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Tuning the Nucleophilicity in Cyclopropenylidenes

Wolfgang W. Schoeller,*[a, b] Guido D. Frey,[c] and Guy Bertrand[c]

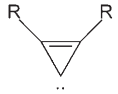
Dedicated to Professor Dr. Dr. h.c. mult. Wolfgang A. Herrmann on the occasion of his 60th birthday

Abstract: Cyclopropenylidenes are Hückel aromatic π systems in which one of the ring atoms is a carbene center. Quantum chemical calculations at the density functional level of theory, supplemented by coupled-cluster calculations, indicate that there is a sizeable energy separation between the lowest-energy singlet and triplet states of these species. Amino groups considerably increase the energy difference between these two states, whereas electron-withdrawing substituents decrease it. The 1,1-dimerization products of cyclopropenylidenes, namely, triafulvalenes, have been investigated. The calculations show that, without steric hindrance and considerable electronic stabilization, cyclopropenylidenes are kinetically unstable and dimerize. Different substituents (alkyl, silyl, terphenyl, amino, and phosphoraneiminato) were probed to tune the frontier orbital energies of 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 · density functional calculations · singlet–triplet energy separation · substituent effects · triafulvalenes

Introduction

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



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Recently, 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 single-crystal X-ray diffraction. In addition, a chiral diamino-substituted cyclopropenylidene has also been isolated by Holschumacher et al.[6] The singlet diphenylcyclopropenylidene **1** (R = Ph) has also been investigated recently by McMahon and co-workers 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 carbene, prompted us to investigate in detail their electronic properties with a variety of substituents (R = CH_3, SiH_3, NH_2, tBu, trimethylsilyl (TMS), Ph, 2,6-diphenylphenyl (Terphen), NMe_2, N(iPr)$_2$, N(tBu)$_2$, and N(pyr)$_2$). The silyl groups exemplify π-electron-withdrawing substituents, whereas amino groups are representatives of π donors. We also included in our study another type of donor substituent, the phosphoraneiminato ligand, which so far has not been used to stabilize 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 were concerned with a detailed spectroscopic analysis of parent **1** or its various valence isomers (e.g., see references [24,29]), and only a few studies have dealt with the singlet–triplet (S–T) energy gap.[8,14] Based on

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[a] Prof. Dr. W. W. Schoeller
Fakultät für Chemie der Universität, Universität Bielefeld
Postfach 10 01 31, 33501 Bielefeld (Germany)
Fax: (+49) 521-106-6467
E-mail: wolfgang.schoeller@ucr.edu

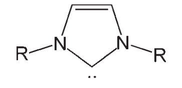
[b] Prof. Dr. W. W. Schoeller
Department of Chemistry, University of California
Riverside, CA 9251-0403 (USA)

[c] Dr. G. D. Frey, Prof. Dr. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California
Riverside, CA 9251-0403 (USA)

multiconfiguration self-consistent field (MCSCF) calculations,[8] the S–T gap for the parent compound was estimated to be approximately 52 kcal mol^{-1}.

Herein we report the results of quantum chemical calculations that deal with some chemical aspects hitherto not analyzed, but which are of key importance to the experimental verification of other cyclopropenylidenes and the assessment of their reactivity. The following points will be considered in more detail:

1) The S–T energy separation in **1** and the substituent effects. This gives a first understanding of the kinetic stability of cyclopropenylidenes.
2) The nucleo- 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 to date.



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3) The possible products from 1,1-dimerization[32] will be studied. It will be shown that the ease of this process depends on the S–T energy separation of the carbene and the steric demands of the substituents.

Results and Discussion

The parent cyclopropenylidene: It is informative to study first the molecular orbital system of parent **1** (R = H). It is formed 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 possesses two π electrons in the cyclic core and thus is isoelectronic with the cyclopropenyl cation.[33,34] According to EH calculations,[35] the two orbitals π_2 and π_3 are similar in energy, the HOMO is the σ orbital, and the π_1 orbital is slightly lower in energy. Consequently, for the lowest-energy singlet state one expects cyclic π delocalization in the ring. These contributions are represented by the canonical structures of **1a** and **1b** (Scheme 1).

