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Strained delocalized carbenoid ring systems – A theoretical investigation

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Abstract. A number of ring compounds containing a divalent carbon center (carbenes) have been studied using *ab initio* quantum chemical methods. The studied systems include: imidazol-2-ylidene, 4-pyranylidene, 9-xanthylidene, cyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene. Extended ANO type basis sets were used. Wave functions and energies were obtained with a multiconfigurational approach (CASSCF), where dynamic correlation effects are treated by using second-order perturbation theory (CASPT2).

The singlet–triplet splitting has been found to depend linearly on the energy separation between the two carbene orbitals. All systems, where this splitting is larger than about 10 eV have been found to have a singlet ground state, while those with a smaller gap have a triplet ground state. A number of excited states have been characterized. Computed excitation energies are in agreement with experiment in cases where such information is available.

Key words: Ring compounds – Carbenes – Quantum chemical methods – CASSCF – CASPT2

1 Introduction

The simplest of all carbenes, methylene (CH_2), has a triplet ground state. The energy difference of the two nonbonding orbitals is not large enough to favor pairing of the two electrons in $^1A_1$. For systems other than methylene the relative orbital energies of the in plane (σ) and out of plane (π) orbitals can be increased or decreased by the effect of different substituents; hence can also the difference in energy between $^1A_1$ and $^3B_1$ state (the singlet–triplet gap) be altered. One way of doing this is to polarize the two bonds at the carbene center and change the hybridization of the σ-orbital [1]. Another way is to mix the out of plane orbital on the carbene carbon atom, p_x, with an aromatically stabilized π system [2]. These effects lead to a lowering of the $^1A_1$ compared to the $^3B_1$ state and can, if the effect is large enough, lead to a change of ground state. A system where the energy difference is large, can become a stable molecule with a di-valent carbon atom.

In spite of the fact that carbenes normally are very reactive, a few stable carbene species have been synthesized in recent years. The first, and perhaps the most important molecule of this kind, 1,3-di(1-adamantyl)imidazol-2-ylidene, was isolated in 1991 [3] and its structure was determined with X-ray crystallography [4]. In this molecule both steric and electronic features contribute in making the carbene stable. Two bulky adamantyl groups on the neighbouring nitrogen atoms hinder reactants to approach the carbene center. The electronic stabilization of this molecule is provided efficiently by the imidazol ring. In this ring there are two electronegative nitrogen atoms directly bound to the carbene carbon atom that diminish the electron density at the carbene center and polarizes the bonds. Due to this the bonds acquire more p-character and the carbenoid angle becomes smaller. As a result, the s-character of the σ lone-pair orbital increases and its energy goes down. The π-system also makes the singlet–triplet gap larger. The carbene π-orbital interacts repulsively with the nitrogen lone-pairs and its energy is as a result pushed up. The overall effect is that the singlet state is favored compared to the triplet and the gap between them is quite large. In general, the singlet carbenes are considerably less reactive than the triplets.

A number of previous studies, experimental and theoretical, have been performed for the carbenes. The spectroscopy of carbenes in matrices was recently reviewed by Sander et al. [5]. The topics discussed concern, except for the singlet–triplet gap, mostly the geometry and its relation to the electronic structure. The theoretical calculations have mainly been performed using MP2 and other single-configuration methods. Experiments concerning carbenes are often limited to ESR-measurements [6, 7] that only give information about triplet species and in addition exclusively of areas close to the carbene center. The information is given by the zero-field splitting parameters. One of them, D, is a measure of the average distance between the two electrons and hence related to the delocalization in conjugated π systems. From the other parameter, E, the bond angle at the carbene center can be estimated since the value is related to the s-character of the in plane singly occupied orbital. In addition to the ESR measurements, spectroscopic investigations have been performed on some of the molecules trapped in inert gas matrices at low temperatures [5]. Also fundamental reactions with oxygen and addition to double bonds have been studied under these conditions and have been helpful in determining the ground state spin multiplicity.

The generation of carbenes are most commonly done by irradiation of monochromatic light on a diazo precursor. The precursors are first isolated in the matrix and then by photolysis converted to the target molecule. Other ways of synthesis are the use of flash vacuum pyrolysis followed by trapping in the matrix or some sort of proton abstracting agent.

Still today this area has not been thoroughly theoretically investigated. The emphasis has been on methylene (cf. [8] and references therein) and the recently synthesized imidazol-2-ylidene neglecting many other compounds of equal interest. The field also lacks the use of more accurate methods and the results are not in all cases reliable. A third carbene of interest is cyclopropenylidene [9], for which single-configuration methods give an asymmetric geometry in the first excited state. The same result is obtained using multiconfigurational (MCSCF) methods [10]. Most studies are concerned with the ground state and the singlet–triplet splitting. Very little has been done on other excited states, which are of considerable interest for experimental spectroscopy.

The present investigation covers five carbenes, which have in common a delocalized π-system. It includes imidazol-2-ylidene, a stable carbene with all the features that give a singlet ground state. The additional choice of molecules includes two with singlet and two with triplet ground states: 4-pyranylidene and

9-xanthylidene (singlets), and cyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene (triplets). Since most experimental information is derived from ESR spectroscopy, very little is known about the singlet states and information about them is instead obtained from the theoretical studies. Further, the influence of electronegative substituents on the carbenes have been studied in several cases by others whereas the influence of the π system is less well understood. The present study includes three states, $^1A_1$, $^3B_1$ and $^1B_1$, for all molecules and in addition the first excited state with the same spin multiplicity as the ground state. In some cases states in between have also been investigated. High level *ab initio* quantum chemical methods have been used together with extended basis sets. Computed structures are accurate to ± 0.01Å and $\pm 5.0°$ and relative energies to 0.2 eV.

2 Methods and details of calculations

The present *ab initio* quantum chemical study has been performed with the complete active space self-consistent field (CASSCF) method followed by a second-order perturbation estimate of the remaining correlation energy. The geometry optimization of the largest system was performed with a more general multiconfigurational restricted active space SCF (RASSCF) type of wave function.

