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Tetracyclo[3.1.0.0(1.3).0(3.5)]hexane: a new C_6H_6 isomer with an unusual bonding situation

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This paper is dedicated to Professor Norman L. Allinger

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Abstract

Quantum chemical calculations at the B3LYP, MP2 and CCSD(T) levels of theory predict that tetracyclo[3.1.0.0(1.3).0(3.5)]hexane (**2**) is an energetically high-lying isomer on the C_6H_6 potential energy surface. **2** is ~70–80 kcal/mol higher in energy than [3]radialene (**3**) and ~150–160 kcal/mol higher in energy than benzene. The activation barrier for the first step of the rearrangement of **2** to **3** is ~10 kcal/mol, which might be high enough to isolate **2** in a low-temperature matrix. The analysis of the bonding situation shows that **2** is a cyclic carbene which is stabilized by charge donation from a C=C double bond to the carbene carbon atom. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: C_6H_6 isomers; Bonding analysis; Carbene

1. Introduction

The search for and prediction of stable molecules with the formula C_6H_6 is a fascinating chapter in the history of organic chemistry. The puzzling chemical stability of benzene was a formidable problem for the bonding models which prevailed in the last century. The correct description as a cyclic delocalized molecule, **1**, which was originally suggested by Kekulé [1] is now known to every chemist. (The original understanding of the two mesomeric forms shown in Scheme 1, which shows a sketch of the planar structures of the C_6H_6 isomers benzene **1**, tetracyclo[3.1.0.0(1.3).0(3.5)]hexane **2** and [3]radialene **3**, was that the two structures are isomers which have oscillating double bonds). Numerous other structures have earlier been suggested for benzene. One example is tetracyclo[3.1.0.0(1.3).0(3.5)]hexane (**2**), which is not known experimentally. Other C_6H_6 isomers such as [3]radialene (**3**) have in the meantime been synthesized [2,3].

The potential energy surface of C_6H_6 has been studied extensively by quantum theoretical methods and numerous energy minima were found (for a leading reference of calculations and a discussion of C_6H_6 isomers see Refs. [4,5]). Casual strolling through historic books aroused our interest in the sketch of the tetracyclic structure **2**. We checked the literature and found that **2** has never been the subject of an accurate quantum chemical study; there are only two theoretical papers which report low-level calculations of the molecule. Lohr and Robin [6] carried out Hückel-type calculations of **2** using an assumed

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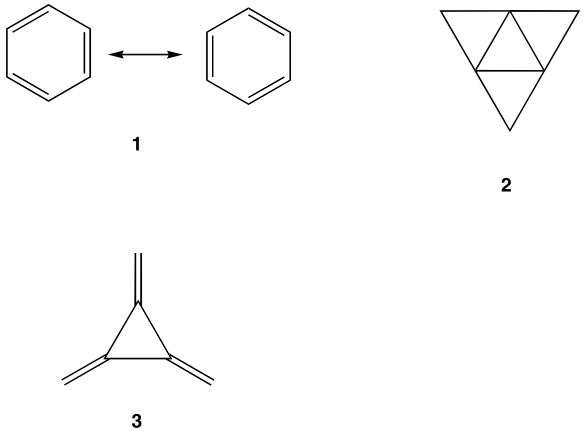


1

2

3

Scheme 1.

planar geometry of the molecule. Pyykkö and co-workers [7] reported about a systematic study of the heats of formation of 48 cyclic hydrocarbons which include **2** using various empirical methods. Both investigations cannot be considered as a reliable theoretical study of the structure and bonding situation of **2**.

