Comparative quantum chemical investigation of structures and properties of diazocyclopropane and other diazoalkanes*

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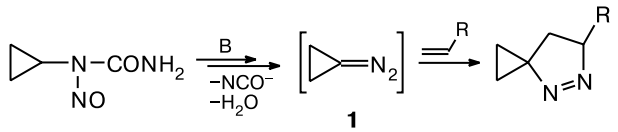
The electronic structures and dissociation energies of diazocyclopropane (**1**), diazomethane (**2**), 2-diazopropane (**3**), and diazocyclobutane (**4**) were calculated at the density functional B3LYP and the *ab initio* MP2 levels using the 6-31G(d) basis set and at the G2(MP2,SVP)//B3LYP/6-31G(d) level. Distinctive features of diazocyclopropane **1** are the low energy of dissociation with loss of the nitrogen molecule; ΔE = 18.7 kcal mol^{-1}, B3LYP; 9.2 kcal mol^{-1}, G2 at 0 K) and a nonplanar structure, in which the C=N bond forms an angle of 115.7° with the plane of the cyclopropane ring. The behavior of molecules **1** and **2** in the 1,3-dipolar cycloaddition to ethylene (**5**), acrylonitrile (**6**), and methyl acrylate (**7**) was studied. The reactions of **1** with **6** and **7** have very low activation barriers (ΔE_a = 4.7 and 4.4 kcal mol^{-1}, respectively; at the B3LYP level). For these reactions, the G2 method gives even smaller activation parameters (1.8 and 0.3 kcal mol^{-1}, respectively). The results of our calculations provide a good explanation for high reactivity of diazocyclopropane **1**.

Key words: diazo compounds, diazocyclopropane, 1,3-dipolar cycloaddition, quantum chemical calculations.

The characteristic feature of diazo compounds is their ability to react as 1,3-dipoles in [3+2]-cycloaddition reactions with unsaturated compounds. Such reactions are well studied both experimentally and theoretically.[1] The reaction mechanisms of cycloaddition[2—4] and the regioselectivity[5,6] of the process were studied in-depth by modern quantum chemical methods. We found that diazocyclopropane (**1**) is distinguished from a whole series of aliphatic diazo compounds by high reactivity.[7]

Diazocyclopropane (**1**) is very unstable and remains undetectable by spectroscopic methods. However, when generated *in situ* in the presence of appropriate trapping agents, compound **1** can give the corresponding trapping products in preparative yields. These reactions afford pyrazolines containing the spiro-fused cyclopropane fragment (Scheme 1).

Scheme 1



1

B is a base

* Dedicated to Academician N. K. Kochetkov on the occasion of his 90th birthday.

Diazocyclopropane **1** is most efficiently trapped by substrates in which the C=C bond is elongated due to the presence of a strained hydrocarbon moiety[8] or is conjugated with electron-withdrawing groups.[9] Attempts to prepare addition products of compound **1** to substrates containing an inactivated double bond (for example, to alk-1-enes) failed. In this case, reactions involving the initial dediazotization of diazocyclopropane **1** play the main role.[10]

The hypothesis of a nonplanar structure of diazocyclopropane **1**, which has been put forward more than 40 years ago,[10] is a possible key to understanding the unusual behavior of this compound. The nonplanar structure of **1** is also supported by the results of quantum chemical calculations at the RHF/6-31G(d) level of theory.[11] However, the geometric structure of diazocyclopropane has not been described in the latter study.

To elucidate the geometric features and the electronic structure of molecule **1** and explain its chemical properties, we carried out quantum chemical calculations by the B3LYP, MP2, and G2 methods.

Experimental

Quantum chemical calculations of the structure, vibrational frequencies, and the potential energy surface (PES) were carried out by the *ab initio* HF and MP2 methods and the B3LYP

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density functional method[12] with the standard 6-31G(d) basis set. In addition, the energies of the stationary points corresponding to the reagents, products, and transition states (TS) were calculated by the G2(MP2,SVP) modification[13] of the quantum chemical GAUSSIAN-2 (G2) scheme.[14] The calculation at the G2(MP2,SVP) level is an approximation of the energy calculations by the QCISD(T)/6-311G+(3df,2pd) method using the geometry and vibrational frequencies evaluated at the B3LYP/6-31G(d) level. The zero-point energy (ZPE) correction was calculated using the scaling factor of 0.9806 suggested[15] for the B3LYP method. The character of the stationary points (a minimum or a saddle point) was determined by calculating the eigenvectors of the second-derivative matrix of the energy. The fact that the transition state belongs to a particular reaction was examined by the intrinsic reaction coordinate (IRC) method.[16] The thermodynamic functions were calculated in terms of the harmonic oscillator—rigid rotator model. Calculations were carried out using the GAUSSIAN-98 program.[17]

