DOI: 10.1002/chem.200600451

Tetrahedrane—Dossier of an Unknown

Adelina Nemirowski, Hans Peter Reisenauer, and Peter R. Schreiner*[a]

Dedicated to Prof. Günther Maier for his seminal contributions to physical-organic and tetrahedrane chemistry

Abstract: To probe whether tetrahedrane should be isolable the thermodynamics and kinetics of C_4H_4 singlet and triplet structures were studied extensively at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVDZ//B3LYP/6–311G**, and B3LYP/6–311G** levels of theory. The reaction of cyclopropene with atomic carbon, which was previously suggested to involve tetrahedrane as a reactive intermediate, was re-examined experimentally with low-temperature matrix-isolation techniques. While experimental and theoretical results exclude the intermediacy of tetrahedrane in the above reaction, it is predicted to be an isolable molecule. Among the many C_4H_4 species, we pay special attention to the electronic effects on the ground state multiplicity of the respective carbenes.

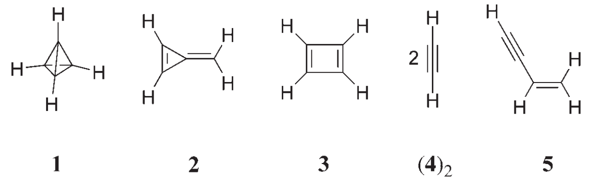
Keywords: carbenes · spherical aromaticity · strained molecules · tetrahedrane

Introduction

Should unsubstituted tetrahedrane (**1**) be isolable? The elusiveness of the parent structure in contrast to its 13 known derivatives[1] and its immense Baeyer strain[2] of 30.7 kcal mol^{-1} per CH unit[3] justify this question. The human tendency to project harmony, balance, and perfection on symmetrical objects, illustrated by the long-lasting efforts to prepare molecular analogues of the Platonic Solids and highly symmetrical structures such as annulenes, diamandoids, fullerenes, prismanes, propellanes, fenestranes, and many more,[4] made **1** an ever valid but never achieved synthetic goal. In the following we attempt to answer the prime question whether **1** should be a kinetically stable molecule. As pulsed laser ablation (PLA) of a rotating graphite disc allows the generation of carbon atoms in their triplet ground state, we also describe our efforts in synthesizing **1** through the reaction of carbon atoms with cyclopropene.

Background

While Eaton and Cole[5] as well as Paquette et al.[6] succeeded in the synthesis of cubane $[CH]_8$ (1964) and dodecahedrane $[CH]_{20}$ (1982), respectively, tremendous efforts to prepare **1**[7–14] resulted only in the detection of the C_4H_4 isomers (Scheme 1) methylenecyclopropene (**2**), cyclobutadiene (**3**), acetylene dimer ((**4**)$_2$), and vinylacetylene (**5**). On three occasions,[7,8a,b] however, reaction products were proposed to be consistent with the intermediacy of **1**. Whereas the outcome of one of these procedures, concerning the decomposition of the dilithium salt of *trans*-butenedial-bistosylhydrazone,[7] could not be reproduced,[14] the second set of experiments,[8a,b] dealing with the reaction of cyclopropene and carbon atoms, generated from C_2O in the gas phase by photolysis or by nuclear reactions, was largely left unnoticed. To probe the validity of the proposal regarding the intermediacy of **1** in the second case, the reaction of carbon atoms with cyclopropene under conditions excluding photoreactions is therefore of particular relevance.



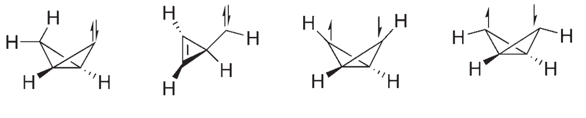
Scheme 1. Selected C_4H_4 isomers.

---

[a] Dipl.-Chem. A. Nemirowski, Dr. H. P. Reisenauer,
Prof. Dr. P. R. Schreiner
Institut für Organische Chemie, Justus-Liebig-Universität
Heinrich-Buff-Ring 58, 35392 Giessen (Germany)
Fax: (+49) 641-99-34309
E-mail: prs@org.chemie.uni-giessen.de

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

Quantum-chemical computations should in principle be able to predict whether **1** is isolable at a given temperature on both thermodynamic and kinetic grounds. Despite a multitude of published studies,[2,15–34] no clear picture regarding the accessibility of **1** emerges. All investigations find vinylacetylene to be the global minimum on the C_4H_4 potential energy surface (PES), followed by butatriene, methylenecyclopropene, cyclobutadiene, and tetrahedrane. The most comprehensive study, performed at the semiempirical MINDO/3 level,[15] places the traditional tetrahedrane precursors (Scheme 2), bicyclo[1.1.0]butaneylidene (**6**) as well as *exo,exo*-bicyclo[1.1.0]butane-2,4-diyl ($\mathbf{8_{xx}}$) 26 kcal mol^{-1} and 18 kcal mol^{-1}, respectively, above, and cycloprop-3-enemethylene (**7**) as well as *endo,endo*-bicyclo[1.1.0]butane-2,4-diyl ($\mathbf{8_{dd}}$) 13–14 kcal mol^{-1} and 10 kcal mol^{-1}, respectively, below **1**. Surprisingly, only very few publications address the activation energies for the various rearrangement pathways of tetrahedrane; these yield three key pieces of information:



6 **7** $\mathbf{8_{dd}}$ $\mathbf{8_{xx}}$

Scheme 2. Proposed reactive intermediates on the way to tetrahedrane.

- the bond cleavage of **1** to $\mathbf{8_{xx}}$ is predicted to be accompanied by a barrier of $\Delta H^{\neq} = 11$ kcal mol^{-1}[15]
- tetrahedrane should be too short-lived to be observable if the bond dissociation to **8** is thermoneutral[16]
- there are non-concerted rearrangements of **8** to D_{4h}-symmetric **3** as well as **1** to **8**, based on rather simple orbital symmetry considerations (vide infra).[17]

Such an obvious lack of reliable information about the kinetic stability of tetrahedrane complicates the interpretation of the known experimental data and leaves the fundamental question regarding the isolability of **1** unanswered. This necessitates a study of the corresponding part of the C_4H_4 PES with high-level ab initio methods as presented here first. In the second part we report our experimental attempts at making **1**.