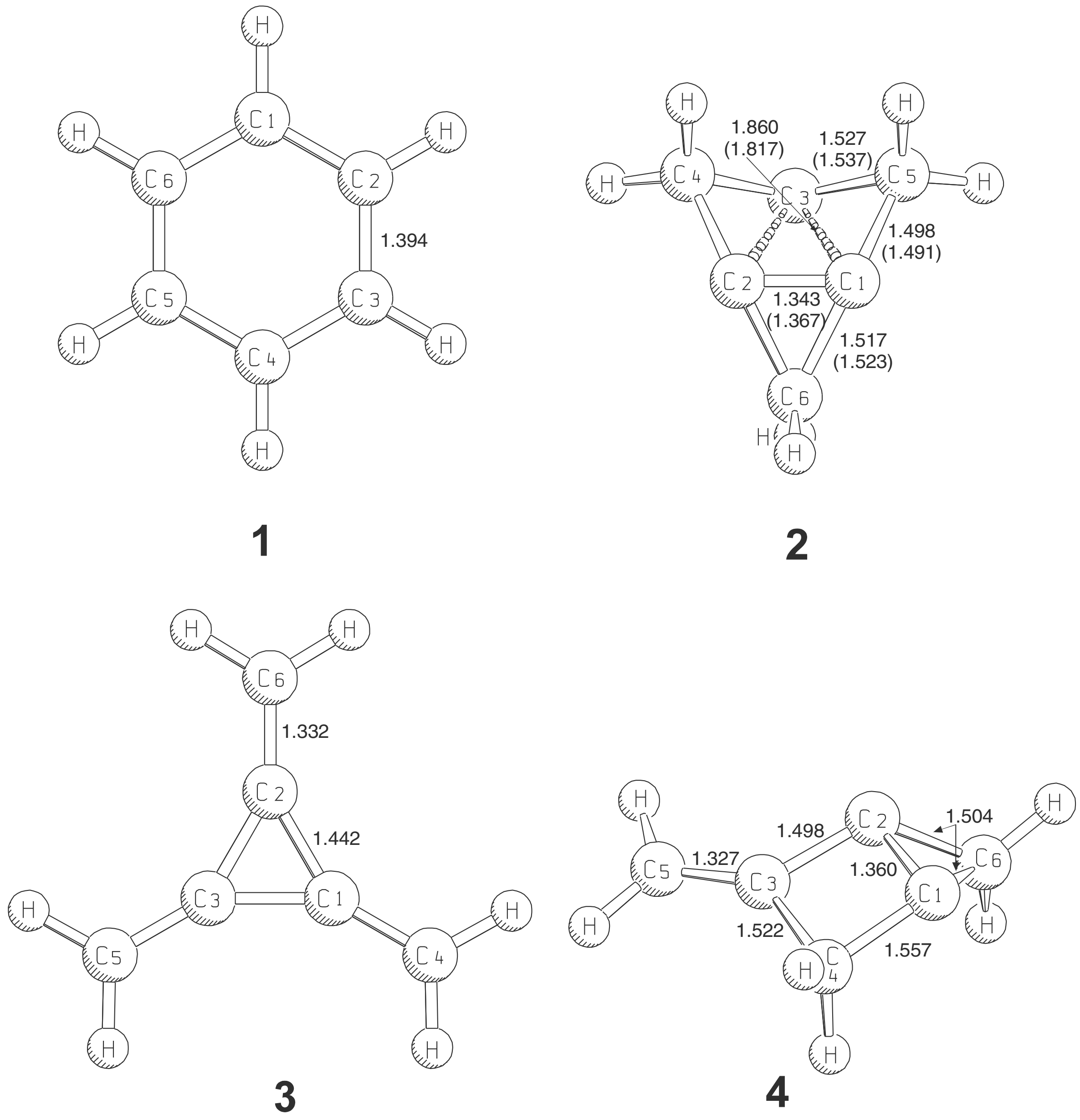
In this paper we report about the first quantum chemical calculation of the equilibrium geometry of tetracyclo[3.1.0.0(1.3).0(3.5)]hexane **2** using gradient-corrected density functional theory at the B3LYP level [8,9] and Møller–Plesset perturbation theory terminated at second order (MP2) [10,11]. We analyzed the bonding situation with the help of the natural bond orbital (NBO) [12] partitioning scheme. The kinetic stability of **2** was probed theoretically by calculating the transition states and intermediates for the rearrangement of **2** → **3**.

2. Methods

The equilibrium geometries have been optimized at the B3LYP [8,9] and MP2 [10,11] levels using 6-311G(d,p) basis sets [13]. Harmonic vibrational frequencies have been calculated at B3LYP/6-311G(d,p). The energy minima and transition states have been verified by inspection of the Hessian matrix, which showed only positive eigenvalues for the former and one negative eigenvalue for the latter species. Improved single-point energy calculations were carried out with coupled-cluster theory at the CCSD(T) level [14–19] using the B3LYP optimized geometries. The program package GAUSSIAN 98 [20] was used for the calculations.