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

Whereas the electronic configuration of the singlet ground state is readily defined 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 orbitals 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 $|\pi_1{}^2\sigma^1\pi_2{}^1\rangle$ ($^3A_2$) represented by the canonical structures **1c** and **1d** (Scheme 2).

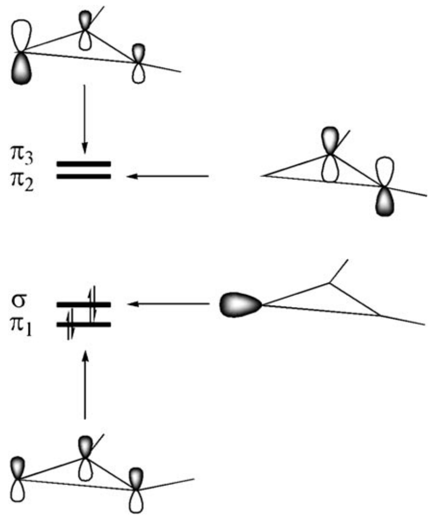
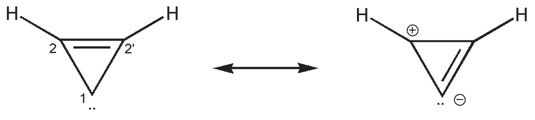
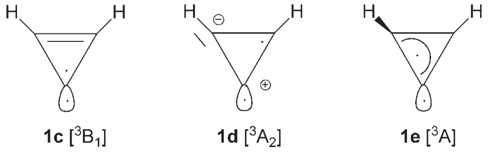


Figure 1. Frontier orbital system of parent **1** according to extended Hückel (EH) calculations.



Scheme 1.



Scheme 2.

These considerations are derived from the C_{2v} symmetry of the overall wavefunction, and **1c** and **1d** can be discussed in terms of a Jahn–Teller distortion.[37] A third alternative must be considered, **1e**, which is derived from the superimposition of **1c** and **1d**. Canonical structure **1d** implies a negative charge on the ring atoms and overall one expects a nonplanar equilibrium structure with pyramidalization of the substituents on the ring atoms and different C–C bond lengths. Such a conformation is preferable because it is known that cyclopropenyl radicals prefer a nonplanar conformation.[38] More details of the triplet energy hypersurface are given in the Theoretical Methods section.

To determine the S–T energy gap of parent **1**, we performed quantum chemical calculations at different levels of sophistication. This gives information about the validity of the different quantum chemical procedures used to evaluate the various species. For all investigations, a triplet-zeta basis set (TZVP; see the Theoretical Methods section) was employed to obtain a reliable bonding description. The results are summarized in Table 1.

Table 1. Bonding parameters and orbital energies for the parent cyclopropenylidene (**1**) calculated at various levels of theory.[a]

Method	State	C(1)–C(2) [Å]	C(1)–C(2′) [Å]	C(2)–C(2′) [Å]	$-E_\sigma$ [eV]	$-E_{S-T}$[b] [kcal mol^{-1}]
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[c] (52.7)[d]

[a] The TZVP basis set was imposed throughout. C(1) is the carbene carbon and C(2) and C(2′) are the olefinic carbon atoms. [b] Energies include the zero-point vibrational energy (ZPE) correction. [c] ZPE correction from B3LYP calculations. [d] Value without ZPE correction.

