The Role of Conjugative Interaction in Stable Carbenes of the 1,2,4-Triazol-5-ylidene Type and their Energy of Dimerization. An *Ab Initio* Study *

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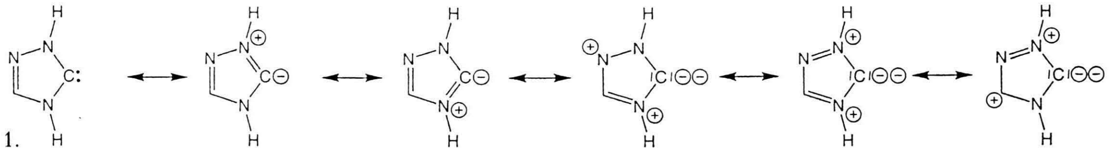
The role of conjugative interaction in stable carbenes of the 1,2,4-triazol-5-ylidene type was studied at different levels of *ab initio* theory employing model compounds. In the case of parent 4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene this type of interaction was found to be of similar importance as in 1,2,4-triazole and pyridine.

Five stationary points were located on the hypersurface of the dimer $(C_2N_3H_3)_2$. ΔE for all considered dimerization reactions was found to be negative, and the change of energy associated with the formation of the most stable isomer is about $-9.5^{kcal}/_{mol}$. In spite of a high value for the singlet-triplet gap of about $90^{kcal}/_{mol}$ for the carbene, the heavy atom skeleton of the most stable dimer is close to planarity. This finding is in perfect accordance with the predictions of other authors regarding the geometry of dimers from singlet carbenes stabilized by π-conjugation.

1. Introduction

Recently we reported synthesis, structure, and reactivity of the stable singlet carbene 1,2,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene [1, 2] (cf. Figure 1).

The five-membered ring of the carbene is essentially planar (sum of bond angles: 540°) and a simple electron count results in 6 "π electrons" (C2 = N2 double bond, lone pairs on N1 and N3) for this molecular fragment. Thus the question arises whether the observed *relatively* low reactivity of the carbene is at least in part due to conjugative stabilization of its ground state which would be cancelled by typical carbene reactions like dimerization or insertion. Scrutinizing calculated and measured electron densities in other stable carbenes of type **1** (cf. Scheme 2), Arduengo et al. [3] concluded that the stability of these singlet [4] species is not governed by conjugative interaction within the five-membered ring. According to these authors the carbenes are stabilized kinetically in that electron density accumulated in the vicinity of the divalent carbon atom prevents the molecule not only from dimerization but also serves as a protection against the attack of nucleophiles. Moreover, based on the combined results of nonlocal density functional and semiempirical calculations, they even predicted an endothermic dimerization reaction for the case where $R = CD_3$. Using an approximate relationship between the strength of a planar C = C bond and the singlet-triplet separation (ΔE_{st}) of the corresponding carbene fragments [5] [1], Heinemann and Thiel [6] predicted a dissociation energy for the central C = C double bond of the dimer of **1** (R = H) as low as 1.0 kcal/mol.


Scheme 1.

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* Presented by one of us (G.R.) at the 16th European Crystallographic Meeting (ECM 16), Lund, Sweden, 6–11 August 1995.

Reprint requests to Dr. Gerhard Raabe.

[1] $D(XYC = CX'Y') = D_{int}(C = C) - [\Delta E_{st}(:CXY) + \Delta E_{st}(:CX'Y')]$ where $D(XYC = CX'Y')$ is the double bond energy of a substituted olefin, $D_{int}(C = C)$ the so-called intrinsic CC double bond energy which is usually equated with the C = C bond energy in ethene. The ΔE_{st} are the singlet-triplet gaps in :CXY and :CX'Y', which have singlet ground states.