Methods

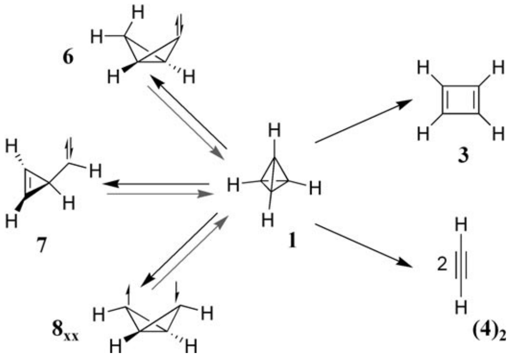
Computational: Geometries of all stationary points were optimized with density functional theory (DFT) approaches, utilizing the Becke, Lee, Yang, and Parr three-parameter hybrid functional B3LYP,[35] in conjunction with a Pople-type triple split-valence contracted basis set, containing polarization functions on all atoms (6–311G**). Higher level energies were computed with coupled-cluster theory[36] comprising single and double excitations as well as perturbatively included triple contributions [CCSD(T)][37] using correlation-consistent polarized-valence double-zeta basis set cc-pVDZ.[38] Single-point energies for all structures optimized at B3LYP/6–311G** were obtained with CCSD(T)/cc-pVDZ {in curly brackets without ZPVE contribution}. To test the thermodynamics of the investigated part of the C_4H_4 PES all minima were reoptimized at the CCSD(T)/cc-pVDZ level of theory (given in parentheses), the most important of them being confirmed at CCSD(T)/cc-pVTZ, and single-point energy calculations computed with CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ for the rest of the structures [in square brackets] (full core for all). Closed-shell species were computed with a restricted and all open-shell structures (triplet and singlet multiplicity) with unrestricted HF reference wave functions. Vibrational frequencies were obtained by using analytic gradients; transition structures, possessing one imaginary frequency, were additionally characterized by computing the intrinsic reaction coordinate (IRC) connecting the corresponding minima. Despite the generally high precision of results acquired with CCSD(T) theory, called therefore "the effective gold standard for single reference computations"[39] emphasizing its comparability with experimental data, and hence predictive power, the validation for the numerously dominant structural moieties of molecules, found on the C_4H_4 PES was carried out along with B3LYP/6–311G**. Keeping in mind the best experimental estimate of the singlet–triplet separation of parent methylene $\Delta E_{ST} =$ 9.1 kcal mol^{-1},[40] CCSD(T)/cc-pVDZ with $\Delta E_{ST} = 12.1$ kcal mol^{-1} performs better than B3LYP/6–311G** giving $\Delta E_{ST} =$ 12.6 kcal mol^{-1}. While the CCSD(T)/cc-pVTZ result $\Delta E_{ST} =$ 10.9 kcal mol^{-1} is even closer to experiment, single-point energies CCSD(T)/cc-pVDZ//B3LYP/6–311G** $\Delta E_{ST} =$ 12.0 kcal mol^{-1} and CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVDZ $\Delta E_{ST} = 10.9$ kcal mol^{-1} show negligible deviations from the optimized structure values. Considering the well known tendency of single-reference computational methods to describe singlet closed-shell carbenes insufficiently,[41] T_1-diagnostics[42] based on CCSD(T)/cc-pVDZ data were evaluated to judge their multireference character. T_1-diagnostics have also been computed for biradicaloid species, as the overestimation of single excitations (these are allowed by symmetry for all conformers of **8**) could lead to an inappropriate description with coupled-cluster methods.[43] Since the energy differences between the acetylene van der Waals dimers of varying structure and two separate acetylene molecules are negligible compared to the energy values under discussion, reported data concern two separate acetylenes.

Experimental Section

The reaction of cyclopropene with atomic carbon was carried out as a combination of matrix isolation with PLA techniques. For this, products of the ablation from a rotating graphite disc by a KrF-excimer laser, $\lambda =$ 248 nm, were co-condensed with 5 mmol of a cyclopropene/Ar 4/1000 gas mixture on a 10–12 K CsI window of a matrix-isolation apparatus.[44] To enable diffusion and hence reaction of species trapped in the Ar matrix, the deposited material was annealed up to 30 K for 10 min. Changes in composition of condensed samples were detected by IR spectroscopy in the range between 4000 and 400 cm^{-1}. Control experiments with the aim of excluding gas-phase reactions by depositing both reaction partners in pulsed mode with alternating pulse sequence were also conducted. To avoid misinterpretations, the individual behavior of cyclopropene and the ablation products under annealing was monitored separately in series of experiments.

Results and Discussion

Isolability of tetrahedrane: Judging the synthesizability of tetrahedrane in general and from the synthons utilized thus far requires an investigation of its kinetic stability towards isomerization reactions (Scheme 3). As can be seen from Figure 1, among the reactions of traditional tetrahedrane synthons, only an intramolecular double-bond addition of **7** to give **1** is predicted to be (strongly) exergonic, which undermines earlier studies on the relative stability of the C_4H_4 isomers.[15,20] At all employed levels of theory, the reactions of **6** to **5**, **8** to **3**, and **7** to **4** and **2** show that for each of the "classical" tetrahedrane precursors there is a thermodynamically more favorable isomerization path to energetically lower lying species *not involving* **1**. Remarkably, despite the enormous strain of **1**, there is almost *no* thermodynamic benefit from cleaving one of the C−C bonds to form a biradical, owing to the destabilization through the unpairing of two electrons. That is, tetrahedrane is kinetically stable towards C−C bond scissions just as the cubane cage and the central bond in [1.1.1]propellane are well known to be. Of the three possible conformers of the resultant biradicaloids, $\mathbf{8_{dx}}$ and $\mathbf{8_{dd}}$ can be located at CCSD(T)/cc-pVDZ, while $\mathbf{8_{xx}}$ is the only energy minimum at B3LYP/6–311G** with $\mathbf{8_{dx}}$ being the interconversion transition state between the conformers $\mathbf{8_{dd}}$ (converges to **1**) and $\mathbf{8_{xx}}$. However, **8** should not be isolable as it is predicted to rearrange remarkably easily to **3**.



Scheme 3. Ways to and from **1**.

The activation energies for the isomerizations of **1** to bicyclo[1.1.0]butaneylidene (**6**) (33.4 {31.4} kcal mol^{-1}), bicyclo[1.1.0]butane-2,4-diyl (**8**) (29.9 {36.3} kcal mol^{-1}), and cycloprop-3-enemethylene (**7**) (>27.3 (>26.4) [>30.8] kcal mol^{-1}) are of the same order of magnitude. That is, even if tetrahedrane forms through one of these precursor struc-