The CASSCF method [11] is a particular case of a more general multiconfigurational (MC)SCF method. All configurations are included in the wave function, which can be formed by distributing a certain number of electrons among a given set of active orbitals, restricted only by point group and spin symmetry.

RASSCF is the restricted active space SCF method, a generalization of the CASSCF method. Instead of a single active space, three subspaces are distinguished, and are called RAS-1, RAS-2 and RAS-3, respectively. Again, a certain number of electrons are distributed among the three orbital spaces, but now with the added restriction that, at most a specified number of holes are allowed in the RAS-1 space and, at most a specified number of electrons in RAS-3.

CASPT2 [12–14] is a method for calculating a second-order perturbation estimate of the remaining error in the total energy – the dynamic correlation energy – based on a CASSCF reference function. A Möller–Plesset-like partitioning of the Hamiltonian is used, with the CASSCF wave function as the unperturbed wave function.

The geometry optimization for the ground state and a few of the lowest excited states has been carried out at the CASSCF level of theory with the MOLCAS gradient facility. The corresponding geometries have been used in the calculation of the adiabatic and vertical excitation energies at the CASPT2 level. For the spin and symmetry allowed transitions, the oscillator strengths at the CASSCF level are also reported.

The detailed studies of the simplest of the carbenes, methylene show, that a quantitative description of the system by the MRCI method can be obtained with a reference space equivalent to the CAS space obtained by distributing two electrons among the σ and π nonbonding orbitals on the carbenoid center. The reference weight in the corresponding CI wave function is 94–95% in both the singlet and the triplet state. In the case of aromatic molecules, however, we may expect substantial near-degeneracy effects involving excitations within the extended π space plus the lone pair. This is also the active space used in the CASSCF calculations (for details see Table 1). It turned out that many of the states considered in this work have a multiconfigurational character. The weight of the

Table 1. Active electrons and orbitals

	No. of active electrons	No. of active orbitals	No. CSFs
$C_3H_4N_2$	8	6	20–40
C_6H_4O	8	8	400–600
C_6H_6	6	6	40–55
C_5H_4O	8	7	100–150
$C_{13}H_8O$	16/14	15/14	55 000/700 000[a]

[a] The first number refers to the RASSCF geometry optimization and the second to the CASSCF energy calculation

leading configuration is usually below 90% (for a couple of states it is close to 80%, see Table 2). A balanced treatment of all states is obtained with the present multiconfigurational approach.

Generally contracted Gaussian basis sets of the atomic natural orbital (ANO) type [15] have been used. The basis sets are based on a 10*s*6*p*3*d* primitive set for first row atoms and 7*s*3*p* for hydrogen. They are thus more compact than the ANO sets usually used, but are more practical for larger systems and perform equally well for tight contractions [16]. The contracted sets were 4*s*3*p*2*d* for C,N,O and 2*s*1*p* for hydrogen. All calculations were performed with the MOLCAS-3 [17] quantum chemistry software.

The largest molecule considered in this study is 9-xanthylidene with 14 first row atoms. Including the σ lone pair and all the π orbitals into the active space in the CASSCF wave function (16 electrons in 15 orbitals) leads to an expansion in about 1 000 000 CSFs. Such a calculation, although time consuming, is possible but only at the CASSCF level. Subsequent CASPT2 calculations cannot be performed with the present code. This molecule is therefore only treated at the MCSCF level of theory and the results are less accurate. Instead of performing full CASSCF calculations, only up to quadruple excitations from the occupied orbitals (in the closed-shell SCF wave function) were included in the MCSCF wave function. This RAS-type wave function was used in the geometry optimization of the ground state. The vertical excitation energies were calculated at this geometry with the corresponding CASSCF wave function. This time, the oxygen π lone-pair orbital, which in the RAS wave function was found to be almost doubly occupied, was kept inactive. The basis set was reduced to 3*s*2*p*1*d* for first row atoms and 2*s*1*p* for hydrogen. This basis set was found to give equivalent results as the 4*s*3*p*2*d* contraction for 4-oxocyclohexa-2,5-dienylidene.

3 Results and discussion

Five carbenes have been studied. Three of them are singlets in the ground state (imidazol-2-ylidene **1**, 4-pyranylidene **2**, 9-xanthylidene **3**) and two are triplets (cyclohexa-2,5-dienylidene **4**, 4-oxocyclohexa-2,5-dienylidene **5**). The structures are shown in Fig. 1.

In aliphatic nonstrained carbenes, like methylene, methyl carbene or dimethylcarbene [8], the carbenoid angle changes substantially between $^1A_1$ and the $^3B_1$ states. It is small, ca. 100°, for the singlet state (indicating a large *s*-character in the σ lone-pair) and large for the triplet state, ca. 130° (with one of the electrons occupying an sp^2-like hybrid). The cyclic carbenes are expected to follow that

Table 2. Major configurations and their weights in the CASSCF wave functions; the occupations of active orbitals are listed

$C_3N_2H_4$	$9a_1$	$2b_1$	$3b_1$		$1a_2$	$2a_2$	
$^1A_1$	2	2			2		94.5%
	2				2	2	2.5%
$^3B_1$	1	2	1		2		95.9%
	1		1		2	2	3.5%
$^1B_1$	1	2	1		2		95.8%
	1		1		2	2	2.9%
$^3B_2$	2	1			2	1	97.6%
		1	2		2	1	1.5%
$^1A_2$	1	2			2	1	90.5%
	1	1	1		2	1	4.4%
C_5H_4O	$11a_1$	$2b_1$	$3b_1$		$1a_2$	$2a_2$	
$^1A_1$	2	2			2		90.9%
	2	1	1		1	1	1.2%
$^3B_1$	1	2	1		2		89.2%
	1	2	1			2	1.5%
$^1B_1$	1	2	1		2		86.9%
	1	2	1		1	1	5.7%
$C_{13}H_8O$	$22a_1$	$4b_1$	$5b_1$		$3a_2$	$4a_2$	
$^1A_1$	2	2			2		78.3%
	2	1	1		1	1	1.0%
C_6H_6	$11a_1$	$2b_1$	$3b_1$		$1a_2$	$2a_2$	
$^1A_1$	2	2			2		88.9%
	2	1	1		1	1	1.7%
$^3B_1$	1	2	1		2		88.2%
	1	2	1			2	1.6%
$^1B_1$	1	2	1		2		85.0%
	1	2	1			2	7.5%
$^3A_2$	1	2			2	1	52.2%
	1	2	2		1		30.2%
C_6H_4O	$11a_1$	$2b_1$	$3b_1$	$4b_1$	$1a_2$	$2a_2$	
$^1A_1$	2	2			2		83.6%
	2		2		2		1.8%
$^3B_1$	1	2	1		2		83.6%
	1	1	1	1	2		1.9%
$^1B_1$	1	2	1		2		83.9%
	1	2	1		1	1	2.8%
$^3A_2$	1	2	2		1		66.9%
	1	2			2	1	15.8%

pattern; however the rigid ring structure determines to great extent the geometry and the carbenoid angle cannot vary over the wide range. The observed difference is only about 10°.