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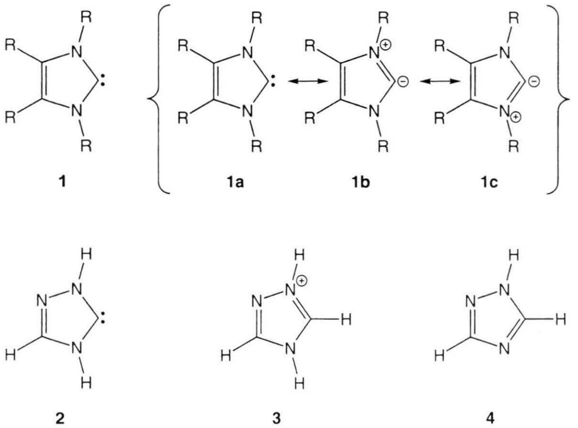
The conclusion that delocalization does not play a significant role in **1**, and that Arduengo-type carbenes might be adequately described by the resonance structure **1a**, has recently been challenged, based on the results of different *ab initio* methods [7].

In order to evaluate the possible role of conjugative stabilization in the case of 1,2,4-triazol-5-ylidene-type carbenes [1, 2], we performed quantum chemical *ab initio* calculations for a model compound (**2**, cf. Scheme 2), where the phenyl groups were replaced by hydrogen atoms.



Scheme 2.

We then applied the hypothetic *isodesmic* bond separation reactions (**A**–**D** cf. Scheme 3), and the *non-isodesmic* reductive ring cleavage reactions (**E**–**H**) (cf. Scheme 4), not only to our model carbene but also to 1,2,4-triazole **4**, which is chemically classified as an *aromatic*. In addition we calculated the change of energy associated with hydrogen transfer reaction **I**. Additional calculations were carried out for cation **3** (cf. Scheme 2), where conjugative stabilization is expected to play an important role.

2. Computational Methods

All calculations were performed employing the GAUSSIAN 92 suite of quantum chemical routines [8]. Final geometry optimizations for most compounds were carried out at the restricted Hartree-Fock (RHF) level with either the 6-31G** or 6-31+G* [9–13] basis sets. In these cases correlation energy was included in single point calculations at RHF-optimized geometries using second order Møller-Plesset perturbation theory [14]. To obtain more reliable molecular geometries, the structures of **2**, **3**, **4**, and some reference compounds were optimized including correlation energy in the calculation of the gradients (MP2/6-31G** and MP2/6-31+G*, respectively). All MP2 calculations included the core electrons. The stationary points obtained at the one-determinant level were characterized as either minima or saddle points by calculation of their normal frequencies [15, 16]. The harmonic zero point energies obtained in these calculations were then used to calculate the energies of reaction. Total energies and harmonic zero point energies are listed in Table 1, while the structural parameters of **2**, **3**, and **4**, either obtained at the MP2/6-31G** or MP2/6-31+G* level, are listed in Tables 2–4.

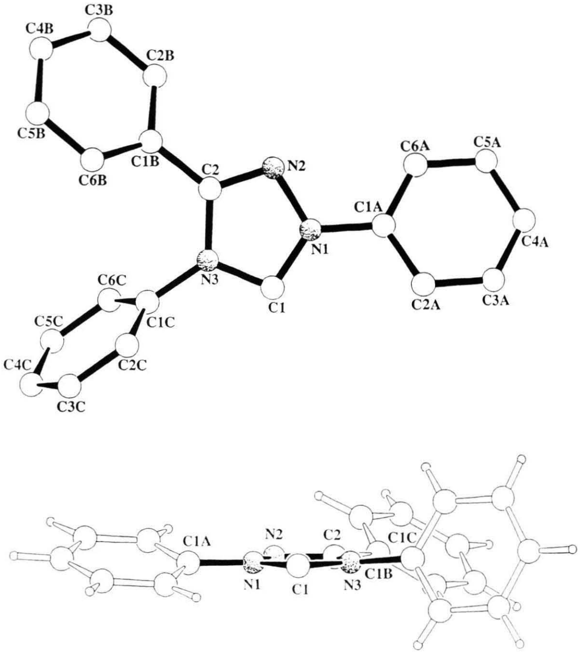


Fig. 1. Solid state structure of 1,2,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene [1, 2][2].