3. Geometry and bonding situation

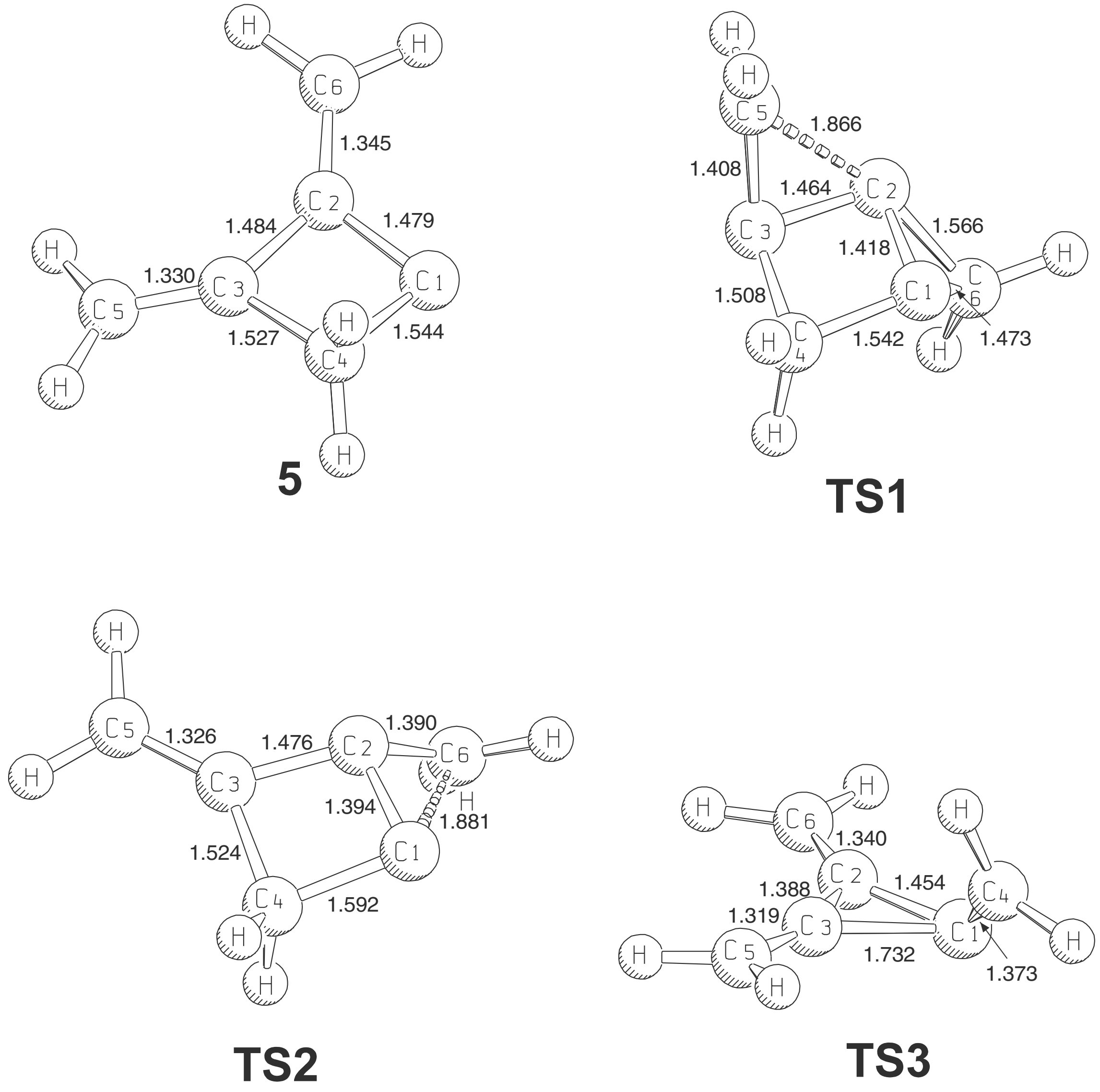
Fig. 1 shows the optimized geometry of **2** at B3LYP/6-311G(d,p). As expected, the equilibrium structure is not planar. The molecule has C_s symmetry and exhibits some surprising features. The C1–C2 bond length of the central three-membered ring is rather short (1.343 Å), which is typical for a C–C double bond (1.35 Å), while the other two bond lengths C1–C3 and C2–C3 are very long (1.860 Å). The interatomic distance of 1.860 Å is much longer than the average value of a typical C–C single bond (1.52 Å). The MP2 values of **2** are very similar to the B3LYP results, which supports the theoretically predicted unusual equilibrium geometry of **2**. There must be some kind of bonding interactions between C1–C3 and C2–C3, which are clearly weaker than those of a C–C σ bond. The C–CH_2 bond lengths of the peripheric three-membered cycles are in the range of a typical C–C single bond.



1 **2** **3** **4**

Fig. 1. Calculated bond lengths (Å) at B3LYP/6-311G(d,p) of C_6H_6 isomers **1**–**5** and transition states **TS1**–**TS3**. The MP2/6-311G(d,p) values of **2** are given in parentheses.

