722. [PubMed: 16614171] b) Lavallo V, Ishida Y, Donnadiou B, Bertrand G. Angew. Chem 2006;118:6804. Angew. Chem., Int. Ed 2006;45:6652.
6. Holschumacher D, Hrib CG, Jones PG, Tamm M. J. Chem. Soc., Chem. Commun 2007:3661.
7. DePinto JT, deProphetis WA, Menke JL, McMahon RJ. J. Am. Chem. Soc 2007;129:2308. [PubMed: 17279747]
8. Shepard R, Banerjee A, Simons J. J. Am. Chem. Soc 1979;101:6174.
9. Tsang HT, Li WK. J. Mol. Struct 1983;13:95.
10. Lee TJ, Bunge A, Schaefer HF. J. Am. Chem. Soc 1985;107:137.
11. DeFrees DJ, McLean AD. Astrophys. J 1986;308:L31. [PubMed: 11542031]
12. Bofill JM, Farras J, Olivella S, et al. J. Am. Chem. Soc 1988;110:1694.

13. Miki S, Ohno T, Iwasaki H, Yoshida Z-I. *J. Phys. Org. Chem* 1988;1:333.
14. Jonas V, Böhme M, Frenking G. *J. Phys. Chem* 1992;96:1640.
15. Herges R, Mebel A. *J. Am. Chem. Soc* 1994;116:8229.
16. Montgomery JA Jr, Ochterski JW, Petersson GA. *J. Chem. Phys* 1994;101:5900.
17. Jursic BS. *Int. J. Quantum Chem* 1996;58:41.
18. Takahashi J, Yamashita K. *J. Chem. Phys* 1996;104:6613.
19. delRio E, Barrientos C, Largo A. *J. Phys. Chem* 1996;100:14643.
20. a) Kaiser RI, Ochsenfeld C, Head-Gordon M, Lee YT, Suits AG. *J. Chem. Phys* 1997;106:1729. b) Ochsenfeld C, Kaiser RI, Lee YT, Suits AG, Head-Gordon M. *J. Chem. Phys* 1997;106:4141.
21. Seburg RA, Patterson EV, Stanton JF, McMahon RJ. *J. Am. Chem. Soc* 1997;119:5847.
22. Dateo CE, Lee TJ. *Spectrochim. Acta A Mol. Biomol. Spectrosc* 1997;53:1065.
23. Ikuta S. *J. Chem. Phys* 1997;107:4579.
24. Gauss J, Stanton JF. *Chem. Phys. Lett* 1997;276:70.
25. Apeloig Y, Boese R, Halton B, Maulitz AH. *J. Am. Chem. Soc* 1998;120:10147.
26. Stanton JF, Byun KS. *Mol. Phys* 1999;96:505.
27. a) Redondo P, Redondo JR, Largo A. *J. Mol. Struct* 2000;505:221. b) Redondo P, Redondo JR, Barrientos C, Largo A. *J. Phys. Chem. A* 2000;104:9733.
28. Hess BA, Schaad LJ. *Mol. Phys* 2000;98:1107.
29. Kassae MZ, Hossaini ZS, Haerizade BN, Sayyed-Alangi SZ. *J. Mol. Struct* 2004;681:129.
30. Johnson LE, DuPré DB. *J. Phys. Chem. A* 2007;111:11066. [PubMed: 17929776]
31. a) Arduengo AJ III, Harlow RL, Kline M. *J. Am. Chem. Soc* 1991;113:361. b) Dixon DA, Arduengo AJ III. *J. Phys. Chem. A* 2006;110:1968. [PubMed: 16451031], and further references therein.
32. a) Woodward RB, Hoffmann R. *J. Am. Chem. Soc* 1965;87:395. Woodward, RB.; Hoffmann, R. *The Conservation of Orbital Symmetry*. Weinheim/Bergstr, Germany: Verlag Chemie; 1970.
33. Heilbronner, E.; Bock, H. „*Das HMO-Modell und seine Anwendung*“, Band 1–3. Weinheim, Germany: Verlag Chemie; 1968.
34. a) Breslow R. *J. Am. Chem. Soc* 1957;79:5318. b) Breslow R, Yuan C. *J. Am. Chem. Soc* 1958;80:5991. c) Breslow R, Groves JT, Ryang G. *J. Am. Chem. Soc* 1967;89:5048.
35. For these studies the YaeHMOP program was used, the default values for the ionization potentials and orbital exponents were chosen. The EH method is described in a) Hoffmann R. *J. Chem. Phys* 1963;39:1397. b) Hoffmann R. *J. Chem. Phys* 1964;40:2245. c) Hoffmann R. *J. Chem. Phys* 1964;40:2474. d) Hoffmann R. *J. Chem. Phys* 1964;40:2480.
36. Schoeller WW. unpublished results.
37. Davidson ER, Borden WT. *J. Chem. Phys* 1976;64:663.
38. a) Barone V, Adamo C, Brunel Y, Subra R. *J. Chem. Phys* 1996;105:3168. b) Glukhovtsev MN, Laiter S, Pross A. *J. Phys. Chem* 1996;100:17801.
39. Chong DP, Gritsenko OV, Baerends EJ. *J. Chem. Phys* 2002;116:1760.
40. Stowasser R, Hoffmann R. *J. Am. Chem. Soc* 1999;121:3414.
41. Twamley B, Haubrich ST, Power PP. *Adv. Organomet. Chem* 1999;44:1.; and references therein.
42. Alder RW, Allen PR, Murray M, Orpen AG. *Angew. Chem* 1996;108:1211. *Angew. Chem., Int. Ed. Engl* 1996;35:1121.
43. Heinemann C, Thiel W. *Chem. Phys. Lett* 1994;217:11.
44. Dixon DA, Arduengo AJ III. *J. Phys. Chem* 1991;95:4180.
45. a) Effenberger F, Fischer P, Schoeller WW, Stohrer W-D. *Tetrahedron* 1978;34:2409. b) Knoche W, Schoeller WW, Schomäcker R, Vogel S. *J. Am. Chem. Soc* 1988;110:7484.
46. Tolman C. *Chem. Rev* 1977;77:313.
47. The reader might refer for the distinction of different cones to simple mathematical considerations, e.g. www.mathwords.com.
48. Moss RA. *Acc. Chem. Res* 1980;13:58. Moss RA. *Acc. Chem. Res* 1989;22:15.
49. Sander W, Kötting C, Hübing R. *J. Phys. Org. Chem* 2000;13:561.