3. Results and Discussion

Our results obtained by means of the isodesmic bond separation reactions (**A**–**D**) indicate significant

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[2] Lists of structure factors, anisotropic displacement parameters, hydrogen atom coordinates, and tables of bond distances may be obtained through the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH; D-76344 Eggenstein-Leopoldshafen, FRG, refering to CSD-58839, the authors and the bibliographical data of [1].

Table 1. Total energies (E_{tot}) at the RHF/6-31G**- and MP2/6-31G**- and harmonic zero point energies (ε_0) at the RHF/6-31G** level. All geometries were optimized at the RHF/6-31G** level. The energies are in a.u.

Molecule	RHF/6-31G**	MP2/6-31G**	ε_0
H_2	−1.131334	−1.157660	0.010555
CH_4	−40.201705	−40.369855	0.047404
NH_3	−56.195545	−56.386599	0.036797
$H_2C=CH_2$	−78.038841	−78.326829	0.054503
H_3C-CH_3	−79.238235	−79.553683	0.079212
$H_2C=NH$	−94.035706	−94.347852	0.043079
H_3C-NH_2	−95.221862	−95.558711	0.068510
H_2N-NH_2	−111.183524	−111.542404	0.057773
$H_2C=CHNH_2$	−133.075149	−133.534988	0.073914
$H_2N-C-NH_2$	−149.057002	−149.528938	0.062003
$HN=CHNH_2$	−149.089597	−149.573476	0.062795
$H_2N-CH^+-NH_2$	−149.482077	−149.959110	0.077829
$H_2C=CHCH=CH_2$	−154.930324	−155.490004	0.091121
Pyrrol	−208.819705	−209.545362	0.088629
$H_2NCH=CHCH=CH_2$	−209.965966	−210.698916	0.109990
2	−240.773690	−241.536451	0.065124
4	−240.811967	−241.585605	0.065190
3	−241.174294	−241.941371	0.079408
$H_2C=NNH-C-NH_2$	−241.899972	−242.670774	0.085150
6	−241.910358	−242.684978	0.089258
$HN=CHNHN=CH_2$	−241.937866	−242.720352	0.085741
7	−241.940395	−242.727565	0.089468
5	−243.109549	−243.918615	0.116455
Pyridine	−246.704612	−247.549322	0.095112
$H_2C=CHCH=CH-CH=NH$	−247.822419	−248.678494	0.115901
D1	−481.549352	−483.089310	0.132223
D2	−481.549035	−483.089993	0.132154
D3	−481.548356	−483.089410	0.132172
D4	−481.543158	−483.083347	0.131293
D5	−481.540808	−483.082562	

conjugative interaction between the N=CH moiety and the adjacent $(HN)_2C$: segment in **2**.

Moreover, the calculated energies of reaction suggest that, as far as energetics are concerned, this interaction is only slightly less important than that between the corresponding segments in **4** and pyridine. This conjugative stabilization is also reflected by the differences between the C=N and N−C: bond lengths in **2** on the one hand, and $H_2C=NH$ (MP2/6-31+G*: 1.283 Å, $E_{tot} = -94.331288$ a.u.; MP2/6-31G**: 1.280 Å, $E_{tot} = -94.349286$ a.u.) and $(H_2N)_2C$: (MP2/6-31+G*: 1.344 Å, $E_{tot} = -149.510547$ a.u.; MP2/6-31G**: 1.343 Å, $E_{tot} = -149.529690$ a.u.) on the other. With both basis sets the corresponding bonds in the cyclic carbene are longer than in formaldehydimine and diaminocarbene, respectively.

The elongation of the N2=C2 bond in **2** relative to the unperturbed value for $H_2C=NH$ is somewhat weaker than in **3** and **4** (cf. Scheme 2 and Tables 2−4).