The NBO analysis of the optimized structure of **2** reveals a very unusual bonding pattern which gives a plausible explanation for the geometry. Table 1 gives the most important results of the NBO partitioning scheme. The bonding situation of **2** according to the NBO method is as follows. There are two C1–C2 bonding orbitals which have nearly σ and π symmetry, although there is no mirror plane which contains the C1–C2 axis. Table 1 shows that the C1–C2 "σ" bond is



5 **TS1** **TS2** **TS3**

Fig. 1. (*continued*)

∼sp^3 hybridized at the carbon atoms, while the "π" bond has 99% p(π) character. The carbon atom C3 has two single bonds to C4 and C5 and a lone-pair orbital which is ∼sp hybridized. Thus, *the NBO analysis suggests that **2** is a carbene!* The unusual C1–C3 and C2–C3 bond lengths of 1.860 Å are the result of electron donation from the C1–C2 π bond into the formally empty p AO of the carbene carbon atom C3. This is revealed by the NBO analysis in two ways. First, the NBO of **2**, which describes the formally empty p(π) AO of C3 is significantly occupied with 0.45 electrons. Secondly, the estimate of the intramolecular orbital interactions via perturbation theory analysis gives a very large value of 169.3 kcal/mol for the orbital pair

Table 1
Results of the NBO analysis of **2** at B3LYP/6-311G(d,p)

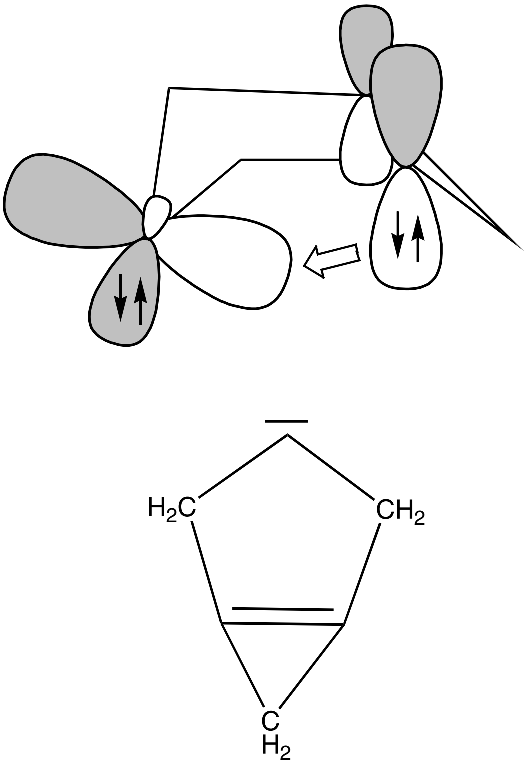
A–B	Population	A			B	
		% A	% s	% p	%s	%p
C_1–C_2	1.96	50.0	27.22	72.59	27.22	72.59
C_1–C_2	1.59	50.0	–	99.53	–	99.53
C_1–C_5	1.93	52.00	42.71	57.20	21.50	78.39
C_1–C_6	1.94	52.41	29.81	70.05	21.52	78.37
C_3–C_5	1.92	45.14	24.55	75.27	27.39	72.48
C_3(lp)	1.90	100.0	46.39	53.48	–	–

C1–C2(π)/C3p(π). The bonding situation at the carbene center of **2** can thus be described as shown in Scheme 2 [21].[1,2]

Further support for the bonding picture depicted in Scheme 2 comes from the shape of the canonical Kohn–Sham orbitals. Fig. 2 shows the HOMO of **2**, which is clearly a lone-pair MO at the carbene carbon atom C3. The HOMO − 1 is mainly the C1–C2 π bond, but it has also a significant coefficient at C3. The LUMO is the C1–C2 "π*" orbital, while the LUMO + 1 is the antibonding combination of the HOMO − 1.

It is interesting to learn about the atomic charge distribution in the molecule. The carbon atoms C1 and C2 carry a weak positive charge of 0.07*e*, while the carbene carbon atom C3 has a small negative charge of −0.11*e*. The peripheric carbon atoms are more negatively charged (C4, C5: −0.45*e*; C6: −0.35*e*).

We optimized the geometry of **2** in the triplet state. The calculations gave a structure which is 32.3 kcal/mol (B3LYP) higher in energy than the singlet state. Therefore, we did not consider triplet states of any C_6H_6 species which is calculated in this work.



Scheme 2.

Fig. 1 gives also the optimized structures of other C_6H_6 species which are relevant for the rearrangement of **2** to the [3]radialene **3** which is discussed below. **3** is the only species investigated here for which an experimental geometry has been reported. The B3LYP/6-311G(d,p) values for the bond lengths of the exocyclic (1.332 Å) and endocyclic (1.442 Å) C–C bonds are in very good agreement with the experimental values which are 1.343(20) and 1.453(20) Å, respectively [22].