The singlet–triplet splitting for the aliphatic carbenes is governed by the hybridization of the σ-orbital; an increased p-character in this orbital decreases the

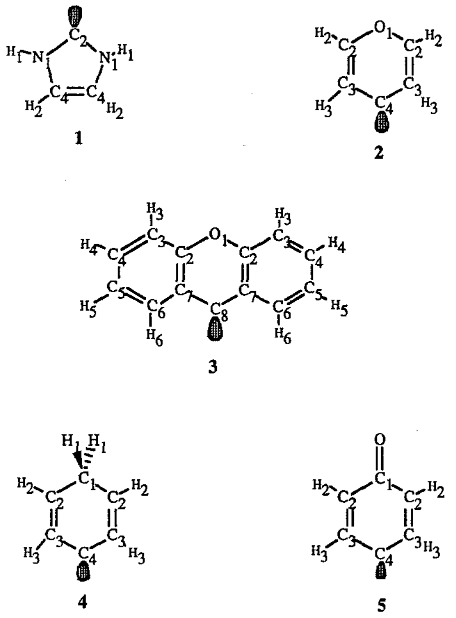

Fig. 1

energy gap between the σ- and the π-orbitals favoring single occupancy in each of them. A detailed description, including the analysis of the factors leading to the preference of one type of hybridization, over the other has been given in Refs. [1, 18]. For the molecules considered in this work we found a similar type of hybridization of the σ-orbital in the $^1A_1$ and $^3B_1$ states as in methylene. For **2**, **4** and **5** in particular, the relative contributions of the C(2*s*) and C(2*p*) orbitals to the σ-orbital are essentially the same. However, the order of the states and their relative energies varies considerably indicating that other effects than hybridization determines the properties of cyclic carbenes. This problem has been dealt with before by Gleiter et al. [2] who considered the divalent carbon atom coupled to polyenes. According to their results, a triplet ground state is found for polyenes with a $4n$ π system. The carbene out-of-plane orbital, (p_x), mixes with an *unoccupied* symmetric combination of the π-orbitals, thus lowering its energy. On the other hand the $4n+2$ systems are likely to be singlets; the (p_x) orbital here mixes with a *doubly occupied* π-orbital, which raises its energy and favors the singlet state. The above conclusions are qualitative and therefore expected to work for a rather limited set of molecules. However, the correlation between the orbital energy gap and the singlet–triplet splitting is intuitively expected.

Figure 2 shows a diagram correlating the singlet–triplet energy gap (at the CASPT2 level) with the HF orbital energy difference for the $^1A_1$ (closed-shell) state. The excitation energies are assumed to be negative if the ground state of the molecule is triplet. The HF orbital energies for the two carbene orbitals were obtained for the $^1A_1$ state at the equilibrium geometry of the ground state. The σ-orbital energy varies only little through the series of molecules, so the diagram reflects mostly the variation of the energy of the π-orbital. The tendency for the ring carbenes is clear: a large orbital energy gap favors the singlet state of the ring carbenes. The switch over from a triplet to a singlet ground state occurs at an orbital energy difference of about 10.0 eV. The data given in Fig. 2 shows that the

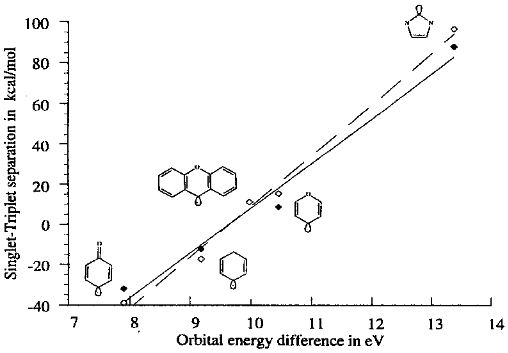

Fig. 2. Correlation diagram for the cyclic carbenes, The CASPT2 adiabatic and vertical energies are plotted vs. the orbital energy difference at the SCF level of the $^1A_1$ state obtained at the ground state geometry; ◆ Adiab. CASPT2, ◇ Vert. CASPT2

qualitative description given by Gleiter et al. [2] may lead to errors in the predicting the order of states. It seems clear that the $4n + 2$ rule cannot be applied when hetero-atoms are present in the π system. In many cases it is, however, possible to determine the ground state spin multiplicity from a simple HF calculation (the diagram is virtually unchanged when geometry of the closed shell $^1A_1$ state is used instead of the ground state geometry). Such a simplified procedure is obviously not valid in cases where the energy separation is small.

3.1 Imidazol-2-ylidene

Imidazol-2-ylidene and derivatives of it have been synthesized and isolated, which shows that steric hindrance is not an absolute necessity for stable carbenes [3]. Instead, a large singlet–triplet gap, which favors the $^1A_1$ state, accounts for the low reactivity. A large electron density close to the carbene center makes the molecule nucleophilic (Mulliken population analysis gives a charge on the C_2 atom of -0.16, cf. Table 3).