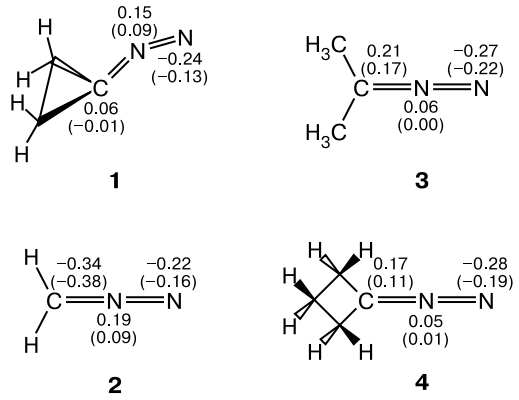

Fig. 1. Total charge distribution in diazoalkane molecules calculated at the B3LYP/6-31G(d) level; the corresponding values calculated at the MP2/6-31G(d) level are given in parentheses.

Results and Discussion

To compare the electronic structure, the geometry, and the dissociation energy of diazocyclopropane (**1**) with the corresponding parameters of other diazo compounds, we performed calculations for several simple and relatively stable diazoalkanes, *viz.*, diazomethane (**2**), 2-diazopropane (**3**), and diazocyclobutane (**4**), which have been studied in-depth by experimental methods.[18—20]

Charge distribution. Calculations by the MP2 and B3LYP methods demonstrated (Fig. 1) that the total charge distribution in the C=N=N fragment in molecules **1** and **2** somewhat differs from that observed in molecules **3** and **4**. In molecules **3** and **4**, the main positive charge is localized on the carbon atom (0.21 and 0.17, respectively), whereas the charge in molecules **1** and **2** is shifted to the nearest nitrogen atom. By contrast, the charge on the terminal nitrogen atom remains virtually unchanged, and this tendency persists regardless of the calculation method.

Structural parameters of diazoalkanes. A comparison of the structural parameters of the diazoalkanes calculated by the B3LYP method (Table 1) showed that the structure of the CNN fragment depends substantially on the nature of the substituent at the carbon atom.

Some differences are observed in the bond lengths in the C=N=N fragment. The longest C=N bond (1.298 Å; B3LYP) is observed in diazocyclopropane (**1**), whereas this bond in molecules **2** and **3** is shorter (1.293 Å), and it is further shortened to 1.283 Å in diazocyclobutane (**4**). At the same time, diazocyclopropane **1** has the shortest N=N bond (1.144 Å, see Table 1). Interestingly, the N=N bond in diazoalkanes is only ~0.05 Å longer than the distance between the nitrogen atoms in the free N_2 molecule (1.096 Å; B3LYP). In the diazo compounds under consideration, the most substantial differences are observed in the C=N=N angle. The CNN fragment is virtually linear in compounds **2**, **3**, and **4**, whereas the C=N=N angle in diazocyclopropane (**1**) is 171.7° (B3LYP). The torsion angle between the alkyl fragment and the C=N bond changes dramatically. The CH_2 (or CCC) fragment in molecules **2**, **3**, and **4** lies in a plane with the C=N bond, whereas the angle between the plane of the ring and the C=N bond in diazocyclopropane (**1**) is 115.7° (B3LYP). The planar structure of **1** corresponds to the transition state, and its energy is 2.6 (B3LYP) or

Table 1. Selected geometric parameters of diazoalkanes calculated at the B3LYP/6-31G(d) and MP2/6-31G(d) (in parentheses) levels and the experimental values[19] (in brackets)

Parameter	1	2	3	4
Bond		*d*/Å		
C=N	1.298 (1.320)	1.293 (1.314) [1.32]	1.293 (1.319)	1.283 (1.318)
N=N	1.144 (1.162)	1.146 (1.150) [1.12]	1.154 (1.156)	1.155 (1.155)
Angle		ω/deg		
C=N=N	171.7 (169.8)	180.0 (178.5) [180.0]	180.0 (176.5)	180.0 (175.4)
R—R—C—N*	115.7 (107.2)	180.0 (163.3) [180.0]	180.0 (157.2)	180.0 (141.8)

* The dihedral angle between the R—C—R plane and the C—N bond.

Table 2. Dissociation energies, enthalpies, and free energies of diazo compounds calculated at the B3LYP/6-31G(d) level (the corresponding values calculated at the G2(MP2/SVP)//B3LYP/6-31G(d) level are given in parentheses)

Compound	ΔE (0 K)	ΔE_0 (0 K)[a]	ΔH (298 K)	ΔG (298 K)
	kcal mol^{-1}			
1	24.1 (14.5)	18.7 (9.2)	20.0 (10.4)	9.2 (−0.4)
2	54.5 (42.2)	48.5[b] (36.2)	50.0 (37.7)	40.1 (27.8)
3	33.6 (25.0)	28.4 (19.8)	39.2 (20.9)	25.6 (9.8)
4	33.7 (22.1)	28.7 (17.1)	29.7 (18.2)	19.3 (7.7)

[a] At $T = 0$ K, taking into account the ZPE correction.
[b] The experimental dissociation energy measured at 0 K [21] is 51.3 kcal mol^{-1}.