4. Kinetic stability

It is unlikely that **2** can be synthesized as a stable molecule. To explore the possibility that **2** might be isolated in a low-temperature inert matrix we calculated the reaction path of rearrangement of **2** toward more stable C_6H_6 isomers. Many reaction channels leading to different species may be envisaged. We

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[1] The bonding situation which is shown in Scheme 2 suggests that the correct name of **2** should be bicyclo[3.1.0]hex-1(5)-ene-3-ylidene. We decided to keep the name tetracyclo [3.1.0.0(1.3).0(3.5)]hexane because there are clearly chemical bonds between the four-coordinated carbon atom C3 and the carbon atoms C1 and C2.

[2] It is interesting to note that the structure shown in Scheme 2 has not been found in a topological search of C_6H_6 isomers which led to 217 possible forms where the coordination number at carbon $k_C \leq 4$ and $k_H = 1$.

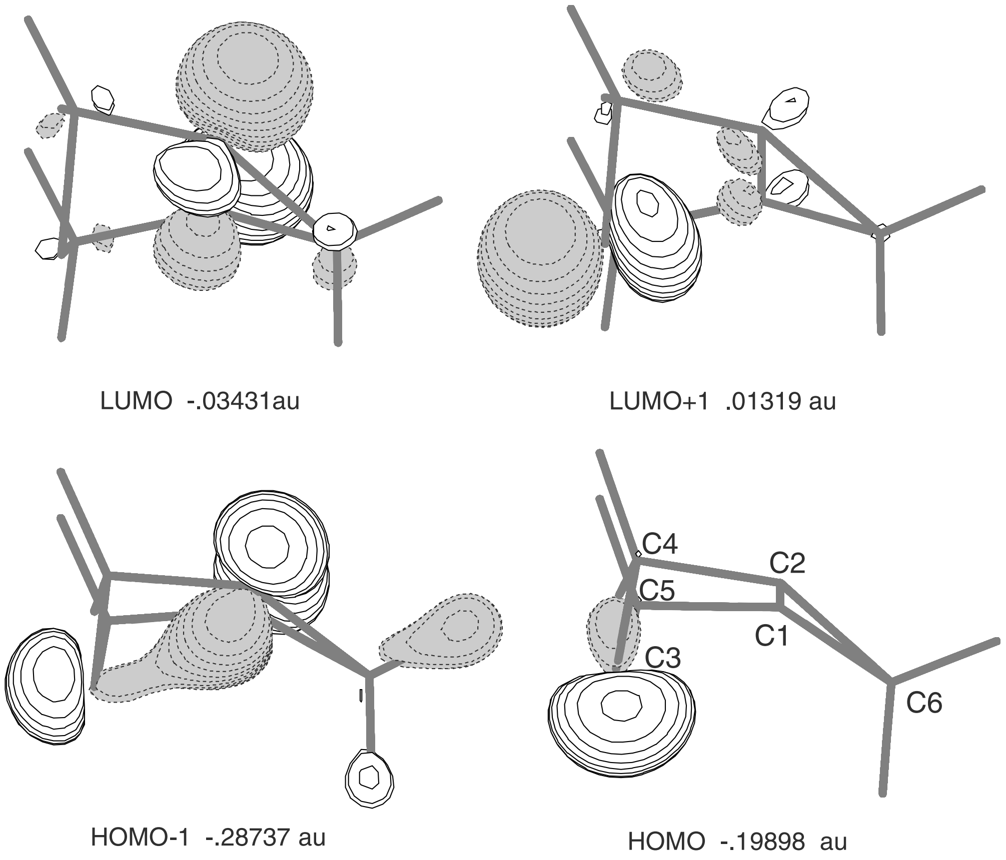

Fig. 2. Plot of the highest-lying occupied orbitals HOMO and HOMO − 1 and the lowest-lying unoccupied orbitals LUMO and LUMO+1 of **2**.

considered the reaction steps leading from **2** to the structurally related isomer [3]radialene **3**. A substantial amount of computer time was spent in order to find the intermediates and the transition states for the reaction. Fig. 3 shows the theoretically predicted reaction pathway for the rearrangement **2** → **3**. Two intermediates **4** and **5** and three transition states **TS1**–**TS3** were located on the potential energy surface. Intrinsic reaction coordinate (IRC) calculations [23] showed that they belong to the reaction course shown in Fig. 3. Fig. 1 shows the optimized geometries of the equilibrium structures. Table 2 gives the theoretically predicted distances and angles. Table 3 shows the calculated energies.