At all levels of sophistication the S–T energy separation appears to be fairly large. The largest was found at the MP2 level of theory and the smallest at the RI-BP86 level. For the singlet state, the calculations reveal a delocalized π system with C–C bonds shorter than the corresponding single bond; for comparison the triplet state has two short and one long C–C bond. This is in accordance with canonical structure **1e**. Of further interest is the σ orbital energy. For a 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 although the scale of orbital energies may well differ, within a given method the relative ordering of orbitals is correctly reproduced.[39,40]

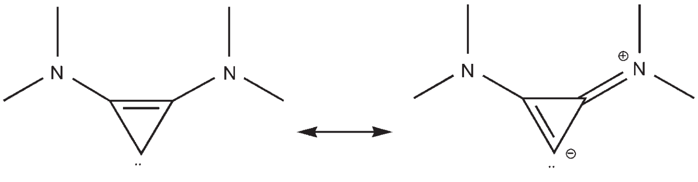
Cyclopropenylidene derivatives: Next the effect of substituents on the S–T energy separation was studied. Because the essential bonding parameters are already well represented at the RI-BP86/TZVP level of theory, this procedure was used. Only symmetrical structures were considered (i.e., identical substituents on the two 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 separations are again sizeable. The separation in the parent cyclopropenylidene is comparable in magnitude to that of the acyclic diaminocarbene,[42,43] but smaller than those of NHCs **2**.[44] Silyl (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 similarly to dimethylamino groups. With respect to the alkyl- and aryl-substituted derivatives, the change in the HOMO energy is approximately 0.5 eV. The effect of an amino group on the S–T energy separation of **1** can be readily understood by consideration of the canonical resonance structures **1f** and **1g** depicted in Scheme 3.

Table 2. Bonding parameters and orbital energies for the singlet states of substituted cyclopropenylidenes **1** calculated at the RI-BP86/TZVP level of theory.

R	C(1)–C(2) [Å]	C(2)–C(2′) [Å]	$-E_\sigma$ [eV]	$-E_{\pi_1}$ [eV]	$-E_{S-T}$ [kcal mol^{-1}]
CH_3	1.423	1.340	4.9	7.3	48.4
t-Bu	1.420; 1.422	1.345	4.9	6.9	49.9[a]
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[a]
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(*t*-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-diphenylphenyl ligand, see ref. [41]. [e] pyr = pyrrolidino.



1f **1g**

Scheme 3.

In **1f** the endocyclic double bond is distal to the carbene function, whereas it is lateral in **1g**. In other words the amino group induces a shortening of the C(1)–C(2) bond and a lengthening of the C(2)–C(2′) bond. This view is confirmed by the results of the calculations (see Tables 1 and 2). The induction of a negative charge at the carbene center increases the p character of the σ orbital, in accordance with the results of a population analysis.[36] It also has the consequence that its orbital energy is lowered (Table 2) and rehybridization in **1g** shortens the lateral ring bonds (with respect to the carbene function) in comparison with **1f**. Hence, these bonds acquire more s character while releasing p electrons to the nonbonding σ orbital.

A special case is provided by the peralkyl-substituted bulky amino derivatives. Although in **1** (R = NH_2, $N(CH_3)_2$, and N(pyr)$_2$) the amino groups are in the plane with the ring moiety, so as to maximize π bonding, in the sterically overloaded systems (R = N(*t*Bu)$_2$ and N(TMS)$_2$) the amino groups tend to rotate out of the plane formed by the three-membered ring. The equilibrium geometries of the singlet states of **1** with $R=N(tBu)_2$ and $N(TMS)_2$ calculated at the RI-BP86/TZVP level of theory are presented in Figure 2.