Table 2. Selected bond lengths, angles, and dihedral angles (Å, °) of **2** at the MP2/6-31+G* ($E_{tot} = -241.535236$ a.u.) and MP2/6-31G** ($E_{tot} = -241.539810$ a.u.) level. The numbering of the ring atoms is the same as in Figure 1.

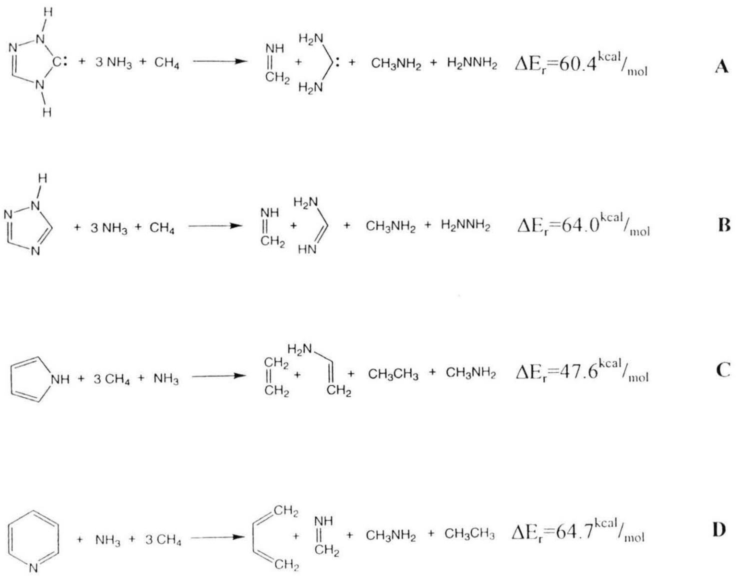
Bond lengths		Bond angles	
MP2/6-31+G*			
N1−C1	1.351	C1−N1−N2	117.9
N1−N2	1.375	N1−N2−C2	101.7
N2−C2	1.317	N2−C2−N3	110.1
N3−C2	1.370	C2−N3−C1	111.9
C1−N3	1.376	N3−C1−N1	98.5
MP2/6-31G**			
N1−C1	1.353	C1−N1−N2	118.3
N1−N2	1.375	N1−N2−C2	101.4
N2−C2	1.315	N2−C2−N3	110.2
N3−C2	1.369	C2−N3−C1	112.1
C1−N3	1.377	N3−C1−N1	98.0

Table 3. Selected bond lengths, angles, and dihedral angles (Å, °) of **3** at the MP2/6-31+G* ($E_{tot} = -241.921566$ a.u.) level and MP2/6-31G** ($E_{tot} = -241.945154$ a.u.) level. The numbering of the ring atoms is the same as in Figure 1.

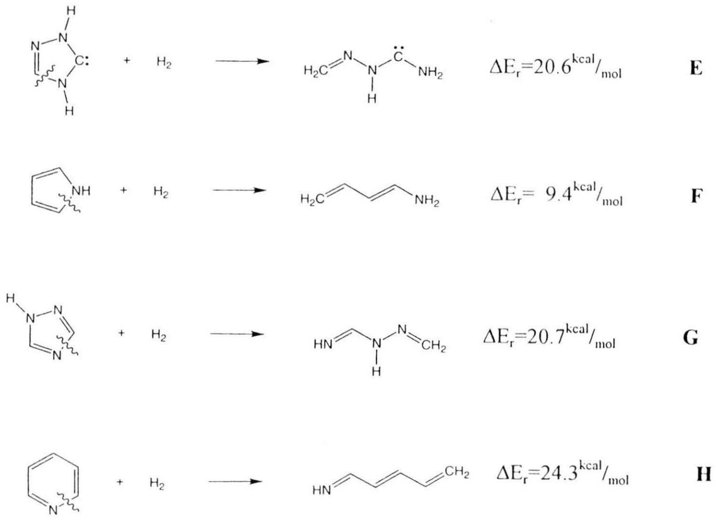
Bond lengths		Bond angles	
MP2/6-31+G*			
N1−C1	1.331	C1−N1−N2	113.2
N1−N2	1.353	N1−N2−C2	103.7
N2−C2	1.322	N2−C2−N3	110.4
N3−C2	1.369	C2−N3−C1	107.8
C1−N3	1.342	N3−C1−N1	105.0
MP2/6-31G**			
N1−C1	1.329	C1−N1−N2	113.3
N1−N2	1.352	N1−N2−C2	103.6
N2−C2	1.320	N2−C2−N3	110.5
N3−C2	1.368	C2−N3−C1	107.7
C1−N3	1.340	N3−C1−N1	104.9