50. In the Hartree-Fock formalism the orbital energy depends on its occupation. Since the virtual orbitals are unoccupied, an orbital energy cannot strictly be defined and orbital energies are not given.
51. Kostikov RR, Molchanov AP, Golovanova GV, Zenkevich IG. Zh. Org. Khim 1977;13:1846. Russ. J. Org. Chem 1977;1712.
52. Houk KN, Rondan NG, Paddon-Row MN, Jefford CW, Huy PT, Burrow PD, Jordan KD. J. Am. Chem. Soc 1983;105:5563.
53. a) Moss RA, Young CM, Perez LA, Krogh-Jespersen K. J. Am. Chem. Soc 1981;103:2413. b) Rondan NG, Houk KN, Moss RA. J. Am. Chem. Soc 1980;102:1770. c) Moss RA, Mallon CB, Ho C-T. J. Am. Chem. Soc 1977;99:4105. d) Fujimoto H, Ohwaki S, Endo J, Fukui K. Gazz. Chim. Ital 1990;120:229.
54. a) Schoeller WW, Brinker UH. Z. Naturforsch. B 1980;35B:475. b) Schoeller WW. Tetrahedron Lett 1980;21:1505. c) Schoeller WW. Tetrahedron Lett 1980;21:1509. d) Schoeller WW, Aktekin N, Friege H. Angew. Chem 1982;94:930. Angew. Chem., Int. Ed. Engl 1982;21:932.
55. a) Dewar MJS, McKee ML. Pure Appl. Chem 1980;52:1431. b) Dewar MJ. J. Am. Chem. Soc 1984;106:669.
56. Cremer D, Kraka E. J. Am. Chem. Soc 1985;107:3811.
57. Moran D, Manoharan M, Heine T, Schleyer PvR. Org. Lett 2003;5:23. [PubMed: 12509881]
58. Fowler PW, Baker J, Lillington M. Theor. Acc 2007;118:1432.
59. Pelloni S, Lazzeretti P, Zanasi R. J. Phys. Chem. A 2007;111:8163. [PubMed: 17665879]
60. Göller A, Clark T. J. Mol. Model 2000;6:133.
61. Schoeller WW. Eur. J. Inorg. Chem 2000;369. Schoeller WW, Rozhenko AB. Eur. J. Inorg. Chem 2001;845. Schoeller WW. Z. Anorg. Allg. Chem 2003;629:816. Benk Z, Streubel R, Nyulászi L. Dalton Trans 2006;36:4321. [PubMed: 16967115]
62. Schoeller, WW. Multiple Bonding and Low Coordination in Phosphorus Chemistry. Regitz, M.; Scherer, OJ., editors. Stuttgart, Germany: Thieme Verlag; 1990.
63. Halton B, Cooney MJ, Jones CS, Boese R, Blaser D. Org. Lett 2004;6:4017. [PubMed: 15496088]
64. Halton B. Eur. J. Org. Chem 2005:3391.
65. Hopf, H. Classics in Hydrocarbon Chemistry. Weinheim: Wiley-VCH; 2000.
66. Graham DC, Cavell KJ, Yates BF. J. Phys. Org. Chem 2005;18:295.
67. a) Trinquier G, Malrieu J-P. J. Phys. Chem 1990;94:6184. b) Trinquier G. J. Am. Chem. Soc 1990;112:2130. c) Malrieu J-P, Trinquier G. J. Am. Chem. Soc 1989;111:5916.
68. a) Carter EA, Goddard WA. J. Phys. Chem 1986;90:998. b) Trinquier G, Malrieu J-P. J. Am. Chem. Soc 1987;109:5303. c) Malrieu J-P, Trinquier G. J. Am. Chem. Soc 1989;111:5916. Trinquier, G.; Malrieu, J-P. "The chemistry of the double-bonded functional groups", Suppl. A. Patai, S., editor. Vol. 2. Chichester: Wiley; 1989. p. 1
69. Driess M, Gruetzmacher H. Angew. Chem 1996;108:900. Angew. Chem., Int. Ed. Engl 1996;35:828.
70. a) Alder RW, Blake ME, Chaker L, Harvey JN, Paolini F, Schütz J. Angew. Chem 2004;116:6020. Angew. Chem. Int. Ed 2004;43:5896. b) Alder RW, Blake ME. Chem. Commun 1997:1513.
71. Graham DC, Cavell KJ, Yates BF. J. Phys. Org. Chem 2005;18:298.
72. a) Liu Y, Lemal DM. Tetrahedron Lett 2000;41:599. b) Lemal DM, Lovald RA, Kawano KI. J. Am. Chem. Soc 1964;86:2518.
73. Arduengo AJ III, Goerlich JR, Marshall WJ. Liebigs Ann. Chem 1997:365.
74. McQuarrie, DA.; Donald, A.; Simon, JD. Physical Chemistry: A Molecular Approach. University Science Books; 1999.
75. Nyulászi L, Veszpremi T, Forro A. Phys. Chem. Chem. Phys 2000;2:3127.
76. Taton TA, Chen P. Angew. Chem 1996;108:1098. Angew. Chem., Int. Ed. Engl 1996;35:1011.
77. Schäfer A, Huber C, Ahlrichs R. J. Chem. Phys 1994;100:5829.
78. Chen W, Schlegel HB. J. Chem. Phys 1994;101:5957.
79. Auer AA, Gauss J. J. Chem. Phys 2001;115:1619.
80. Ahlrichs R, Bär M, Häser M, Horn H, Kölmel C. Chem. Phys. Lett 1989;162:165.

81. Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Montgomery, JA., Jr; Vreven, T.; Kudin, KN.; Burant, JC.; Millam, JM.; Iyengar, SS.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, GA.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, JE.; Hratchian, HP.; Cross, JB.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, RE.; Yazyev, O.; Austin, AJ.; Cammi, R.; Pomelli, C.; Ochterski, JW.; Ayala, PY.; Morokuma, K.; Voth, GA.; Salvador, P.; Dannenberg, JJ.; Zakrzewski, VG.; Dapprich, S.; Daniels, AD.; Strain, MC.; Farkas, O.; Malick, DK.; Rabuck, AD.; Raghavachari, K.; Foresman, JB.; Ortiz, JV.; Cui, Q.; Baboul, AG.; Clifford, S.; Cioslowski, J.; Stefanov, BB.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, RL.; Fox, DJ.; Keith, T.; Al-Laham, MA.; Peng, CY.; Nanayakkara, A.; Challacombe, M.; Gill, PMW.; Johnson, B.; Chen, W.; Wong, MW.; Gonzalez, C.; Pople, JA. Gaussian 03, Revision C.02. Wallingford CT: Gaussian, Inc.; 2004.

Figure 1. Frontier orbital system of parent cyclopropenylidene **1** according to extended Hückel (EH) calculations.

Figure 2.

Plot of the geometries (singlet states) of **1** with $R = N(tBu)_2$ (first entry), and $N(Si(Me)_3)_2$ (third entry) at RI-BP86/TZVP level.