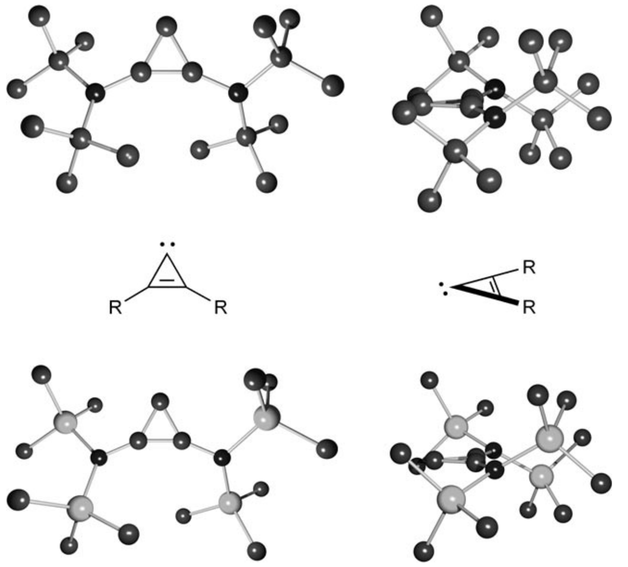


Figure 2. Geometries (singlet states) of **1** with $R=N(tBu)_2$ (top row) and $N[Si(Me)_3]_2$ (bottom row) at the RI-BP86/TZVP level of theory.

The relative rotations of the NR_2 groups with respect to each other (the gearing effect) are 55.2 and 43.2° for R=*t*Bu and TMS, respectively. Interestingly, the triplet equilibrium geometry for $R=N(tBu)_2$ could not be determined by calculations. The corresponding triplet state is not a stable entity on the electronic hypersurface and the steric strain exerted by the $N(tBu)_2$ groups is so large that the cyclopropadienyl ring opens to the corresponding propadienylidene biradical without an activation energy barrier.

Some considerations regarding the steric effects of these large substituents compared with diisopropylamino groups (the substituents used for the experimentally characterized derivative) must be discussed here on the basis of Tolman's concept.[46] For the *tert*-butyl group, the substituents on the tetrahedral carbon atom are similar in size and can be described as a right circular cone. For isopropyl groups, the three substituents on the central carbon atom are different in size leading to an oblique cone (Scheme 4).[47]

Scheme 4.

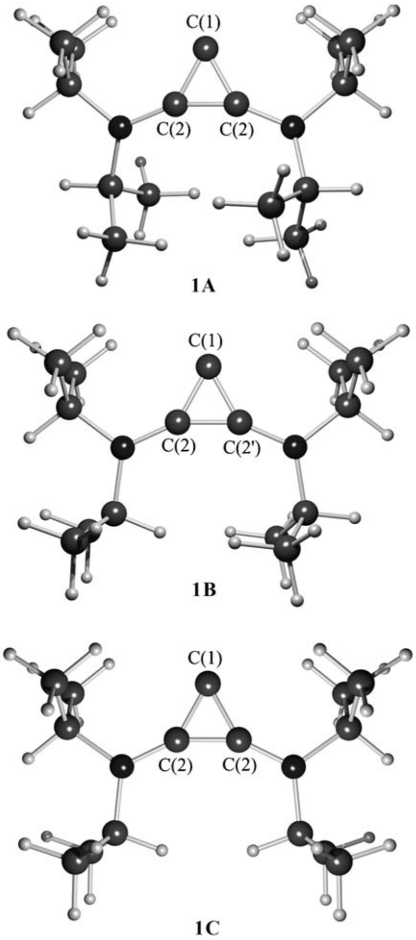


Figure 3. Geometries (singlet states) of **1** with $R=N(iPr)_2$ at the RI-BP86/TZVP level of theory. Relative energies are 0.0 (**1A**), −5.1 (**1B**), and −7.0 kcal mol^{-1} (**1C**).

Hence, it is clear that various conformations are possible with diisopropylamino substituents 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 the plane of the three-membered ring system; the corresponding twisting angle is 34.2°. In **1B** and **1C**, the methyl groups can minimize the eclipsing of the hydrogen atoms, and it is optimum for **1C**.