Table 4. Selected bond lengths, angles, and dihedral angles (Å, °) of **4** at the MP2/6-31+G* ($E_{tot} = -241.581890$ a.u.) level and MP2/6-31G** ($E_{tot} = -241.589446$ a.u.) level. The numbering of the ring atoms is the same as in Figure 1.

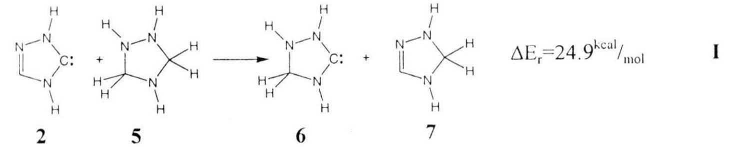
Bond lengths		Bond angles	
MP2/6-31+G*			
N1−C1	1.354	C1−N1−N2	111.0
N1−N2	1.352	N1−N2−C2	101.5
N2−C2	1.340	N2−C2−N3	115.3
N3−C2	1.362	C2−N3−C1	102.8
C1−N3	1.330	N3−C1−N1	109.5
MP2/6-31G**			
N1−C1	1.353	C1−N1−N2	111.0
N1−N2	1.350	N1−N2−C2	101.2
N2−C2	1.338	N2−C2−N3	115.6
N3−C2	1.360	C2−N3−C1	102.5
C1−N3	1.327	N3−C1−N1	109.6



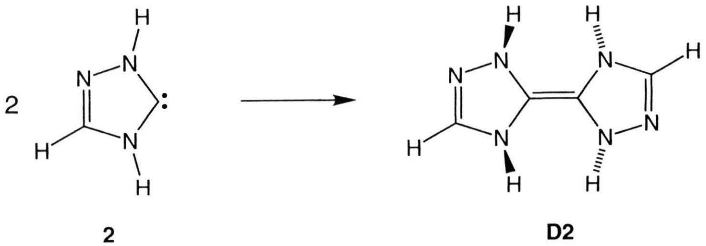
Scheme 3. (ZPE + MP2/6-31G**//RHF/6-31G**)



Scheme 4. (ZPE + MP2/6-31G**//RHF/6-31G**)



Scheme 5. (ZPE + MP2/6-31G**//RHF/6-31G**)



Scheme 6.

It is nevertheless clearly indicative of a certain degree of conjugative interaction between this structural element and the rest of the five-membered ring. With both basis sets the angle at the carbene center C1 of **2** (MP2/6-31+G*: 98.5°, MP2/6-31G**: 98.0°) is quite close to the experimentally determined value of 100.6(2)° for **1** [1].

Part of the conjugative interaction is retained in the open chain products resulting from *non-isodesmic* reductive ring cleavage (**E**–**H**). However, these reactions allow one to estimate the role of *cyclic* conjugation.

Again this type of interaction seems to be of similar importance in **2**, **4** and pyridine.

The *isodesmic* hydrogen transfer reaction **I** (cf. Scheme 5) allows one to determine the additional stabilization of the diamino carbene fragment carbon atom by the presence of a C=N double bond in the five-membered ring.

The change of energy associated with this reaction also emphasizes the non-negligible role of the conjugative interplay of the different molecular segments in **2**.