The B3LYP calculations predict that **2** is 82.3 kcal/mol higher in energy than **3**, which is 80.4 kcal/mol less stable than benzene (Table 3). The CCSD(T) calculations give similar results: the energy difference between **2** and **3** is 69.8 kcal/mol and the energy difference between **3** and benzene is 83.3 kcal/mol. Thus, **2** is an energetically very high-lying isomer on the C_6H_6 potential energy surface. But what about the kinetic stability? Fig. 3 shows that the first step of the reaction course is the formation of the bicyclic structure **4** via transition state **TS1**. One of the long C1/C2–C3 bonds of **2** is broken and the other becomes a normal single bond while the $C5H_2$ group forms an exocyclic double bond with carbon atom C3 during the reaction step **2** → **4**. The rearrangement is highly exothermic. The calculated reaction energy is −29.9 kcal/mol at B3LYP and −27.3 kcal/mol at

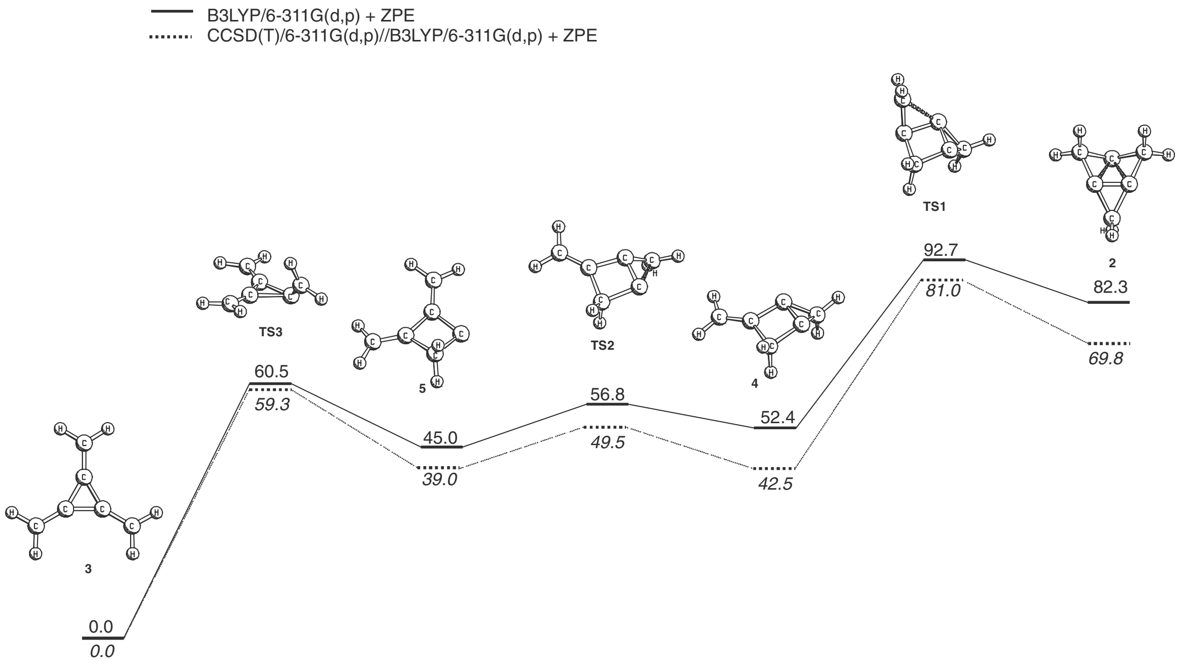

Fig. 3. Calculated reaction path for the rearrangement **2** → **3**. Energy values in kcal/mol.

CCSD(T). We want to point out that B3LYP and CCSD(T) predict not only similar reaction energies but also comparable activation barriers of 10.4 and 11.2 kcal/mol, respectively (Fig. 3 and Table 3). The calculated barriers are high enough to keep **2** in the potential well at low temperatures.

The second step of the reaction pathway shown in Fig. 3 is the rearrangement **4** → **5** via **TS2**. **5** is a four-membered cyclic carbene which has two exocyclic C=C double bonds. The carbene center is stabilized by conjugation of the formally empty p(π) AO of the carbene carbon atom C1 with the C2–C6 π bond. This becomes obvious by the calculated C1–C2 bond length which is significantly shorter (1.479 Å) than the C1–C4 bond (1.544 Å) and by the population of the natural orbital which describes the formally empty p(π) AO of C1 (0.21*e*). This is clearly less than the occupation of the C3 carbene p(π) AO of **2** (0.45*e*). The perturbation analysis of the intramolecular orbital interaction between the C2–C6 double bond and the p(π) AO of **5** gives only 33.1 kcal/mol, which is much less than the stabilization which is estimated for the carbene **2** (169.3 kcal/mol). Thus, the NBO analysis indicates that the carbene carbon atom C1 of **5** is electronically less stabilized than C3 in **2**.