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

Nucleophilicity of cyclopropenylidenes in comparison with other carbenes: The philicity is one of the most important aspects of a singlet carbene and has been scrutinized for the cyclopropanation reaction in terms of Hammett-type substituents,[48] frontier orbital considerations, and on the basis of the electron affinities and ionization potentials of the singlet carbenes.[49] Hence, the orbitals depicted in Figure 4[50] give a good rationale of the philicity of carbenes, which is determined by the frontier orbital model of carbene reactivity.[51–54] Kohn–Sham energies were used for this purpose because it has been shown that these parallel Hartree–Fock-type calculations.[39,40]

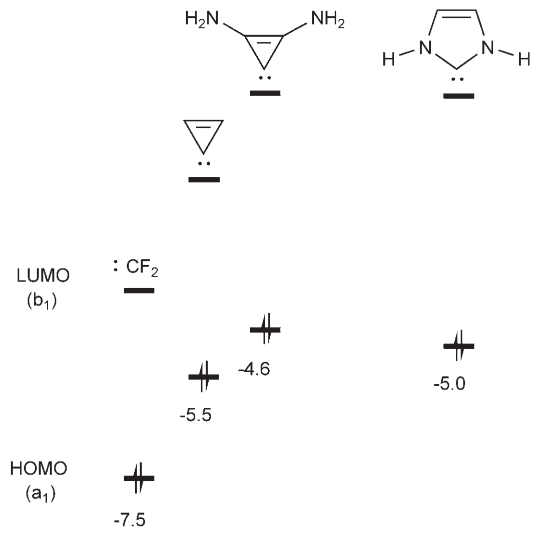


Figure 4. Kohn–Sham frontier orbitals of various singlet carbenes obtained at the RI-BP86/TZVP level of theory. HOMO (a_1) energies are given in eV and LUMO refers to the lowest-energy b_1 orbital.

CF_2 has an energetically low-lying LUMO and is accordingly a typical electrophilic carbene. On the other hand, NHC **2** (R = H was chosen) has so far been considered as one of the most nucleophilic carbenes; it has a very high-lying HOMO and also an extremely large S–T energy separation.[44] With respect to these extremes, the cyclopropenylidenes are of very much interest; they have frontier orbitals characteristic of NHCs and thus are nucleophilic carbenes. The amino-substituted derivative of **1** ($R = NH_2$) 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, because 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. The two amino groups ($R = NH_2$) modify the energy level of the HOMO (of parent R = H) by 0.9 eV (see Tables 1 and 2 and Figure 4), almost 0.5 eV per group. Imino-,[61] or even better, iminato-type substituents should be even more effective because they possess a lone pair within the ring plane that could transmit electron density onto the HOMO of the carbene. We have evaluated two different phosphoraneiminato-substituted cyclopropenylidenes **3** (Figure 5).

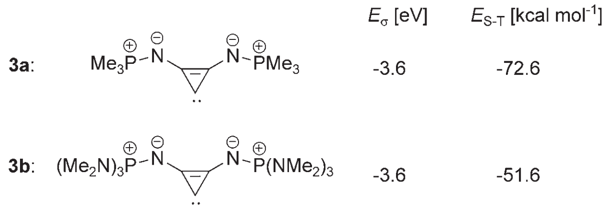
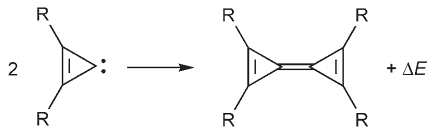


Figure 5. Energies (including ZPE corrections) of the phosphoraneiminato-substituted cyclopropenylidenes (**3**).

The structures in Figure 5 have been described within an ylide formalism, that is, 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, rarely participate in these structures.[62] The phosphoraneiminato substituents with the phosphorane group *cis* to the carbene center is more stable than all other possible conformations. The *cis* conformation arises from the attraction of the positively charged phosphonium groups by the negatively charged carbene center, as revealed by the corresponding population analysis.[36] Two representatives of **3** have been investigated: derivative **3a** with PMe_3 and **3b** with $P(NMe_2)_3$ as the substituents. The energies of the σ orbitals (HOMOs) of **3a** and **3b** are similar, but are 1.9 and 1.0 eV higher (i.e., a lower ionization potential) than **1** and the diamino-substituted cyclopropenylidene, respectively. Thus, one can predict that these compounds should be extremely nucleophilic. Importantly, at the same time they are also predicted to feature large S–T separations, which should make them very stable towards dimerization (see below).