Although these interactions determine the ground state properties of the molecule beyond any doubt, it is difficult, if not impossible, to estimate their *absolute* effect on the experimentally observed overall *reactivity* not only of the highly substituted carbene **1** but also on that expected for parent **2**. Due to donation of the lone pairs of the neighbouring nitrogen atoms into the formally vacant $2p_z$ orbital at the divalent carbon atom, the *electrophilic* reactivity of the carbene will be reduced. However, participation of this orbital in a resonance hybrid might leave unchanged or even enhance the *nucleophilic* reactivity of the species. Thus at −245.1 kcal/mol (ZPE+MP2/6-31G**//RHF/6-31G**) the change of energy associated with protonation of the carbenoid lone pair is very high for a neutral organic molecule. Dixon and Arduengo [4] obtained an even higher value of approximately $-250^{\mathrm{kcal}}/_{\mathrm{mol}}$ for protonation of **1** at a comparable level of accuracy. Since dimerization involves both the carbenic lone pair as well as the partly occupied $2p_z$ orbital of the divalently bonded carbon atom, examination of this reaction seems to be more informative. Some stationary points located (RHF/6-31G**) on the $(C_2N_3H_3)_2$ surface are shown in Fig. 2 (**D1**–**D5**).

The relative energies given in Fig. 2 were calculated at the MP2/6-31G**//RHF/6-31G** level, and the following discussion of the geometries refers to the RHF/6-31G**-optimized structures. While **D1**–**D4** are local minima, the least stable isomer **D5** is a saddle point, characterized by one imaginary frequency in the spectrum of its normal vibrations. The most stable isomer is **D2**.

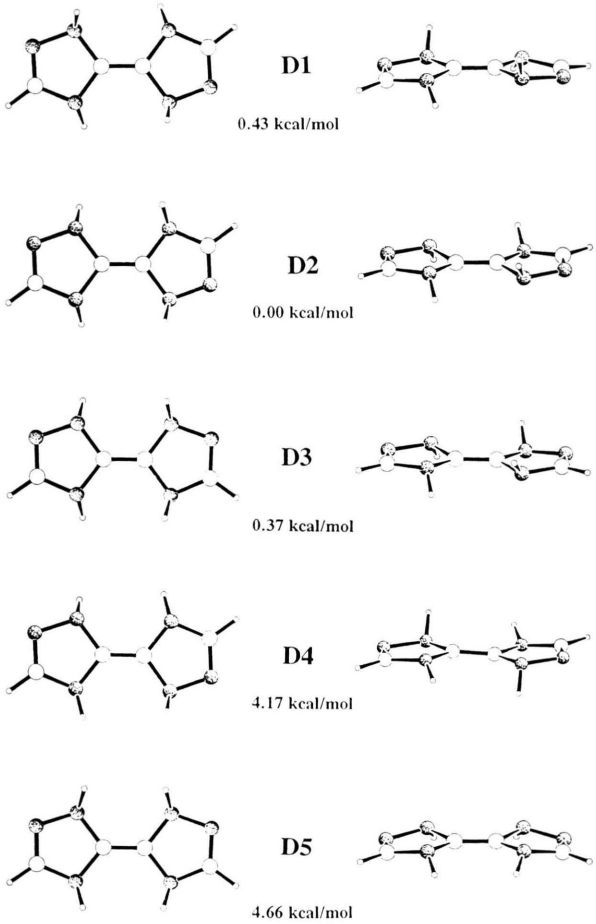


Fig. 2. Structures (RHF/6-31G**) and relative energies (MP2/6-31G**//RHF/6-31G**) of five dimers of **2**.