The geometry of **1** is summarized in Table 4. In the $^1A_1$ state the carbenoid angle is 101.5° and in the $^3B_1$ it is 112.7°. The short C_2–N bonds in the $^1A_1$ state (1.35 Å) indicate a delocalized π system that partially occupies the p_x-orbital on C_2. In the first excited state, $^3B_1$, the π-orbital with a node between atoms C_2 and N is occupied. Consequently the bond length is increased. The geometry of the $^3B_1$ state is different from that of the ground state; the latter is planar (C_{2v} geometry) whereas the former has two nonplanar isomers with almost the same energy, *cis* and *trans* (the *cis* structure has C_s symmetry and is less than 1 kcal/mol higher in energy than the *trans* structure with C_2 symmetry). The overall lowering of the symmetry stabilizes the $^3B_1$ state with about 7 kcal/mol compared to the corresponding C_{2v} geometry. The ring is slightly bent out of plane with a dihedral angle of 3.3° and

Table 3. Mulliken charges on the carbene centers

	$C_3H_4N_2$	C_6H_4O	C_6H_6	C_5H_4O	$C_{13}H_8O$
$^1A_1$	-0.16	$+0.04$	-0.07	-0.14	-0.33
$^3B_1$	$+0.09$	$+0.10$	$+0.07$	$+0.05$	
$^1B_1$	-0.16	$+0.10$	$+0.06$	$+0.03$	

Table 4. Bond distances (Å), angles (°) and relative energies (kcal/mol) in $C_3H_4N_2$; C_{2v} symmetry if no other specification

	$^1A_1$	$^3B_1$	Trans (C_2)	Cis (C_s)	$^3B_2$	$^1A_2$	$^1B_1^a$
Bond (Å)							
$R(C_2–N_1)$	1.350	1.402	1.414	1.414	1.353	1.316	1.388
$R(C_4–N_1)$	1.382	1.398	1.427	1.426	1.399	1.410	1.388
$R(N_1–H_1)$	0.989	0.984	0.999	1.000	0.988	0.989	0.984
$R(C_4–H_2)$	1.067	1.067	1.068	1.069	1.062	1.061	1.067
$R(C_4–C_5)$	1.346	1.341	1.334	1.336	1.527	1.470	1.349
Angle (°)							
$\theta_1(N_1–C_2–N_1(x)^b)$	101.5	106.8	112.7	113.0	104.5	110.9	109.4
$\theta_2(C_2–N_1–C_4)$	113.6	107.6	102.7	102.4	115.1	110.2	106.0
$\theta_3(C_4–N_1–H_1)$	124.6	126.6	113.0	113.4	123.9	125.9	127.6
$\theta_4(N_1–C_4–H_2)$	123.5	121.9	120.6	120.5	125.5	122.0	121.9
$\theta_5(N_1–C_4–C_4(x))$	105.6	109.0	110.9	111.0	102.6	104.3	109.3
$\phi_1(C_2–N_1–C_4–C_4(x))$			3.3	2.5			
$\phi_2(C_2–N_1–C_4–H_2)$			177.7	172.8			
$\phi_3(H_1–N_1–C_4–H_2)$			55.3	62.8			
T_e, CASSCF	0.0	87.2	76.8	77.4	94.6	123.0	135.4
T_e, CASPT2	0.0	88.6	81.3	81.7	94.0	110.3	120.5
T_v, CASSCF	0.0	95.5			111.5	137.7	145.5
T_v, CASPT2	0.0	97.2			111.1	124.7	130.2
μ (D)	−3.08	−0.50	−1.12	−1.151	−2.39	2.78	−1.43

[a] States in other symmetries between $^1A_2$ and $^1B_1$ are possible

[b] The notation $N_1(x)$ refers to a symmetry related atom

the vinyl hydrogen bonds make an angle of 2.3° with the plane of the ring. The hydrogen atoms bound to the nitrogen atoms are, however, more distorted with a dihedral angle of 55.3°. Also the carbenoid angle is increased; the angle is 6° smaller in the optimal C_{2v} geometry. Only the ground and the first excited state have been investigated for planarity. It is, however, likely that also other states are significantly nonplanar. The energies reported in Table 4 for the $^3B_2$, $^1A_2$, and $^1B_1$ states are therefore not truly adiabatic but refer to the C_{2v} constrained geometries.

Because of the large difference between the σ- and π-orbital energies, the singlet–triplet separation is expected to be large. Two different effects are responsible for the large energy gap. The relatively small NCN angle gives the CN bonding orbitals more *p*-character and consequently the σ lone-pair more *s*-character and a lower energy. The energy gap is further increased since the interaction of the carbene π-orbital with the rest of the π system is antibonding (the $4n + 2$ case). The corresponding a_1 and b_1 orbitals are depicted in Fig. 3. The antibonding character of the π-orbital is illustrated. Both orbitals are well localized at the carbene center.

All this favors the $^1A_1$ state over the $^3B_1$ state and gives a singlet–triplet gap of 81.3 kcal/mol (CASPT2). This is the largest energy separation found for any of the carbenes studied in this work. The stabilization of the σ lone-pair also has the consequence that the second excited state is not $^1B_1$ but instead the $\pi \rightarrow \pi^*$ excited $^3B_2$ state. The first excited singlet state is $^1A_2$ where one electron has been excited