Dimerization of cyclopropenylidenes—triafulvalenes: The fate of a carbene, whether or not it remains a stable species under laboratory conditions, essentially depends on its ability to undergo 1,1-dimerization.[32] In the case of cyclopropenylidenes **1**, this process leads to the corresponding triafulvalenes (Scheme 5), which are highly reactive compounds and hitherto have not been structurally characterized.[63–65]



Scheme 5.

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, they have a very low ionization potential. The extreme electron-richness of triafulvalenes has been discussed before in the light of skillfully performed quantum chemical calculations.[66] At our quantum chemical level (RI-BP86/TZVP) of optimization we obtained the following orbital energies for the HOMOs of the various olefinic systems: 1) ethene −6.8 eV, 2) tetraaminoethene −4.2 eV, 3) parent triafulvalene −3.8 eV, and 4) its tetraamino derivative −2.2 eV. These values are in accordance with the recent analysis.[66] If these orbital energies are assigned to Koopman energies, the tetraaminotriafulvalene is extremely electron-rich and should be amenable to easy oxidation.

The energy gain for the dimerization reaction is rather large because a σ and 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] and Carter and Goddard.[68,69] Another aspect is the proton-induced dimerization of a carbene by a catalytic cycle;[66,70–72] this aspect will not be explored further herein. The dimerization energies of a variety of differently substituted cyclopropenylidenes were calculated. To reveal the importance of the entropy contributions in these reactions, we first performed vibration analyses (within the harmonic approximation) and secondly calculated the free-energy contributions by standard thermodynamic formula for the gas phase.[73] The results are summarized in Table 3.

Table 3. Dimerization energies of substituted cyclopropenylidenes and bond lengths of the dimers determined at the RI-BP86/TZVP level of theory.

Substituent R	C−C[a] [Å]	$-\Delta E$[b] [kcal mol^{-1}]	$-\Delta G$[c] [kcal mol^{-1}]
H	1.303	60.9	48.2
CH_3	1.321	53.1	36.3
*t*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(*t*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] Free energies for the dimerization reaction ($T=298$ K, $p=0.1$ MPa).

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.[74] In this study the 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 monomer formation.[66,75] In the cases presented herein, only the amino-substituted cyclopropenylidenes reveal endothermic behavior, largely driven by the entropy contributions. The difference in energy between the electronic and entropic energy contributions for the dimerization reaction range from 12.7 (R = H) to 20.4 kcal mol^{-1} (R = SiH_3).

The most sterically overloaded carbene studied is **1D** with the terphenyl substituents. As a consequence of strain the C(2)−C(2′) bond lengthens slightly, whereas the C(1)−C(2) bonds shorten in comparison with the parent compound **1** (R = H). Despite the large steric shielding of the carbene center (see Figure 6), 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 resulting triafulvalene is an energy minimum; in the corresponding equilibrium geometry the Terphen substituents move away from each other to minimize mutual steric hindrance (Figure 7). However, would **1D** dimerize? This question remains unanswered because the necessary conformational changes might well cause a barrier towards dimerization. This aspect will be studied in future investigations.

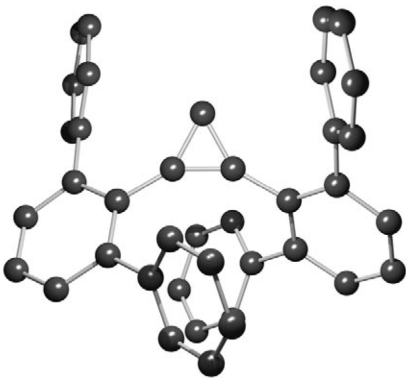


Figure 6. Geometry (singlet state) of cyclopropenylidene with Terphen substituents (**1D**) at the RI-BP86/TZVP level of theory. For clarity the hydrogen atoms have been omitted.