At an energy of reaction of $-9.53^{\mathrm{kcal}}/_{\mathrm{mol}}$ (MP2+ZPE/6-31G**//RHF/6-31G**) the dimerization resulting in **D2** (cf. Scheme 6) is clearly exoenergetic. However, compared with the double bond energy of, e.g., ethene ($171.3^{\mathrm{kcal}}/_{\mathrm{mol}}$ [3]), this value is rather low. Using this value in the approximate relationship between the double bond energy and ΔE_{st} of the fragments[1] results in a ΔE_{st} value of approximately

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[3] Calculated from experimentally determined values for the heats of formation of H_2C: ($91.9 \pm 1^{\mathrm{kcal}}/_{\mathrm{mol}}$ [20]) and $H_2C{=}CH_2$ ($12.5^{\mathrm{kcal}}/_{\mathrm{mol}}$ [21]).

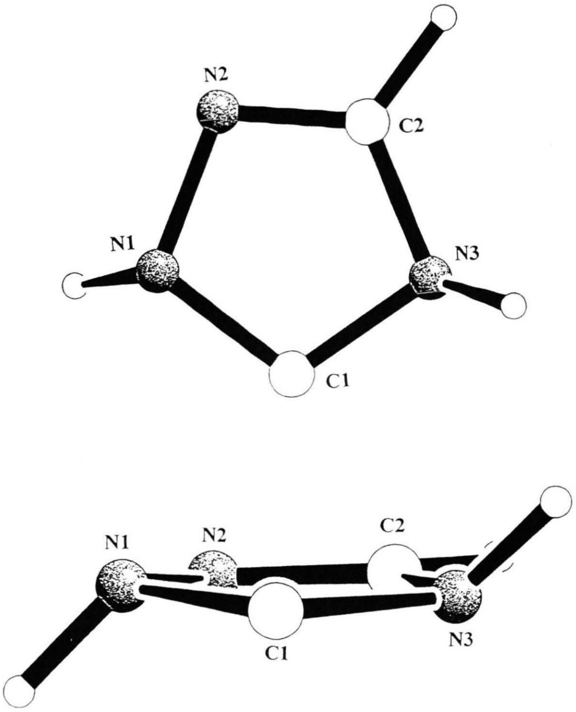

Fig. 3. Structure of the lowest triplet state of **2** and selected structural parameters at the UHF/6-31G** (ROHF/6-31G**) level: C1–N1: 1.411 (1.413) Å, N1–N2: 1.412 (1.411) Å, N2–C2: 1.258 (1.256) Å, C2–N3: 1.394 (1.397) Å, C1–N3: 1.408 (1.411) Å, N1–C1–N3: 108.8 (108.9)°, C1–N3–C2: 102.0 (101.7)°, N3–C2–N2: 115.8 (115.9)°, C2–N2–N1: 107.4 (107.5)°, N2–N1–C1: 105.5 (105.4)°.

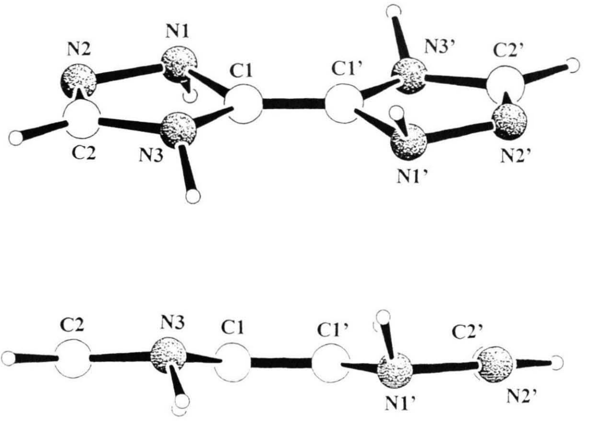

Fig. 4. The structure of the most stable dimer **D2**. Selected structural parameters at the RHF/6-31G** level: C1–C1′: 1.314 Å, N3–C1: 1.416 Å, C1–N1: 1.423 Å, N1–N2: 1.407 Å, N2–C2: 1.254 Å; N1–C1–C1′: 127.1°, N3–C1–N1: 105.7°, C2–N2–N1: 107.0°, N3–C1–C1′: 126.7°, N3–C2–N2: 115.4°.