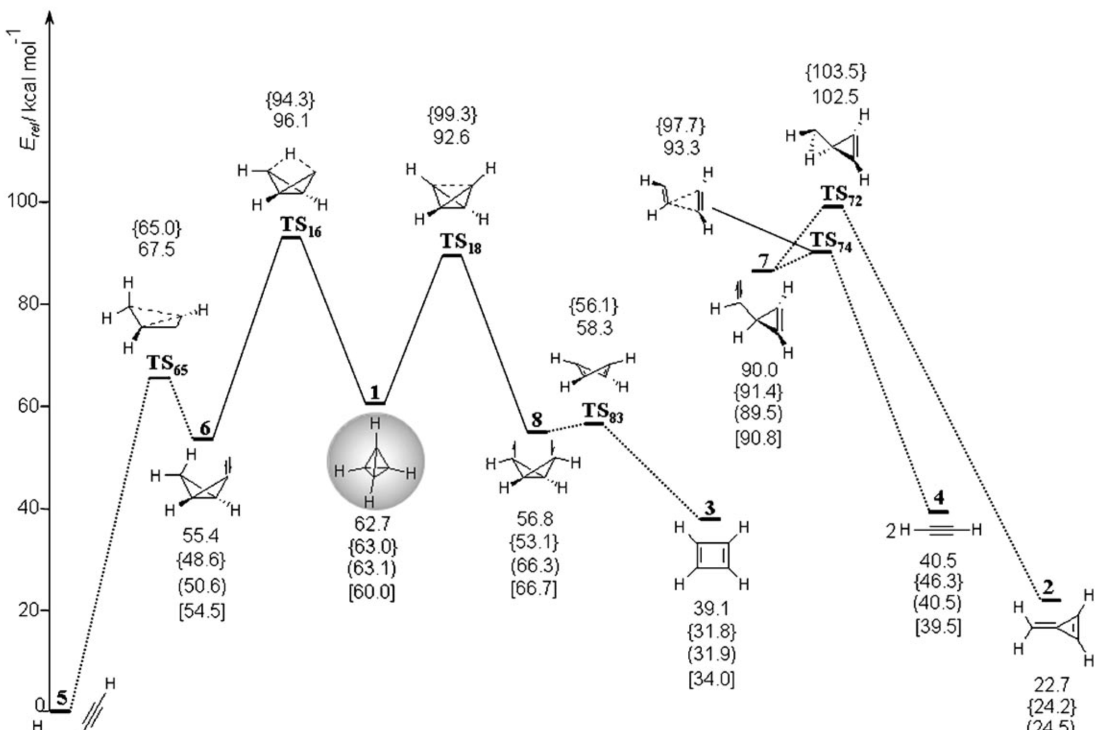


Figure 1. Isomerization reactions of tetrahedrane and related C_4H_4 species; electronic energies and ZPVEs computed at B3LYP/6–311G**, {CCSD(T)/cc-pVDZ//B3LYP/6–311G**}, (CCSD(T)/cc-pVDZ), [CCSD(T)/cc-pVTZ fully optimized except **8**, **6**].

tures, for example, in an intramolecular double-bond addition of **7**—the activation energies for cheletropic reactions range from 5 to 10 kcal mol^{-1}—further rearrangements to the other isomers may take place readily if the excess energy is not removed quickly. This finding possibly explains the permanent failure to synthesize tetrahedrane from the above precursor structures.

Figure 2 and Figure 3 present correlation diagrams for thermal concerted pericyclic isomerizations of **1** to D_{2h}-cyclobutadiene and two molecules acetylene, based on group orbitals, which mainly describe changes in bonding in the course of the respective reactions.[45] The transformation of a bonding orbital of **1** into one of the antibonding orbitals of cyclobutadiene or the perpendicular arrangement of two acetylene molecules and vice versa clearly identify these reactions as *forbidden* by symmetry. High activation energies for both processes are the consequence. The change of electronic configuration between the precursors and products of both reactions may explain the inability of B3LYP/6–311G** to describe the respective transition structures. Thus, the rearrangement of tetrahedrane to cyclobutadiene or two acetylenes is strongly unfavorable, as reactions to **6–8** are, since the corresponding reaction barriers are sizable, in marked contrast to previous lower-level predictions.[15,24] Although **1** is highly strained,[13,19,20,23,29,32] it is *not reactive*, and should, in principle, be isolable. This is even more intriguing in light of the fact that strain, measured as a net effect is generally underestimated because of the neglect of thermodynamically stabilizing factors. One of them operating on *all* T_d tetrahedrane derivatives originates from the interactions of the radially oriented p orbitals, comprising the 3a$_1$ MO (Figure 4): these are similar to the σ-delocalization of the 1a$_1$ Walsh MO of cyclopropane. This stabilizing delocalization, indicated by negative nonadditive NICS[34] values was termed spherical aromaticity[46,47] in inorganic molecules by analogy to the σ-aromaticity[48] of cyclopropane. The role of the exocyclic delocalized 1e orbitals in **1** can be compared with the contributions of the appropriate e Walsh MOs of cyclopropane.

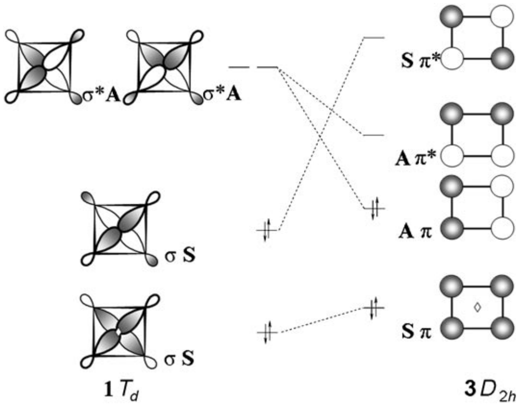


Figure 2. Correlation diagram for the tetrahedrane **1**–cyclobutadiene **3** cycloreversion/cyclobutadiene-tetrahedrane cycloaddition; orbital ordering with increasing energy from bottom to top; **S** and **A** indicate orbital symmetry with respect to the common C_2 axes, marked for the first set of orbitals; top view of the cyclobutadiene p-atomic orbitals.

Additionally, due to the p-contributions to the 1e and 3a$_1$ MOs, the C–H bonds gain s-character, resulting in increased thermodynamic stability of **1**. The shortening of C–H bonds is reflected in the stretching vibrational frequency shift into the acetylenic area (Figure 5). This also helps rationalize the extremely short inter-cage C–C bond observed experimentally in hexa-trimethylsilyl-tetrahedranyltetrahedrane.[1j,49]

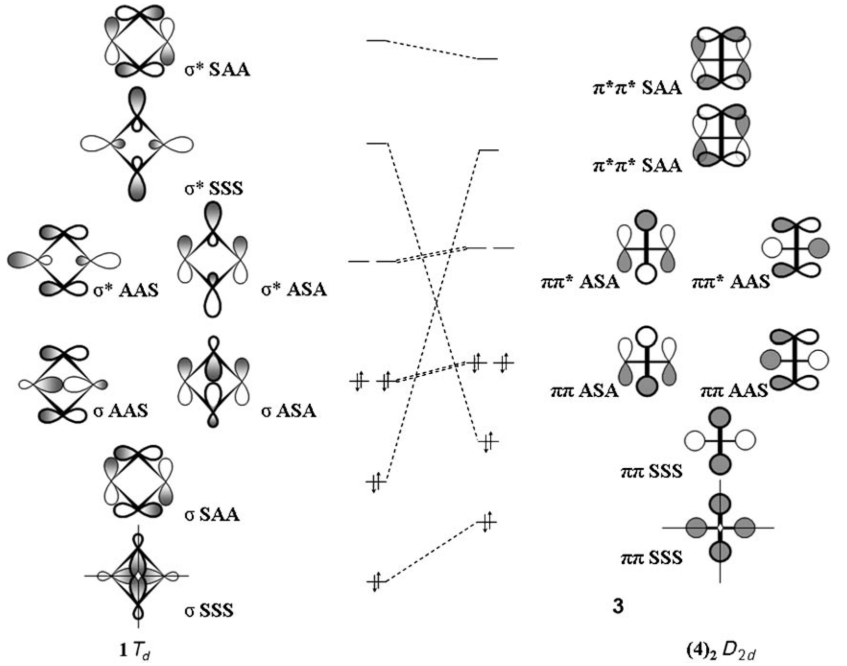


Figure 3. Correlation diagram for the dissociation of tetrahedrane **1** into two perpendicular molecules acetylene (**4**)$_2$; symmetry designations **S** and **A** refer to the elements C_2, σ_v, and σ_h, shown for the first set of orbitals; orbital ordering with increasing energy from bottom to top; p-atomic orbitals of the two acetylenes are shown as a projection onto the plane between the molecules.