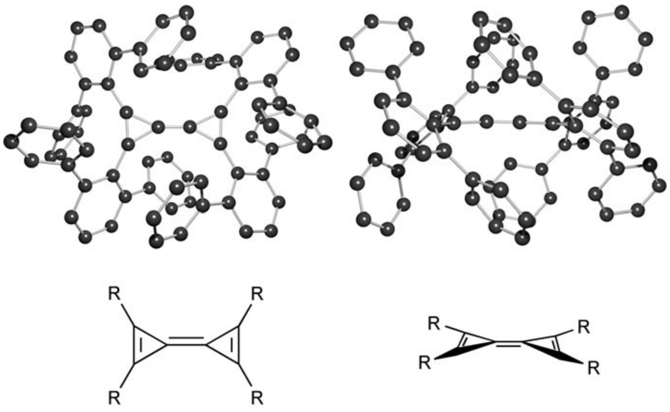


Figure 7. Graphical representation of the equilibrium geometry of the dimer of **1D**.

Conclusion

Cyclopropenylidenes are Hückel π-conjugated cyclic systems with two electrons in the cyclic moiety. Different states are feasible a priori for the triplet. Calculations show that the lowest-energy triplet 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 those of acyclic bis(amino)carbenes, but smaller than those of NHCs. Compared with the parent cyclopropenylidene, amino substituents increase the S–T energy difference by approximately 20 kcal mol^{-1}. At the same time, the HOMO (σ orbital) is lower in energy and thus the cyclopropenylidenes become more nucleophilic than their five-membered ring analogues **2**. The phosphaneiminato substituents are even stronger donors. They lower the vertical ionization potential by almost 2 eV. Hence our investigations verify the different synthetically observed substituted cyclopropenylidenes, which are predicted to be extremely nucleophilic. Overall, by a suitable choice of substituents at the olefinic positions, cyclopropenylidenes are predicted to be more nucleophilic than their five-membered ring congeners, the imidazol-2-ylidenes.

On the basis of the electronic energies, the dimerization reactions of the cyclopropenylidenes are exothermic, albeit to a much lesser extent in the case of the amino derivatives. The inclusion of entropy contributions mediates the exothermic energy balance, which favors more the monomers; this is a consequence of the $T\Delta S$ term in the free-energy expression. The central π bond of dimeric triafulvalenes is extremely electron-rich, and therefore, they are predicted to undergo easy oxidation.

Theoretical Methods

Calculations: For all calculations the TZVP basis set of Ahlrichs and coworkers was employed.[76] The basis set is of triple-zeta quality and was augmented by polarization functions for all atoms. All of the triplet states were investigated within unrestricted wavefunctions. For the singlet state the spin contamination through the UMP2 procedure was fairly small ($<S^2> \approx 0$) and needed no correction with the spin projection procedure of Chen and Schlegel.[77] The coupled-cluster calculations included triple corrections to the overall correlation energy.[78] The single-point calculations were performed by using the MP2 (UMP2)-energy-optimized geometries. All of the structures were identified as energy minima by 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[79] and Gaussian 03[80] program systems.

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 wavefunction for a planar C_{2v}-symmetrical triplet can thus be described by Equation (1) in which $c=1$ for $^3A_2$ and $c=0$ for the $^3B_1$ component.

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

Equation (1) refers to the canonical structures **1c** and **1d**. Because the $^3A_2$ component bears a negative charge on one of the ring carbon atoms, the lowest-energy geometry is expected to exhibit pyramidalization at the ring atoms. This is taken into account by assuming a C_1-symmetrical structure for the lowest-energy triplet and is supported by the data in Table 4, obtained by UMP2/TZVP calculations.

Accordingly, the $^3B_1$ component of the wavefunction 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 the lowest-energy planar and pyramidal conformations is less than 10 kcal mol^{-1}.

Table 4. UMP2/TZVP calculations on the triplet states.

State	Symmetry	$-E$ [a.u.]	ΔE [kcal mol^{-1}]	ZPE[a]	NIMAG[b]	$<S^2>$[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). [b] NIMAG = number of imaginary frequencies. [c] $<S^2>$ = value for spin projection; these values were calculated according to ref. [77].

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