$81\,^{\mathrm{kcal}}/_{\mathrm{mol}}$ for **2**. To test the reliability of this approach, we optimized the structure of the carbene's lowest triplet state at the UHF and ROHF level, employing the 6-31G** basis set[4]. Including correlation and zero point energy, the lowest triplet state of the carbene lies $88.6\,^{\mathrm{kcal}}/_{\mathrm{mol}}$ above its singlet ground state. The geometry of the triplet is no longer planar. Selected structural parameters are given in Figure 3.

Orienting calculations regarding the dimerization path indicate a significant barrier of $19.4\,^{\mathrm{kcal}}/_{\mathrm{mol}}$ at the MP2/6-31G**//RHF/6-31G** level (RHF/6-31G**//RHF/6-31G**: $32.7\,^{\mathrm{kcal}}/_{\mathrm{mol}}$). As expected, dimerization results in a decrease of the N2=C2 and increase of the C1–N1 and C1–N3 bond lengths as compared with the values for the free carbene. While the length of the N2=C2 double bonds in **D2** (1.254 Å) is almost identical with the value for the isolated bond in $H_2C=NH$ (1.250 Å), the average value for the C_1–N_1, N_3 distances (1.419 Å) is only by 0.033 Å smaller than for the C–N single bond in H_3C–NH_2.

The dimers of ylides with singlet ground states (Y_2X:) usually show significant trans bending about the X=X bond [17–19], which is strongly decreased when divalently bonded X is involved in a mesomeric system. Thus like for other dimers of singlet carbenes with π conjugation [17], the central C=C bond is only slightly trans bent (sum of bond angles on C1 and C1′: 359.6°) although the expected singlet-triplet gap amounts to about $89\,^{\mathrm{kcal}}/_{\mathrm{mol}}$ (cf. Figure 4). Such a weak deviation from planarity is not expected to affect the length of the C=C bond in **D2** significantly, and the C=C bond distance is identical with that calculated for ethene at the same level of computational accuracy.

4. Conclusion

The results of isodesmic and non-isodesmic reactions applied to 4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene emphasize the role of conjugative interaction between the molecular fragments of this species. Com-

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[4] UHF/6-31G**//UHF/6-31G**: $E_{\mathrm{tot}} = -240.669682$ a.u., $\langle s^2 \rangle = 2.025$, $\varepsilon_0 = 0.061693$ a.u.; UMP2/6-31G**//UHF/6-31G**: $E_{\mathrm{tot}} = -241.391848$ a.u.; ROHF/6-31G**//ROHF/6-31G**: $E_{\mathrm{tot}} = -240.664473$ a.u., $\varepsilon_0 = 0.062120$ a.u.; MP2/6-31G**//ROHF/6-31G**: $E_{\mathrm{tot}} = -241.392310$ a.u.

parison with the results obtained for other compounds reveals that it is only slightly less important than in 1,2,4-triazole and pyridine. Involvement of the divalently bonded carbon atom in a ground state resonance hybrid is expected to predominantly reduce the electrophilic reactivity of the ylide, while its nucleophilicity might remain uneffected or even be enhanced. Thus, at about 240 – 250$^{\text{kcal}}/_{\text{mol}}$ the energy of protonation of the carbene is very high for a neutral organic compound. On the contrary, the energy of dimerization of about 9.5$^{\text{kcal}}/_{\text{mol}}$ is quite low compared with that for non- or only weakly stabilized carbenes. This is not surprising since the dimerization reaction of singlet carbenes involves both the doubly occupied lone pair and the partly occupied $2p_z$ orbital of the carbenic center *.

Acknowledgement

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* *Note Added in Proof:* After our paper had been accepted for publication an *ab initio* study of some other heterocyclic 6π carbenes appeared [7a] in which aromatic stabilization energies ranging from 7.6 to 25.5 kcal/mol are reported.

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