Reactions of cyclopropene with carbon atoms: One can envision four modes of attack of a carbon atom onto cyclopropene (Figure 6): The insertions in aliphatic or vinylic C–H bonds, giving rise to cycloprop-3-enemethylene (**7**) and cycloprop-2-enemethylene (**9**), respectively, the insertion in one of the C–C bonds, resulting in cyclobutenylidene (**10**), and a double-bond addition, yielding **6**. Among them the stepwise

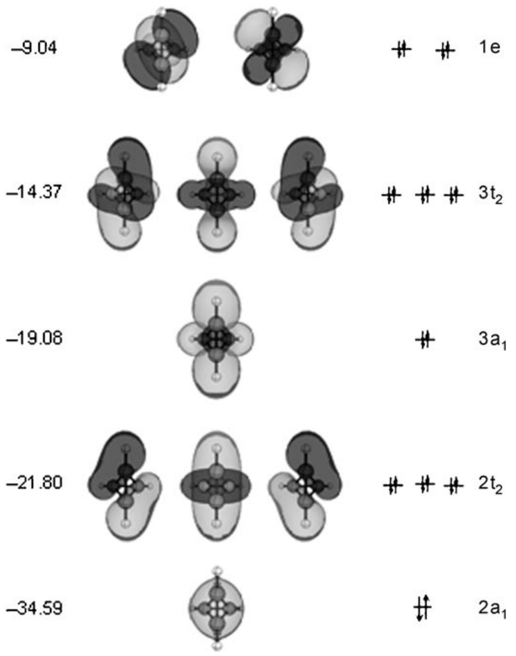


Figure 4. Occupation scheme of the valence MOs of tetrahedrane; increasing energy [eV] ordering from bottom to top (CCSD(T)/cc-pVDZ); designations on the right: symmetry types.

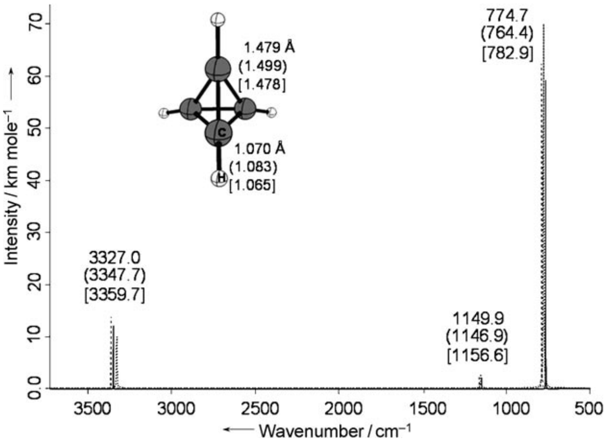


Figure 5. Computed unscaled IR spectrum of tetrahedrane: B3LYP/6–311G** (dotted); CCSD(T)/cc-pVDZ (solid); CCSD(T)/cc-pVTZ (dashed).

abstraction/recombination mechanism seems unlikely for the insertion in either C–H bond, as radical intermediates are found to be less stable than separate starting materials in the gas phase by 16.3 and 25.9 kcal mol^{-1}, respectively, at the B3LYP/6–311G** level of theory. Without exception, these reactions are strongly exergonic owing to the high energy of atomic carbon, and they are predicted to occur activationless in accordance to the Bell–Evans–Polanyi principle, as, for instance, demonstrated for the double-bond addition (Figure 7).

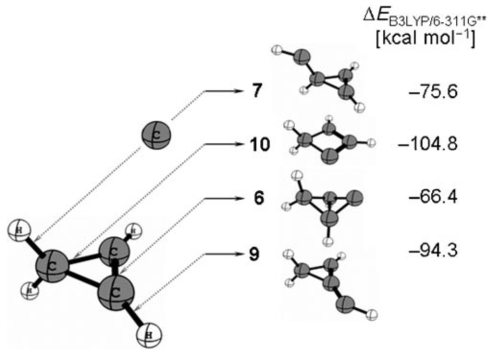


Figure 6. Primary products of the reaction of cyclopropene with a ground state ^3P carbon atom.

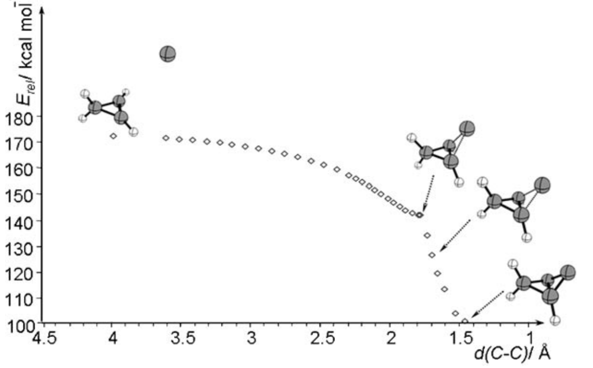
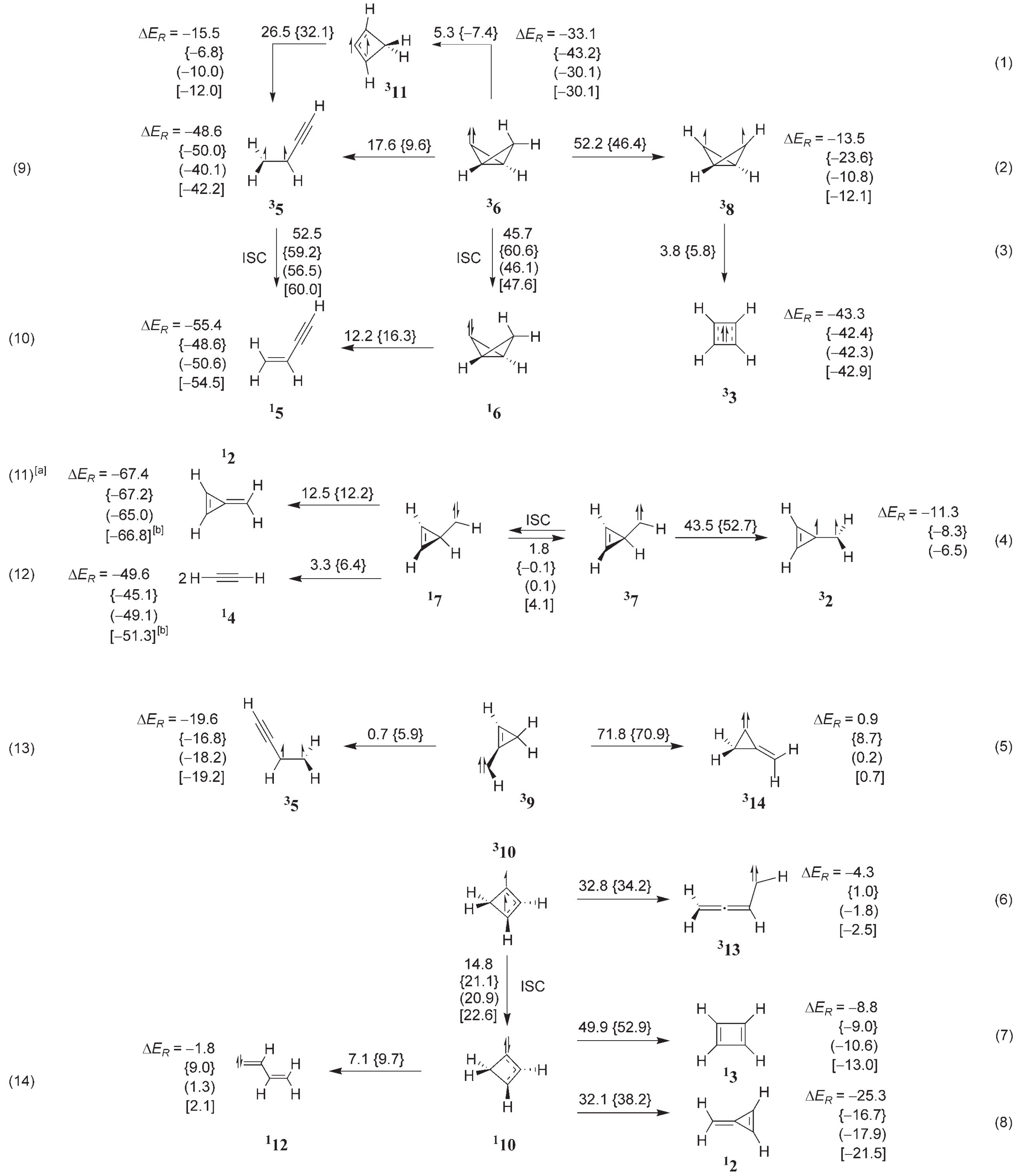