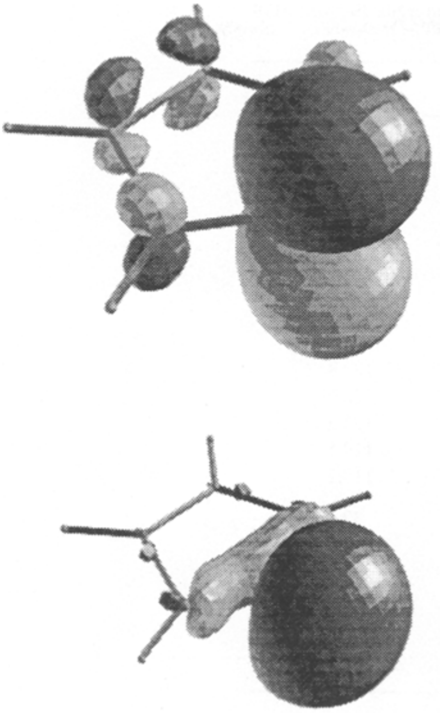

Fig. 3

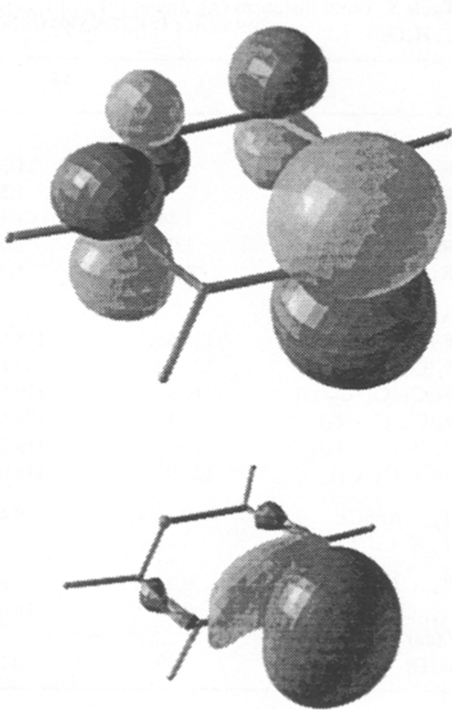

Fig. 4

Fig. 3. The two radical orbitals in the $^3B_1$ state of imidazol-2-ylidene. The surface value is 0.06 for the σ-orbital and 0.0676 for the π-orbital. Negative parts of the orbitals are drawn with a lighter grey tone

Fig. 4. The two radical orbitals in the $^3B_1$ state of 4-pyranylidene. The surface value is 0.06 for the σ-orbital and 0.0676 for the π-orbital. Negative parts of the orbitals are drawn with a lighter grey tone

from the σ lone-pair to the CC π^*-orbital (cf. Table 2 for details). The excitation energies are 94.0 ($^3B_2$) and 110.3 kcal/mol ($^1A_2$), respectively.

The dipole moment changes considerably between states described by $(\sigma)^2$ and $(\sigma)(\pi)$ configurations. In the first case the two electrons occupy the lone-pair orbital, which is directed away from the molecule, while in the latter case this orbital is only singly occupied. The other electron is in a π-orbital, which is located on the carbene center. In imidazol-2-ylidene, the dipole moment changes from -3.08 to -1.12 D between the $^1A_1$ and $^3B_1$ states.

As can be seen in Table 2, the ground state wave function is well described by a single configuration, as expected. The weight of the leading configuration is 95%. In contrast to other carbenes no near-degeneracy effects are present in the wave functions for the ground and lower excited states of imidazol-2-ylidene. The geometry obtained in the SCF approximation [19] also agrees with that obtained here with the CASSCF method.

3.2 4-Pyranylidene

4-Pyranylidene has not been isolated experimentally. It may serve, however, as a reference molecule for the analogous 9-xanthylidene, which has been observed.

Table 5. Bond distances (Å), angles (°) and relative energies (kcal/mol) of C_5H_4O

	$^1A_1$	$^3B_1$	$^1B_1$
Bond (Å)			
$R_1(O_1–C_2)$	1.326	1.360	1.364
$R_2(C_2–C_3)$	1.352	1.353	1.376
$R(C_3–C_4)$	1.440	1.416	1.384
$R_3(C_2–H_2)$	1.071	1.070	1.067
$R_4(C_3–H_3)$	1.074	1.072	1.072
Angle (°)			
$\theta_1(C_2–O_1–C_2(x))$	118.4	118.5	119.3
$\theta_2(O_1–C_2–C_3)$	122.6	123.1	121.9
$\theta_3(C_3–C_4–C_3(x))$	110.3	119.5	122.6
$\theta_4(C_3–C_2–H_2)$	125.5	124.8	125.3
$\theta_5(C_2–C_3–H_3)$	117.0	119.5	119.5
$\theta(C_2–C_3–C_4)$	123.0	118.0	117.2
T_e, CASSCF	0.0	9.4	32.4
T_e, CASPT2	0.0	9.2	24.5
T_v, CASSCF	0.0	14.8	42.6
T_v, CASPT2	0.0	16.0	35.1
f (au)			4.2×10^{-3}
μ (D)	3.53	−0.12	−0.13

The π system is occupied by six electrons. Two of them occupy the oxygen π lone-pair orbital, the remaining four are distributed among the π-orbitals of the diene system. This arrangement favors the singlet state over the triplet state and thus the order of the states is $^1A_1$, $^3B_1$, and $^1B_1$.

The properties of **2** are summarized in Table 5. The $^1A_1$ ground state has a well localized electron structure. The double bond C_2–C_3 is quite short (1.352 Å), and the C_3–C_4 bond is substantially longer than the C–C bond in benzene indicating that it acquires character of a single bond. The carbenoid angle, as expected for singlet carbenes, is small (110.3°). It also follows the pattern of the other carbenes under $\sigma \rightarrow \pi$ excitation. The B_1 states have a more delocalized π-electron structure. The C–C bonds approach the lengths they have in benzene. This effect is very pronounced for $^1B_1$. The delocalization of the electron influences also the dipole moment of **2**. The large value (3.53 D) for the ground state (due to the lone-pair and not compensated by the electronegative substituent in the ring) is much smaller for the B_1 states. The effect can be attributed to the single occupancy of the σ-orbital accompanied by the delocalization of the other electron over the molecule. This is nicely illustrated in Fig. 4, which shows the two carbene orbitals in the $^3B_1$ state. While the σ-orbital is well localized to the carbene center, the π-orbital is delocalized over the entire molecule with a sizable contribution from the oxygen atom.