The final step of the reaction is the formation of [3]radialene **3**. The calculations predict that the highly exothermic reaction step has a substantial activation energy. The theoretically predicted barrier is 15.5 kcal/mol at B3LYP and even 20.3 kcal/mol at CCSD(T).

The calculated reaction pathway for rearrangement of **2** suggests that the compound might be isolable in a low-temperature matrix. In order to help in the identification of the molecule we present in Table 4 the calculated harmonic vibrational frequencies and IR intensities. We think that the IR intensive modes 9a′, 13a′ and the triple 8a″, 9″ and 10″ should be particularly useful for the purpose of identification.

5. Summary

Tetracyclo[3.1.0.0(1.3).0(3.5)]hexane **2** is predicted

Table 2
Calculated bond distances *r* (Å), bond angles *a* and dihedral angles *d* (degree) at B3LYP/6-311G(d,p). MP2 values for **2** are given in parentheses

1 (D_{6h})		**5** (C_1)		**TS2** (C_1)	
r(C1,C2)	1.394	*r*(C1,C2)	1.479	*r*(C3,C2)	1.476
2 (C_s)		*r*(C2,C3)	1.484	*r*(C2,C1)	1.394
r(C1,C2)	1.343 (1.367)	*r*(C3,C4)	1.527	*r*(C1,C4)	1.592
r(C2,C3)	1.860 (1.817)	*r*(C4,C1)	1.544	*r*(C4,C3)	1.524
r(C2,C4)	1.498 (1.491)	*r*(C2,C6)	1.345	*r*(C5,C3)	1.326
r(C4,C3)	1.527 (1.537)	*r*(C3,C5)	1.330	*r*(C2,C6)	1.390
r(C2,C6)	1.517 (1.523)	*a*(C3,C2,C1)	93.7	*r*(C1,C6)	1.881
a(C3,C4,C2)	75.8 (73.8)	*a*(C2,C1,C4)	86.8	*a*(C4,C3,C2)	84.9
a(C2,C6,C1)	52.5 (53.3)	*a*(C4,C3,C2)	87.2	*a*(C3,C2,C1)	100.0
a(C1,C2,C6)	63.7 (63.3)	*a*(C1,C4,C3)	89.5	*a*(C2,C1,C4)	85.1
a(C4,C2,C6)	149.3 (148.6)	*a*(C6,C2,C1)	127.5	*a*(C1,C4,C3)	89.7
a(C4,C3,C5)	110.4 (109.6)	*a*(C6,C2,C3)	138.1	*a*(C1,C6,C2)	47.6
d(C6,C2,C1,C3)	116.5 (114.0)	*a*(C5,C3,C2)	135.7	*a*(C5,C3,C2)	136.4
d(C4,C2,C3,C1)	144.9 (143.3)	*a*(C5,C3,C4)	136.0	*a*(C5,C3,C4)	138.8
d(C4,C3,C2,C6)	159.9 (160.8)	*d*(C5,C3,C2,C1)	156.1	*a*(C2,C1,C6)	47.4
3 (D_{3h})		*d*(C6,C2,C1,C4)	159.1	*d*(C3,C2,C1,C4)	4.9
r(C1,C2)	1.442	*d*(C3,C4,C1,C2)	12.3	*d*(C5,C3,C2,C1)	174.3
r(C2,C6)	1.332			*d*(C6,C2,C1,C4)	129.1
4 (C_1)		**TS1** (C_1)		**TS3** (C_1)	
r(C3,C2)	1.498	*r*(C2,C1)	1.418	*r*(C2,C1)	1.454
r(C2,C1)	1.360	*r*(C2,C3)	1.464	*r*(C1,C3)	1.732
r(C1,C4)	1.557	*r*(C1,C4)	1.542	*r*(C3,C2)	1.388
r(C4,C3)	1.522	*r*(C3,C4)	1.508	*r*(C6,C2)	1.340
r(C2,C6)	1.504	*r*(C1,C6)	1.473	*r*(C4,C1)	1.373
r(C6,C1)	1.504	*r*(C6,C2)	1.566	*r*(C5,C3)	1.319
r(C3,C5)	1.327	*r*(C2,C5)	1.866	*a*(C2,C1,C3)	50.7
a(C4,C3,C2)	89.3	*r*(C5,C3)	1.408	*a*(C3,C2,C1)	75.1
a(C3,C2,C1)	92.9	*a*(C1,C2,C3)	84.0	*a*(C1,C3,C2)	54.2
a(C2,C1,C4)	93.2	*a*(C2,C3,C4)	98.5	*a*(C6,C2,C1)	142.5
a(C1,C4,C3)	84.6	*a*(C4,C1,C2)	99.0	*a*(C6,C2,C3)	142.5
a(C5,C3,C2)	133.2	*a*(C1,C4,C3)	78.4	*a*(C4,C1,C2)	119.9
a(C5,C3,C4)	137.3	*a*(C1,C6,C2)	55.5	*a*(C4,C1,C3)	85.3
a(C2,C6,C1)	53.8	*a*(C2,C5,C3)	50.8	*a*(C5,C3,C2)	160.5
a(C3,C2,C6)	128.8	*a*(C6,C1,C2)	65.6	*a*(C5,C3,C1)	145.3
a(C4,C1,C6)	129.4	*a*(C6,C2,C1)	65.6	*d*(C5,C3,C2,C1)	179.3
a(C1,C2,C6)	63.1	*a*(C3,C2,C5)	48.1	*d*(C6,C2,C3,C1)	179.8
a(C6,C1,C2)	63.1	*a*(C5,C3,C2)	81.0	*d*(C4,C1,C3,C2)	135.6
d(C4,C3,C2,C1)	0.6	*d*(C4,C1,C3,C2)	177.1		
d(C5,C3,C2,C1)	175.3	*d*(C6,C1,C2,C3)	127.6		
d(C6,C2,C1,C4)	133.2	*d*(C5,C3,C2,C1)	124.3		