Figure 7. Double-bond addition of a carbon atom to cyclopropene (energies at B3LYP/6–311G**, without ZPVE, with respect to vinylacetylene) conserving C_s symmetry.

As the initial reaction products **6**, **7**, **9**, and **10** are energetically high-lying ((101.1 (96.6) [102.1] kcal mol^{-1} for **6**, 91.8 (89.6) [94.9] kcal mol^{-1} for **7**, 72.1 (74.7) [79.2] kcal mol^{-1} for **9**, and 62.7 (63.3) [69.6] kcal mol^{-1} for **10** with respect to vinylacetylene), they are expected to undergo further isomerizations readily even if the reaction energy in the primary step dissipates efficiently. The examination of possible exergonic and thermoneutral deactivation routes reveals that besides reactions requiring high activation energies [Eq. (1)–(8)] (Scheme 4), there are some isomerizations of **6**, **7**, **9**, and **10** that should take place easily [Eq. (9)–(14)].

Considering the tendency of DFT to overestimate strain,[50] the electrocyclic ring opening of ^{3}**6** to the smallest cyclic cumulene, 1,2-cyclobutadiene (**11**), is likely to be associated with a higher barrier than predicted. Destabilizing strain due to the inclusion of an allenic moiety in ^{1}**11** versus allyl stabilization of its triplet counterpart, makes the singlet and triplet species almost isoenergetic {$\Delta E_{ST} = -2.7$ (−3.8) [0.1] kcal mol^{-1}}. This favors ISC and the subsequent reaction to ^{1}**5,** which is about 70 kcal mol^{-1} more stable. Since the energy separation between the singlet and triplet states of bicyclo[1.1.0]butaneylidene and vinylacetylene as well as the energy barriers for the respective reactions to **5** for both multiplicities are similar, either of the reaction sequences



Scheme 4. Possible exergonic and thermoneutral deactivation routes of the initial products of the reaction of ^{3}PC with cyclopropene. Reaction energies, abbreviated as ΔE_R, are arranged in line with the respective equations while the numbers, placed above the arrows reflect the activation energies; data for intersystem crossing (ISC) are singlet–triplet energy splittings between the respective energy-minimum geometries of both multiplicities; all energies are in kcal mol^{-1} and the kind of brackets corresponds to the description in the computational methods section. [a] Employing UHF reference decreases E_A slightly by 1.6 kcal mol^{-1} indicating modest (bi)radicaloid character of the transition structure. [b] Energy differences for fully optimized structures.

[Eq. (9) and (10)] inevitably leads to ^{1}**5**. The rearrangement of bicyclic triplet carbene ^{3}**6** to the triplet biradical ^{3}**8**, which is 13.5 (10.8) [12.1] kcal mol^{-1} more stable, followed by isomerization to cyclobutadiene cannot compete with these reactions. The same is true for the intramolecular insertion of exocyclic carbene ^{3}**7** ($E_a = 43.5$ {52.7} kcal mol^{-1}) to give methylencyclopropene ($\Delta E = -11.3$ (-6.5) kcal mol^{-1}) in its lowest-lying triplet state. Accordingly, as the triplet and singlet states of cycloprop-3-enemethylene are predicted to be nearly isoenergetic {$\Delta E_{ST} = 0.6$–1.8 (-0.4–0.1) kcal mol^{-1} depending on the conformation}, reactions (11) and (12) should predominantly determine the experimentally observed products derived from **7**, although it forms in the triplet state. Another exocyclic carbene, **9**, possesses a triplet ground state, lying 13–14 kcal mol^{-1} below its singlet at B3LYP/6–311G** which is by 2.1 kcal mol^{-1} less stable than ^{3}**9** at CCSD(T)/cc-pVDZ; for this reason the reactions of **9** were investigated on the triplet PES only.

In the experimental re-examination of the reactions of carbon atoms with cyclopropene, we identified methylenecyclopropene (**2**), acetylene (**4**), vinylacetylene (**5**), and butatriene (**18**), by comparison of observed and computed as well as known experimental[51] IR spectra of these compounds. Noteworthy, acetylene can be detected in Ar matrices of graphite ablation products even in the *absence* of cyclopropene. Only qualitative changes of the spectrum obtained after co-deposition of the reactants (Figure 8), for pulsed and continuous co-condensation can be seen after annealing (see Supporting Information).

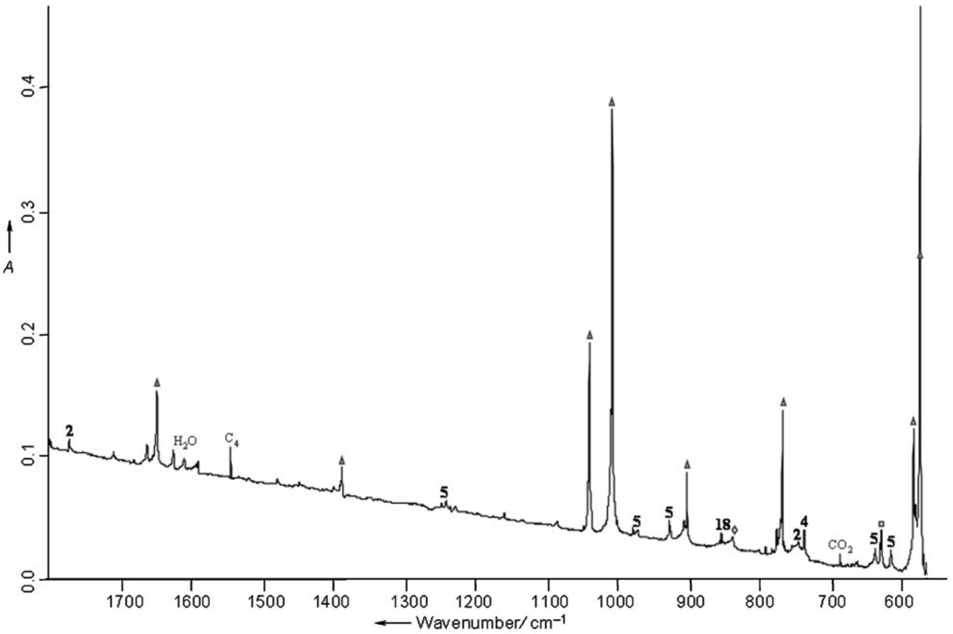


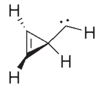
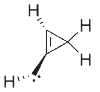
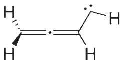
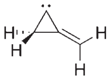
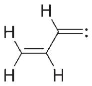
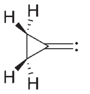
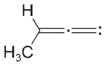
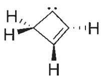
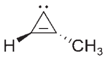
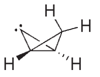
Figure 8. Part of the IR spectrum after the co-condensation of 50 mmol Ar/cyclopropene (1000/4) with graphite deposition products (2 h at 2 Hz) and annealing to 25 K, containing characteristic bands of reaction products **2**, **5**, **4**, and **18**; resolution 0.7 cm^{-1}; △: cyclopropene, □: propane, ◇: allene; gray: bands observable in the sprectra of the precursor, black: bands observable only after reaction.