The first excited state of **2** is $^3B_1$ and the singlet–triplet gap is 9.2 kcal/mol. The small positive excitation energy is contradictory to the reasoning presented by Gleiter and Hoffmann [2]. The diene system contains four electrons (the $4n$ case) and therefore the ground state ought to be a triplet. A comparison with **4**, which is also a $4n$ case and has a triplet ground state, shows that the delocalizing effect of the

Table 6. Bond distances (Å), angles (°) and relative energies (kcal/mol) of $C_{13}H_8O$

Geometry optimized with RAS wave function

Angle	(°)	Bond	(Å)
$\theta_1(C_2{-}O_1{-}C_2(x))$	119.8	$R_1(O_1{-}C_2)$	1.340
$\theta_2(O_1{-}C_2{-}C_3))$	116.3	$R_2(C_2{-}C_7)$	1.400
$\theta_3(C_7{-}C_8{-}C_7(x))$	111.4	$R_3(C_2{-}C_3)$	1.408
$\theta_4(C_7{-}C_2{-}C_3)$	122.2	$R_4(C_3{-}C_4)$	1.383
$\theta_5(C_2{-}C_3{-}C_4)$	118.8	$R_5(C_4{-}C_5)$	1.415
$\theta_6(C_3{-}C_4{-}C_5)$	120.8	$R_6(C_5{-}C_6)$	1.380
$\theta_7(C_4{-}C_5{-}C_6)$	119.6	$R_7(C_3{-}H_3)$	1.080
$\theta_8(H_3{-}C_3{-}C_4)$	121.9	$R_8(C_4{-}H_4)$	1.081
$\theta_9(H_4{-}C_4{-}C_5)$	119.8	$R_9(C_5{-}H_5)$	1.080
$\theta_{10}(H_5{-}C_5{-}C_6)$	120.6	$R_{10}(C_6{-}H_6)$	1.080
$\theta_{11}(H_6{-}C_6{-}C_7)$	117.3	$R(C_7{-}C_8)$	1.448
μ (D)	2.57		

Vertical CASSCF excitation energies

	CASSCF	Dipole moment (D)
$^3B_2$	81.0	2.72
$^3A_2$	79.2	−0.40
$^1A_2$	74.5	−0.41
$^1B_1$	39.0	−0.23
$^3B_1$	11.6	−0.29
$^1A_1$	0.0	2.37

oxygen atom cannot be ignored. The interaction of the oxygen with the diene system will raise the energy of the highest occupied orbital of b_1 symmetry, resulting in a stronger interaction with the carbene π-orbital. As a result, the energy of the latter orbital will raise, which favors a singlet ground state. The 4-pyranylidene molecule is in this sense intermediate between a $4n$ and a $4n + 2$ case. The singlet–triplet splitting correlates with the orbital energy gap and the orbital energy difference, where the states become degenerate, can be estimated to be slightly below 10 eV. It is worth noting that the singlet–triplet excitation is already well described at the CASSCF level. The first dipole allowed transition, to $^1B_1$ occurs at 24.5 kcal/mole with an oscillator strength of 4.2×10^{-3}.

3.3 9-Xanthylidene

EPR measurements and techniques involving elementary reactions show that 9-xanthylidene, **3**, like 4-pyranylidene is a carbene with a singlet ground state [20]. The half-life of the singlet ground state was determined to be 50 μs. Because of the large size of the molecule we have performed geometry optimization only for the ground state.

The geometrical properties of **3** are summarized in Table 6. The carbenoid angle of the ground state is 111.4°. All the bonds in the two outer rings (the benzene-like rings) have bond lengths quite close to those in benzene indicating strong delocalization of the π system. These rings do not affect the remaining bonds

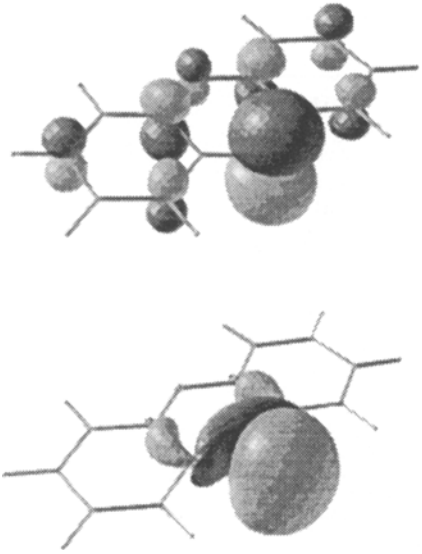

Fig. 5

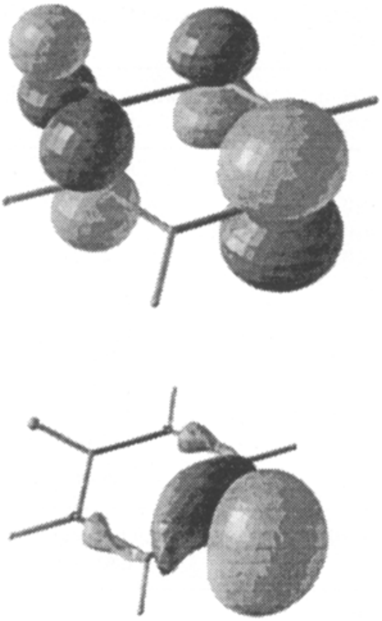

Fig. 6

Fig. 5. The two radical orbitals in the $^3B_1$ state of 9-xanthylidene. The surface value is 0.04 for the σ-orbital and 0.0476 for the π-orbital. Negative parts of the orbitals are drawn with a lighter grey tone

Fig. 6. The two radical orbitals in the $^3B_1$ state of 4-oxocyclohexa-2,5-dienylidene. The surface value is 0.06 for the σ-orbital and 0.0676 for the π-orbital. Negative parts of the orbitals are drawn with a lighter grey tone

in a major way and they remain almost the same as they are in 4-pyranylidene. The general pattern of the charge distribution is also similar to **2**. The ground state has a dipole moment of 2.37 D. In higher excited states (only vertical excitation energies have been computed) the dipole moment has the opposite direction and is slightly larger than it is in **2**.

Also energetically, 9-xanthylidene is similar to 4-pyranylidene. The singlet state is favored but the singlet–triplet energy gap is slightly smaller; the vertical energy at the CASSCF level is 11.6 kcal/mol compared to 14.8 kcal/mol for 4-pyranylidene. The increased *s*-character of the σ-orbital in the $^3B_1$ state (compared to other molecules) ought to place the excitation energy much higher. This effect is, however, compensated by a delocalization of the p_x-orbital towards the benzene-like rings, which lowers its energy. The two orbitals are shown in Fig. 5. They are strikingly similar to those of 4-pyranylidene. The somewhat larger delocalization of the π-orbital in **3** can explain the slightly lower value of the singlet–triplet separation as compared to **2**.