Figure 3.

Plots of the geometries (singlet states) of **1** with R = N(*i*-Pr)₂, at RI-BP86/TZVP level. Relative energies (in kcal/mol) (**A**) 0.0, (**B**) -5.1, (**C**) -7.0.

Figure 4. Kohn-Sham frontier orbitals of various singlet carbenes obtained at RI-BP86/TZVP level. HOMO (a₁) energies in eV, LUMO refers to the energy lowest b₁ orbital.

		E_{σ} (eV)	E_{S-T} (kcal/mol)
3a		-3.6	-72.6
3b		-3.6	-51.6

Figure 5. Phosphaneiminato-type substituted cyclopropenylidenes (**3**), σ -orbital energies are in eV and S-T energy separations in kcal/mol (including ZPE corrections).

Figure 6. Plot of the geometry (singlet states) of cyclopropenylidene **1** with (**D**) Terphen (2,6-diphenylphenyl) substituents, at RI-BP86/TZVP level. For clarity the hydrogen atoms are omitted.

Figure 7.
Graphical representation of the equilibrium geometry of the dimer of **1D**.

Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Table 1

Parent cyclopropenylidene, **1**, calculated at various levels of theory, throughout the TZVP basis set was imposed, C(1) is the carbene carbon, C(2), C(2') are the olefinic carbon atoms.

Method	State	C(1)C(2) [Å]	C(1)C(2') [Å]	C(2)C(2') [Å]	-E ₀ [eV]	-E (S-T) ^a
RI-BP86	S	1.427	1.427	1.330	5.5	0.0
	T	1.309	1.423	1.573	4.5	45.8
B3LYP	S	1.415	1.415	1.320	6.5	0.0
	T	1.297	1.419	1.563	5.3	49.8
MP2	S	1.418	1.418	1.327	8.6	0.0
	T	1.302	1.445	1.535	7.4	57.1
CCSD(t)	S	1.418	1.418	1.322		0.0
	T	1.298	1.446	1.543		51.1 (52.7) ^{bc}

^aEnergies in kcal/mol including zero-point vibrational energy (ZPE) correction

^bZPE correction from B3LYP calculations

^cValue without ZPE correction.

Table 2

Substituted cyclopropenylidenes **1** calculated at RI-BP86/TZVP level of theory. Bonding parameters (in Ångström) and orbital energies (in eV) are for singlet states.

R	C(1)C(2) [Å]	C(2)C(2') [Å]	-E _σ [eV]	-E _π [eV]	-E (S-T) [kcal/mol]
CH ₃	1.423	1.340	4.9	7.3	48.4
<i>t</i> -Bu	1.420; 1.422	1.345	4.9	6.9	49.9 ^d
SiH ₃	1.434	1.353	5.4	7.3	36.4
TMS ^b	1.433	1.358	4.9	6.4	37.3
Ph ^c	1.424	1.351	5.0	6.4	38.8
Terphen ^d	1.421	1.358	4.9	5.8	37.5 ^d
NH ₂	1.413	1.353	4.6	5.7	59.6
N(CH ₃) ₂	1.412	1.364	4.5	4.9	58.6
N(<i>t</i> -Bu) ₂	1.415	1.381	4.3	4.9	-
N(pyr) ₂ ^e	1.418	1.363	4.2	4.7	57.8

^a without ZPE correction

^b TMS = trimethylsilyl

^c Ph = phenyl ligand

^d Terphen = 2,6-diphenyl-phenyl ligand [41]

^e pyr = pyrrolidino.

Table 3

Dimerization energies (in kcal/mol) of substituted cyclopropenylenes, at RI-BP86/ TZVP level of approximation.

Substituent R	CC [Å] ^a	-ΔE [kcal/mol] ^b	-ΔG [kcal/mol] ^c
H	1.303	60.9	48.2
CH ₃	1.321	53.1	36.3
<i>t</i> Bu	1.323	49.2	33.2
SiH ₃	1.314	66.4	46.0
TMS	1.317	59.5	45.3
Ph	1.331	59.3	43.5
Terphen	1.331	42.8	---
NH ₂	1.326	18.2	4.8
N(CH ₃) ₂	1.328	14.9	-3.6
N(<i>t</i> Bu) ₂	1.337	10.0	-4.5

^a Bond lengths of the central double bond

^b electronic energies for the dimerization reaction (without ZPE correction)

^c corresponding free energy values, T = 298 K, p = 0.1 MPa.