None of the computed IR bands of **1** (Figure 5) were detected under any reaction conditions. Since this result is in qualitative agreement with Shevlins report, claiming that "···the data presented rule out all plausible mechanisms for the formation of acetylene other than via tetrahedrane..",[8a] the question arises, whether acetylene can form *without* the intermediacy of **1**. Three of the four observed products (vinylacetylene, methylencyclopropene, and acetylene) are expected from Equation (9)–(14), while butatriene forms from **2** under influence of visible light.[52] Thus, the formation of all observed species can be explained on kinetic *as well as* thermodynamic grounds without the intermediacy of **1**. Moreover, as depicted in Figure 1, the activation energies for the reactions of **6** (40.7 {45.7} kcal mol^{-1}) as well as of **8** (35.8 {46.2} kcal mol^{-1}) to **1** are too high to compete with the rearrangements of Equations (9)–(14). Hence, in marked contrast to Shevlin's hypothesis,[8a] it is *not* necessary to involve tetrahedrane as an intermediate to explain the observed products.

C_4H_4 PES: some general considerations: Besides tetrahedrane and its precursors, the C_4H_4 PES exhibits a number of isomers, for example carbenes (Table 1) that deserve attention. The presented series of carbenes illustrates the interplay of two well known factors effecting ground state multiplicities of carbenes vividly: variation of the internuclear angle at the carbene carbon atom and conjugation with a double bond. In this light the exocyclic carbene **7** is an exception, since its electronic configuration is dominated by conjugation with the cyclopropene ring. In terms of perturbation theory, the interaction of the b_1-MO of methylene with the doubly occupied cyclopropane Walsh e-orbital of the appropriate symmetry leads to the stabilized bonding combination below and destabilized antibonding combination above the a_1 methylene orbital. Since the latter stays empty in the singlet state but is singly occupied in the triplet state, the all over thermodynamic stabilization through conjugatuion is less pronounced in the triplet than in the singlet state and the singlet–triplet energy separation is diminished with respect to parent methylene; ^{1}**7** and ^{3}**7** are practically energetically degenerate. The shift of electron density from the ring to the carbene carbon atom is confirmed nicely by the shortening of the exocyclic C–C bond to 1.412 (1.445) Å.

While the notion of a bonding stabilization of the a_1 orbital with decreasing angle and enlarging energy separation of the a_1 and b_1 orbitals in favor of the singlet state is widely accepted on the grounds of the corresponding Walsh diagram,[53] the role of conjugation cannot be generalized. Indeed, substitution with a double bond operates on the b_1

Table 1. Point groups, PG, (first entry for T, second for S) and singlet–triplet energy separations for carbenes of C_4H_4 stochiometry; according to the IUPAC convention the ΔE_{ST} values for the triplet ground state carbenes are positive.

No	Structure	PG	ΔE_{ST} [kcal mol^{-1}] B3LYP-/6–311G**	CCSD(T)-/cc-pVDZ	CCSD(T)-//cc-pVTZ
7		C_s C_s	−1.8	−0.1	−4.1
9		C_s C_1	13.9	−2.1	−3.9
13		C_s C_s[a]	6.6	5.7	4.6
14		C_s C_s	−3.4	−6.0	−6.5
12		C_s C_s	−51.6	−42.4	−51.5
15		C_{2v} C_s	−55.3	−50.1	−65.4
16		C_s C_s	−32.0	−32.6	−34.1
10		C_s C_1	−14.8	−20.9	−22.6
17		C_s C_1	−49.3	−56.0	−52.6
6		C_s C_s	−45.7	−46.1	−47.6

[a] As B3LYP/6–311++G** is reported to predict ^{1}**13** to be a closed shell C_1 structure, with the 0.2 kcal mol^{-1} higher lying C_s symmetric interconversion TS for the *anti* isomer and ΔE_{ST}=3.9 kcal mol^{-1};[52] we computed the C_1 structure at CCSD(T)/cc-pVDZ: it converges to the C_s-symmetric energy minimum.

orbital, creating three allyl-like orbitals, of which the all over bonding below (or almost isoenergetic) the a_1-MO is doubly occupied and mimics the π bond. The energy difference between the a_1-MO and the nonbonding as well as antibonding orbitals depends on the substitution of a double bond. If the energy of the π orbital differs from that of the b_1-MO in methylene insignificantly, the energy splitting between the a_1 and nonbonding allylic orbital would not vary notably from the SOMO–SOMO gap in the parent triplet methylene. For the parent vinylmethylene such an ordering is found[54] at the MRCI/DZP level of theory. Both CCSD(T)/cc-pVDZ and B3LYP/6–311G** predict closed-shell C_s-symmetric ^{1}**9** not to be a minimum on the singlet PES. Furthermore, coupled-cluster theory gives one imaginary frequency for C_s open-shell ^{1}**9**. Since B3LYP describes the lowest-lying singlet state as a C_s-symmetric open-shell structure, the ΔE_{ST} value, given at this level of theory might be slightly overestimated, as the C_1 structure should gain stability due to nonzero overlap. The difference in the electronic configuration of the lowest-lying singlet state between ^{1}**9** and ^{1}**10** (closed-shell) on the one hand and the parent vinylmethylene (open-shell) on the other, seems to come from the increased interaction between both a_1 and b_1 orbitals with substituents, equalling the s character of both kinds of orbitals. This enables through-space delocalization in ^{1}**10**, which is best described by resonance between the localized ^{1}**10** and the Lewis structure, with the IUPAC name bicyclo[1.1.0]-but-2-ene (both are located as energy minima at B3LYP/6–311G**, but they converge to delocalized ^{1}**10** at CCSD(T)/cc-pVDZ; see Supporting Information). For ^{1}**9**, p-donation of the cyclopropene ring manifests itself in the strengthening of the exocyclic C−C bond to 1.288 Å concomitant with the lengthening of the adjacent ring C−C bond (1.721 Å). The lowest-lying ^{3}**9** and ^{3}**10** triplet states are C_s-symmetric, exhibiting allylic moieties; again triplet bicyclo[1.1.0]-but-2-ene (B3LYP/6–311G**) converges to ^{3}**10** (CCSD(T)/cc-pVDZ). In contrast to **9** and **10**, allenylidene **13**, is predicted to adopt C_s symmetry in the triplet and closed-shell singlet states at both levels of theory. This deviation in geometry from the other vinylmethylene carbenes ^{1}**9** and ^{1}**10** is likely to be due to the presence of a second pair of p orbitals perpendicular to the allyl system and interacting with the a_1 orbital localized on the carbene carbon atom.