Spectroscopic measurements have indicated the presence of three transitions in the area between 72 and 76 kcal/mol [20]. The first symmetry allowed transition found in the present study, $^1A_1 \rightarrow {}^1B_1$, occurs at 39.0 kcal/mol, but this area was not investigated in the experiment. The next state is $^1A_2$, to which the transition is symmetry forbidden. The computed vertical excitation energy is 74.5 kcal/mol. Above this state there are two triplet states close to 80 kcal/mol, but because the transitions to them are spin forbidden they are not likely to be seen in the spectrum.

Table 7. Bond distances (Å), angles (°) and relative energies (kcal/mol) of C_6H_4O

	$^3B_1$	$^1B_1$	$^1A_1$	$^3A_2$
Bond (Å)				
$R_1(O–C_1)$	1.225	1.263	1.210	1.213
$R_2(C_1–C_2)$	1.461	1.430	1.476	1.461
$R_3(C_2–H_2)$	1.073	1.073	1.074	1.072
$R_4(C_2–C_3)$	1.369	1.393	1.348	1.444
$R_5(C_3–H_3)$	1.073	1.072	1.075	1.072
$R(C_3–C_4)$	1.405	1.380	1.476	1.381
Angle (°)				
$\theta_1(C_2–C_1–C_2(x))$	117.9	119.2	117.1	114.7
$\theta_2(C_1–C_2–C_3)$	120.7	120.3	120.4	122.0
$\theta_3(C_3–C_2–H_2)$	122.1	121.7	123.0	120.2
$\theta_4(C_2–C_3–H_3)$	121.3	121.3	119.2	119.5
$\theta_5(C_2–C_3–C_4)$	118.2	117.6	124.2	119.0
$\theta(C_3–C_4–C_3(x))$	124.4	125.0	113.6	123.2
T_e, CASSCF	0.0	14.8	19.5	59.3
T_e, CASPT2	0.0	9.6	31.8	49.7
T_v, CASSCF	0.0	16.9	28.4	66.2
T_v, CASPT2	0.0	11.9	38.8	56.4
f(au)				1.1×10^{-3}
μ (D)	−2.68	−2.20	0.17	−3.64

The most natural assignment is that all observed bands are due to transitions to the $^1A_2$ state combined with vibrational progressions involving asymmetric distortions that make the transition dipole nonzero. It is finally worth noting that the ground state of 9-xanthylidene has a very multiconfigurational character; the weight of the primary CSF is only 78.3%.

3.4 4-Oxocyclohexa-2,5-dienylidene

ESR measurements at low temperature have shown that 4-oxocyclohexa-2,5-dienylidene, **5**, has a triplet ground state [21]. Due to the quinone oxygen, the π system is greatly delocalized and the triplet ground state stabilized. Upon excitation of this carbene to a metastable singlet state, the molecule undergoes a Wolf rearrangement to a bicyclic compound, 1H-bicyclo[3.1.0]hexa-3,5-dien-2-one. The photo induced reaction is totally reversible and can be performed with light in the visible region. This has previously been investigated both experimentally and theoretically [22].

The geometries of **5** are summarized in Table 7. The carbenoid angle is large in the triplet ground state, 124.4°, but is considerably smaller in the $^1A_1$ state, 113.6°. The delocalization of the electron structure in the ground state is due to resonance between a quinoid structure and a structure resembling the phenoxy radical. In the latter case the π system is more delocalized and an aromatic ring is formed at the cost of breaking the CO π bond. This resonance is not possible in the $^1A_1$ state, which is then more localized with shorter $C_1–O$ and $C_2–C_3$ bonds, and longer

C_1–C_2 and C_3–C_4 bonds (cf. Table 7). The shift in electron density between the two states has a substantial effect on the dipole moment. The $\pi \rightarrow \sigma$ excitation localizes the electrons to the carbene lone-pair, which changes the dipole moment from the ground state value 2.68 to 0.17 D in the opposite direction. The delocalization of the carbene electrons in the ground state is also evident from the Mulliken populations. The total charge on the carbenoid carbon is +0.10, which should be compared with the negative (or close to zero) charges found for the other carbenes (cf. Table 3). As shown in Fig. 6, the delocalization occurs in the carbene π-orbital, while the corresponding σ-orbital is well localized at the carbene center.

The energy difference between the σ- and π-orbital is smaller in this system than it is in any of the other molecules studied here. Thus, the ground state should be a triplet and the triplet–singlet gap should be large. The value computed at the CASPT2 level is 31.8 kcal/mol (corresponding to a wave length of about 900 nm). This is more than twice as large as it is in the methylene radical. Since the π-orbital is low in energy, $^1A_1$ is not the first excited state. It is instead the $^1B_1$ state which has been computed to lie 9.6 kcal/mol above the ground state. The first state to which excitation is dipole allowed is the $\pi \rightarrow \pi^*$ excited $^3A_2$ state. An absorption spectrum measured in argon matrices at 10 K [22] exhibits peaks at 56.3, 54.9, 53.5, 51.9, and 50.5 kcal/mol. The calculated vertical (56.4 kcal/mol) and adiabatic (49.7 kcal/mol) excitation energies show that the measured bands are due to a vibrationally resolved transition to the $^3A_2$ state. The oscillator strength was found to be 1.02×10^{-3}. All considered states of **5** are found to have multiconfigurational character. The weight of the primary CSF in the ground state is only 0.84. Inclusion of dynamic correlation affects substantially the excitation energies (cf. Table 7).

3.5 Cyclohexa-2,5-dienylidene

Cyclohexa-2,5-dienylidene, **4**, is a carbenic isomer of benzene. It has a triplet ground state. To our knowledge, this molecule has not been studied experimentally or theoretically before. Here we include it since it is of interest to compare its properties with those of other six membered ring systems.

All the geometrical properties for **4** are summarized in Table 8. The carbenoid angle has roughly the same value as in the other molecules with 6-membered rings (113.1° for $^1A_1$ and 123.9° for $^3B_1$). For B_1 states the C_1–C_2 bonds are almost pure single bonds. Thus, in contrast to 4-pyranylidene, this molecule behaves like a typical $4n$ system and the ground state is a triplet. The dipole moment of the $^1A_1$ state is large (3.97 D) due to the doubly occupied σ lone-pair and the delocalization of the π system. In the $^3B_1$ state it is 1.03 D; the electron density is shifted away from the carbene center. Fig. 7 shows the two carbene orbitals in the $^3B_1$ state. The shape of the σ lone-pair orbital is similar to the other molecules. There is a certain delocalization of the π-orbital similar to that found in the corresponding oxo compound **5**.