to be an energetically high-lying isomer on the C_6H_6 potential energy surface. The activation barrier for the rearrangement of **2** to the more stable structure **4** is ~10 kcal/mol, which makes it possible to isolate **2** in a low-temperature matrix. The analysis of the bonding situation shows that **2** is a cyclic carbene stabilized by charge donation from a C=C double bond to the empty orbital of the carbene carbon atom.

Acknowledgements

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Table 3
Calculated energies at B3LYP/6-311G(d,p) and CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p). ZPE corrected values are given in parentheses

	B3LYP			CCSD(T)	
	E_{tot} (au)	E_{rel} (kcal/mol)	ZPE	E_{tot} (au)	E_{rel} (kcal/mol)
1	−232.308549	−84.3 (−80.4)	62.9	−231.653845	−87.3 (−83.3)
2	−232.044415	81.4 (82.3)	59.8	−231.404954	68.9 (69.8)
3	−232.174200	0.0 (0.0)	58.9	−231.514800	0.0 (0.0)
4	−232.091739	51.7 (52.4)	59.5	−231.448093	41.9 (42.5)
5	−232.101169	45.8 (45.0)	58.1	−231.451319	39.8 (39.0)
TS1	−232.025616	93.2 (92.7)	58.4	−231.384831	81.6 (81.0)
TS2	−232.082880	57.3 (56.8)	58.5	−231.435181	50.0 (49.5)
TS3	−232.074646	62.5 (60.5)	57.0	−231.417177	61.3 (59.3)

Table 4
Calculated harmonic frequencies and IR intensities of compound **2** at B3LYP/6-311G(d,p)

	Irep	ν (cm^{-1})	Intensities (km/mol)
1	a′	334.2	15.4
2	a′	396.2	1.9
3	a′	497.6	5.3
4	a′	693.1	10.2
5	a′	893.9	2.6
6	a′	1010.3	3.7
7	a′	1051.4	3.2
8	a′	1111.6	4.1
9	a′	1144.5	12.1
10	a′	1200.1	2.2
11	a′	1472.1	0.6
12	a′	1500.4	1.9
13	a′	1624.2	20.8
14	a′	2987.0	97.0
15	a′	3080.6	44.3
16	a′	3148.7	7.4
17	a′	3172.3	8.1
1	a″	260.9	8.0
2	a″	483.4	12.4
3	a″	650.3	0.9
4	a″	945.8	1.3
5	a″	972.0	1.5
6	a″	1007.9	7.3
7	a″	1087.9	8.0
8	a″	1102.3	10.1
9	a″	1152.4	0.0
10	a″	1250.6	2.6
11	a″	1484.8	0.4
12	a″	2994.2	28.3
13	a″	3148.5	19.8

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