A further example of the allylic stabilization of b_1, operating however in a completely different context, is given in buta-1,2-dieneylidene (**16**). Another vinylidene-type carbene, differing by more than 10 kcal mol^{-1} from the singlet–triplet energy separation of **16** (depending on the level of theory), buta-1,3-dieneylidene (**12**) lacks the allyl moiety. The ΔE_{ST} values of both carbenes compare well with the experimental estimate of −46.8 kcal mol^{-1} for the parent vinylidene.[55] For the last carbene, **15**, only the triplet configuration can be located with the employed computational methods, while the corresponding singlet structure of C_{2v} symmetry possesses one imaginary frequency leading to the C_s-symmetric potential energy minimum. The same stationary point is found by following the imaginary frequency of another C_{2v}-symmetric Lewis structure, which can be referred to as cyclobutyne and is predicted to be an energy minimum with MP2/6–31G*, MP4SDTQ/6–31G*//MP2/6–31G*, MP4SDTQ/6–311G**//MP2/6–31G*, MCSCF(4,4)/3–21G, MCSCF(4,4)/6–31G*, TCSCF/3–21G[25,56,57] in contrast to HF/6–31G*, B3LYP/6–311G**, CASSCF(12,12)/6–311G**, CCSD(T)/6–311G**[21] as well as its triplet pendant.

Combination of both factors, incorporation of the carbene carbon atom into a small ring and its conjugation with an *exocyclic* π bond, yields a ground-state singlet carbene owing to the preferential stabilization of the a_1 orbital; this also applies to methylenecyclopropylidene (**14**). Incorporation of *both* a double bond and a carbene center into a ring of decreasing size on going from **14** over **10** to methylcyclopropenylidene (**17**), is accompanied by growing stabilization of the closed-shell singlet, leading to a large ΔE_{ST} difference. This can be understood easily considering that the diminishing distance between carbene substituents raises the energy of the nonbonding quasi allyl orbital and lowers the energy of the antibonding MO by the same amount, while the a_1-MO and the bonding allyl orbital are strongly stabilized. In the extreme case of completely symmetric substitution, for example, for cyclopropenylidene, this results in a pair of almost degenerate nonbonding orbitals, energetically well separated from the a_1- and b_1-MOs. As such an orbital ordering would require occupation of *two* energetically comparable orbitals with *one* electron in the triplet state, triplet cyclopropenylidene adopts a C_1 structure, which allows an increase in the orbital energy separation. Similarly, **17** is predicted to possess a C_s-symmetric singlet ground state and an asymmetric (C_1) lowest-lying triplet state; the same is true for **10**. Remarkably, although **6** exhibits a high ΔE_{ST} value comparable to that of cyclopropenylidene (-48.8 (-49.9) kcal mol^{-1}) rather than cyclopropylidene (-13.7 (-20.1) kcal mol^{-1}), in agreement with expected high p-character of the central bond,[58] the rigidity of bicyclo framework prevents its relaxation to C_1 in the lowest triplet state.

Conclusion

While the reaction of atomic carbon with cyclopropene provides no access to tetrahedrane (**1**), **1** is kinetically stable and should in principle be synthesizable. All traditional tetrahedrane precursors react in exergonic low-barrier rearrangements to other C_4H_4 isomers. However, although tetrahedrane is not synthesizable from the classical precursors it still is an exciting synthetic target.

Acknowledgements

We are grateful to the members of Prof. J. Gauß′ group, University of Mainz, for kindly providing the ACESII program with technical support. We thank CSC Frankfurt am Main for generous allotments of CPU time.

---

[1] a) G. Maier, S. Pfriem, U. Schaefer, R. Matusch, *Angew. Chem.* **1978**, *90*, 552–553; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 520–521; b) G. Maier, F. Fleischer, *Tetrahedron Lett.* **1991**, *32*, 57–59; c) G. Maier, S. Pfriem, U. Schaefer, K. D. Malsch, R. Matusch, *Chem. Ber.* **1981**, *114*, 3965–3987; d) G. Maier, D. Born, *Angew. Chem.* **1989**, *101*, 1085–1087; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1050–1052; e) G. Maier, R. Wolf, H.-O. Kalinowski, *Angew. Chem.* **1992**, *104*, 764–766; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 738–740; f) G. Maier, R. Wolf, H.-O. Kalinowski, *Chem. Ber.* **1994**, *127*, 201–204; g) G. Maier, F. Fleischer, H.-O. Kalinowski, *Liebigs Ann.* **1995**, 173–186; h) G. Maier, J. Neudert, O. Wolf, *Angew. Chem.* **2001**, *113*, 1719–1720; *Angew. Chem. Int. Ed.* **2001**, *40*, 1674–1675; i) A. Sekiguchi, M. Tanaka, *J. Am. Chem. Soc.* **2003**, *125*, 12684–12685; j) M. Tanaka, A. Sekiguchi, *Angew. Chem.* **2005**, *117*, 5971–5973; *Angew. Chem. Int. Ed.* **2005**, *44*, 5821–5823.

[2] A. Baeyer, *Chem. Ber.* **1885**, *18*, 2269–2281.

[3] H.-S. Wu, X.-F. Quin, X.-H. Xu, H. Jiao, P. von R. Schleyer, *J. Am. Chem. Soc.* **2005**, *127*, 2334–2338; other strain measures are presented in references [13,19,20,23,29,32]; however, here we prefer the estimate with respect to dodecahedrane, although not completely strainless itself (cf. H.-D. Beckhaus, C. Rüchardt, D. R. Lagerwall, L. A. Paquette, F. Wahl, H. Prinzbach, *J. Am. Chem. Soc.* **1994**, *116*, 11775–11778) but setting its strain to zero gives strain energy consisting of *Baeyer* strain exclusively.

[4] H. Hopf, *Classics in Hydrocarbon Chemistry. Synthesis, Concepts, Perspectives*; Wiley-VCH, Weinheim, **2000**.

[5] P. E. Eaton, T. W. Cole, *J. Am. Chem. Soc.* **1964**, *86*, 3157–3158.

[6] R. J. Ternansky, P. W. Balogh, L. A. Paquette, *J. Am. Chem. Soc.* **1982**, *104*, 4503–4504.

[7] L. B. Rodewald, H. Lee, *J. Am. Chem. Soc.* **1973**, *95*, 623–625.

[8] a) P. B. Shevlin, A. P. Wolf, *J. Am. Chem. Soc.* **1970**, *92*, 406–408; b) R. F. Peterson, R. T. K. Baker, R. L. Wolfgang, *Tetrahedron Lett.* **1969**, *10*, 4749–4752.

[9] H. W. Lage, H. P. Reisenauer, G. Maier, *Tetrahedron Lett.* **1982**, *23*, 3893–3896.

[10] G. Maier, M. Hoppe, H. P. Reisenauer, *Angew. Chem.* **1983**, *95*, 1009–1010; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 990–991.

[11] G. Maier, M. Hoppe, K. Lanz, H. P. Reisenauer, *Tetrahedron Lett.* **1984**, *25*, 5645–5648.

[12] H. P. Reisenauer, cited in M. Christl, S. Freund, *Chem. Ber.* **1985**, *118*, 979–999.

[13] D. A. Kaisaki, D. A. Dougherty, *Tetrahedron Lett.* **1987**, *28*, 5263–5266.