The energetics of **4** is consistent with the prediction based on the orbital mixing proposed by Gleiter. The triplet ground state is favored; the first excited state is $^1A_1$ and is located to 12.0 kcal/mol above the ground state (almost the same as in methylene). The $^1B_1$ state is found only slightly above $^1A_1$. The first symmetry and spin allowed transition, $^3B_1 \rightarrow {}^3A_2$ occurs at 50.0 kcal/mol with an oscillator strength of 6.0×10^{-2}.

Table 8. Bond distances (Å), angles (°) and relative energies (kcal/mol) of C_6H_6

	$^3B_1$	$^1A_1$	$^1B_1$	$^3A_2$
Bond (Å)				
$R_1(C_1–C_2)$	1.507	1.489	1.507	1.500
$R_2(C_2–C_3)$	1.359	1.348	1.386	1.442
$R(C_3–C_4)$	1.417	1.464	1.386	1.385
$R_3(C_1–H_1)$	1.090	1.090	1.092	1.091
$R_4(C_2–H_2)$	1.075	1.076	1.074	1.072
$R_5(C_3–H_3)$	1.074	1.076	1.073	1.071
Angle (°)				
$\theta_1(C_2–C_1–C_2(x))$	113.7	113.2	113.9	115.5
$\theta_2(C_1–C_2–C_3)$	122.5	122.5	121.9	121.1
$\theta_3(C_3–C_4–C_3(x))$	123.2	113.1	126.1	127.3
$\theta(C_2–C_3–C_4)$	119.0	124.4	118.1	117.4
$\theta_4(H_1–C_1–H_1(z))$	105.1	105.2	104.7	105.1
$\theta_5(C_1–C_2–H_2)$	117.5	117.0	118.0	118.5
$\theta_6(C_2–C_3–H_3)$	120.8	118.7	120.7	120.9
T_e, CASSCF	0.0	6.5	22.3	60.8
T_e, CASPT2	0.0	12.0	15.4	50.1
T_v, CASSCF	0.0	12.4	23.9	68.9
T_v, CASPT2	0.0	16.9	17.3	57.5
f(au)				6.0×10^{-2}
μ (D)	1.03	3.97	1.16	1.22

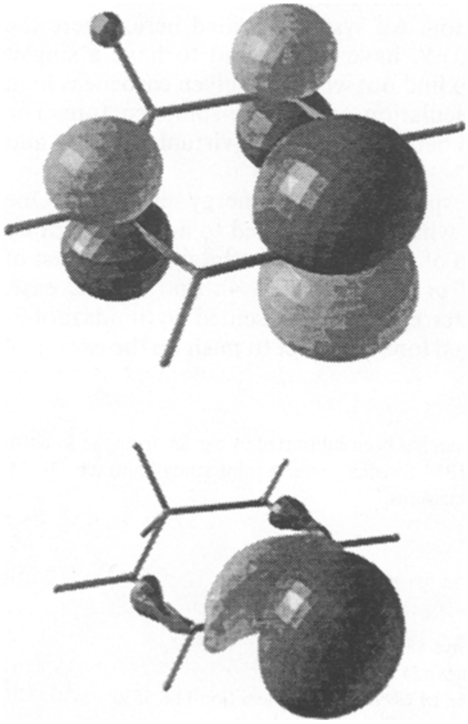

Fig. 7. The two radical orbitals in the $^3B_1$ state of Cyclohexa-2,5-dienylidene. The surface value is 0.06 for the σ-orbital and 0.0676 for the π-orbital. Negative parts of the orbitals are drawn with a lighter grey tone

4 Conclusions

A series of *ab initio* quantum chemical calculations have been performed on some divalent carbon species, carbenes, where the carbene center is located in a 6- or 5-membered ring. The intention has been to understand in a quantitative way the electronic features that determine the spin multiplicity of the ground state and the singlet–triplet splitting. In addition, the structures of the compounds have been determined both for the ground state and a number of excited states. All calculations have been performed with extended basis sets. A multiconfigurational approach with dynamic correlation effects included using second-order perturbation theory has been used. Geometries have been optimized at the CASSCF level, a method which is known to yield structures with errors smaller than -0.01 Å in bond distances and 5° in angles.

The CASSCF/CASPT2 approach has been used to compute a large number of excited states in a variety of molecules with errors in calculated excitation energies not exceeding 5 kcal/mol. We expect that the excitation energies computed in the present study have at least this accuracy. In a few cases it has been possible to compare directly computed excitation energies with measurements. The agreement is for these cases 1–2 kcal/mol.

The Gleiter–Hoffman model for the interaction of a carbene center with a polyene system predicts a triplet ground state for $4n$ systems and a singlet ground state for $4n + 2$ systems. This rule has been found to work well except in cases where the energy separation is small. Small perturbations of the polyene system caused by, for example, the insertion of a hetero atom into the ring may change the order of the states. It has been shown, however, that there is a high degree of correlation between the difference in orbital energy for the carbene π- and σ-orbitals and the singlet–triplet separation. All systems treated here, where the energy difference is larger than about 10 eV, have been found to have a singlet ground state. There is thus a simple way to find out whether a given carbene is high or low spin: perform a Hartree–Fock calculation on the low-spin structure. The spin state is determined by the energy gap between the lowest virtual π-orbital and the highest occupied σ-orbital.

There are two effects that are mainly responsible for the energy separation. One is the *s*-character of the lone-pair orbital, which is determined to a large extent by the bond angle. Another is the interaction of the carbene π-orbital with the rest of the π system, which may be attractive or repulsive (the $4n$ and $4n + 2$ case, respectively). An extreme case of the latter effect is represented by imidazaol-2-ylidene, where the two neighboring nitrogen lone-pairs act to push up the energy of the carbene π-orbital.

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