[14] G. Maier, *Angew. Chem.* **1988**, *100*, 317–341; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309–332.

[15] H. Kollmar, *J. Am. Chem. Soc.* **1980**, *102*, 2617–2621.

[16] N. C. Baird, M. J. S. Dewar, *J. Am. Chem. Soc.* **1967**, *89*, 3966–3970.

[17] R. J. Buenker, S. D. Peyerimhoff, *J. Am. Chem. Soc.* **1969**, *91*, 4342–4346.

[18] N. C. Baird, M. J. S. Dewar, *J. Chem. Phys.* **1969**, *50*, 1262–1274.

[19] N. C. Baird, *Tetrahedron* **1970**, *26*, 2185–2190.

[20] J. M. Schulman, T. J. Venanzi, *J. Am. Chem. Soc.* **1974**, *96*, 4739–4746.

[21] W. J. Hehre, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 6941–6955.

[22] M. C. Böhm, R. Gleiter, *Tetrahedron Lett.* **1978**, *14*, 1179–1182.

[23] J. D. Dill, A. Greenberg, J. F. Liebman, *J. Am. Chem. Soc.* **1979**, *101*, 6814–6826.

[24] H. Kollmar, F. Carrion, M. J. S. Dewar, R. C. Bingham, *J. Am. Chem. Soc.* **1981**, *103*, 5292–5303.

[25] G. Fitzgerald, P. Saxe, H. F. Schaefer, *J. Am. Chem. Soc.* **1983**, *105*, 690–695.

[26] R. L. Disch, J. M. Schulman, M. L. Sabio, *J. Am. Chem. Soc.* **1984**, *106*, 1904–1906.

[27] B. A. Hess Jr., D. Michalska, L. J. Schaad, *J. Am. Chem. Soc.* **1985**, *107*, 1449–1450.

[28] B. A. Hess Jr., W. D. Allen, D. Michalska, L. J. Schaad, H. F. Schaefer III, *J. Am. Chem. Soc.* **1987**, *109*, 1615–1621.

[29] M. N. Glukhovtsev, S. Laiter, A. Pross, *J. Phys. Chem.* **1995**, *99*, 6828–6831.

[30] D. W. Ball, *J. Mol. Struct.* **1996**, *364*, 183–188.

[31] C. W. Earley, *J. Phys. Chem. A* **2000**, *104*, 6622–6627.

[32] B. S. Jursic, *J. Mol. Struct.* **2000**, *499*, 137–140.

[33] B. S. Jursic, *J. Mol. Struct.* **2000**, *507*, 185–192.

[34] D. Moran, M. Manoharan, T. Heine, P. von R. Schleyer, *Org. Lett.* **2002**, *4*, 23–26.

[35] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[36] a) J. Cizek, *J. Chem. Phys.* **1966**, *45*, 4256–4266; b) J. Gauß in *Encyclopedia of Computational Chemistry, Vol. 1*, (Eds.: P. von R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, A. P. Kollman, H. F. Schaefer III, P. R. Schreiner), Wiley, Chichester, **1998**, pp. 615–636.

[37] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.

[38] D. E. Woon, T. H. Dunning Jr., *J. Chem. Phys.* **1993**, *98*, 1358–1371.

[39] C. J. Cramer, *Essentials of Computational Chemistry* 2nd ed., Wiley, Chichester, **2004**.

[40] C. D. Sherrill, T. J. Van Huis, Y. Yamaguchi, H. F. Schaefer, *J. Mol. Struct.* **1997**, *400*, 139–156.

[41] H. F. Bettinger, P. R. Schreiner, P. von R. Schleyer, H. F. Schaefer, *Modern Electronic Structure Theory and Applications in Organic Chemistry*, World Scientific, Singapore, **1997**, pp. 183–196.

[42] T. J. Lee, J. E. Rice, G. E. Scuseria, H. F. Schaefer, *Theor. Chim. Acta* **1989**, *75*, 81–98. As none of the calculated T_1 values (see Supporting Information) exceed the critical limit of 0.02, the multideterminantal nature is of low importance for the description of all singlet carbenes and biradicaloid species discussed here.

[43] P. R. Schreiner, A. Navarro-Vazquez, M. Prall, *Acc. Chem. Res.* **2005**, *38*, 29–37.

[44] The details of apparatus and its uses are described in P. R. Schreiner, H. P. Reisenauer, *ChemPhysChem* **2006**, *7*, 880–885; P. R. Schreiner, H. P. Reisenauer, W. D. Allen, K. W. Sattelmeyer, *Org. Lett.* **2004**, *6*, 1163–1166; P. R. Schreiner, H. P. Reisenauer, K. W. Sattelmeyer, W. D. Allen, *J. Am. Chem. Soc.* **2005**, *127*, 12156–12157.

[45] R. B. Woodward, R. Hoffmann, *Angew. Chem.* **1969**, *81*, 797–869; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781–853. To the best of our knowledge, there is only one analogous correlation diagram on the basis of complete MO sets for both species in D_{2d} symmetry for the reaction of two N_2 molecules to hypothetic tetrahedral N_4: R. G. Pearson, *Symmetry Rules for Chemical Reactions: Orbital Topology and Elementary Process*, Wiley, New York, **1976**.

[46] A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem.* **2001**, *113*, 2916–2920; *Angew. Chem. Int. Ed.* **2001**, *40*, 2834–2838.

[47] A. A. Fokin, B. Kiran, M. Bremer, X. Yang, H. Jiao, P. von R. Schleyer, P. R. Schreiner, *Chem. Eur. J.* **2000**, *6*, 1615–1628.

[48] D. Cremer, E. Kraka, *J. Am. Chem. Soc.* **1985**, *107*, 3800–3810.

[49] Y. Mo, *Org. Lett.* **2006**, *8*, 535–538.

[50] F. Jensen, *Introduction to Computational Chemistry*, 1st ed., Wiley, Chichester, **2004**.

[51] For IR-spectra in Ar matrices: of **4** and **5** see: G. Maier, M. Hoppe, K. Lanz, H. P. Reisenauer, *Tetrahedron Lett.* **1984**, *25*, 5645–56458; for **2** see: W. E. Billups, L-J. Lin, E. W. Casserly, *J. Am. Chem. Soc.* **1984**, *106*, 3698–3699.

[52] R. Wrobel, W. Sander, D. Cremer, E. Kraka, *J. Phys. Chem. A* **2000**, *104*, 3819–3825.

[53] A. D. Walsh, *J. Chem. Soc.* **1953**, 2260–2266.

[54] M. Yoshimine, J. Pacansky, N. Honjou, *J. Am. Chem. Soc.* **1989**, *111*, 2785–2798.

[55] K. M. Ervin, J. Ho, W. C. Lineberger, *J. Chem. Phys.* **1989**, *91*, 5974–5992.

[56] N. Balucani, A. M. Mebel, Y. T. Lee, R. I. Kaiser, *J. Phys. Chem. A* **2001**, *105*, 9813–9818, and references therein

[57] R. P. Johnson, K. J. Dadoust, *J. Am. Chem. Soc.* **1995**, *117*, 362–367, and references therein

[58] H.-U. Wagner, G. Szeimies, J. Chandrasekhar, P. von R. Schleyer, J. A. Pople, J. Binkley, *J. Am. Chem. Soc.* **1978**, *100*, 1210–1213.

Received: March 31, 2006