5.2 kcal mol^{-1} (G2) higher than that of the above-described nonplanar structure. The structures of all the diazoalkanes calculated by the MP2 method are nonplanar (see Table 1). However, the deviations from the planar structure are small for molecules **2**, **3**, and **4**, whereas the torsion angle between the C=N bond and the plane of the cyclopropane ring in **1** is 107.6°.

Dissociation energies of diazoalkane molecules. Although elongation of the C=N bond in diazocyclopropane (**1**) is not so big compared to other diazo compounds (0.05—0.15 Å), our calculations demonstrated (Table 2) that this molecule should decompose much more easily than other diazoalkanes to give the corresponding carbene and the nitrogen molecule. For example, ΔE_0 is 48.5 (B3LYP) and 36.2 kcal mol^{-1} (G2) for diazomethane (**2**), whereas ΔE_0 decreases to 18.7 (B3LYP) and 9.2 kcal mol^{-1} (G2) for diazocyclopropane (**1**). The dissociation energies of diazo compounds **3** and **4** have intermediate values (see Table 2).

The calculated low dissociation energy of diazocyclopropane (**1**) agrees well with the experimental data[7] and explains why this diazo compound remains undetectable by physicochemical methods even at low temperatures (unlike compounds **2**—**4**).[20]

Study of 1,3-dipolar cycloaddition reactions. Our experimental studies[7—9] have demonstrated that, in spite of the low dissociation energy, diazocyclopropane (**1**) exists as a highly labile compound. When generated *in situ* in the presence of certain unsaturated compounds, diazocyclopropane **1** can give spirocyclopropane-containing pyrazolines (see Scheme 1). High reactivity of compound **1** in 1,3-dipolar cycloaddition reactions is, apparently, attributed to its unusual geometry and the fact that the electron density of the highest occupied molecular orbital is localized to a substantial degree on the carbon atom bearing the diazo group and is directed outside the molecule. We calculated the activation energies of the [3+2]-cycloaddition of diazocyclopropane **1** and diazomethane **2** to the C=C bond of ethylene, acrylonitrile, and methyl acrylate (Table 3).

Table 3. Total energies (E/au) of the stationary points on potential energy surfaces and the total energy differences (ΔE, ΔE_0[a]/kcal mol^{-1}), the enthalpy differences (ΔH/kcal mol^{-1}), and the free energy differences (ΔG/kcal mol^{-1}) for the 1,3-dipolar cycloaddition of diazocyclopropane (**1**) and diazomethane (**2**) to ethylene (**5**), acrylonitrile (**6**), and methyl acrylate (**7**) calculated at the B3LYP/6-31G(d) and G2(MP2/SVP)//B3LYP/6-31G(d) levels

Compounds and TS	B3LYP					G2			
	$-E$	ΔE	ΔE_0[a]	ΔH	ΔG	$-E_0$[a]	ΔE_0[a]	ΔH	ΔG
1	226.11005	—	—	—	—	225.71633	—	—	—
2	148.73926	—	—	—	—	148.50662	—	—	—
5	78.58746	—	—	—	—	78.41205	—	—	—
6	170.83155	—	—	—	—	170.53060	—	—	—
7	306.46775	—	—	—	—	305.96811	—	—	—
1 + **5**	304.77479	−48.5	−43.5	−45.0	−31.3	304.20333	−47.0	−48.5	−34.9
1 + **6**	397.00773	−41.5	−37.3	−38.5	−24.7	396.31660	−43.7	−44.9	−31.1
1 + **7**	532.64639	−43.0	−39.0	−40.0	−26.2	531.75740	−45.8	−46.8	−33.0
2 + **5**	227.38575	−37.0[b]	−30.8[b]	−32.5[b]	−19.4	226.96851	−31.3	−33.1	−19.9
2 + **6**	319.61824	−29.8	−24.3	−25.8	−12.2	319.08154	−27.8	−29.3	−15.7
2 + **7**	455.25716	−31.5	−26.1	−27.4	−14.1	454.52224	−29.8	−31.2	−17.9
TS (**1** + **5**)	304.68522	7.7	8.9	8.1	20.4	304.11849	6.2	5.4	17.7
TS (**1** + **6**)	396.93552	3.8	4.7	4.2	16.5	396.24409	1.8	1.3	13.6
TS (**1** + **7**)	532.57188	3.7	4.4	4.1	16.4	531.68402	0.3	−0.1	12.3
TS (**2** + **5**)	227.30399	14.3[b]	16.6[b]	15.3[b]	27.7	226.89422	15.3	14.1	26.4
TS (**2** + **6**)	319.55405	10.5[c]	12.6	11.6	24.0	319.01939	11.2	10.2	22.6
TS (**2** + **7**)	455.19116	9.9	11.9	11.0	23.5	454.46024	9.1	8.3	20.7

[a] At $T = 0$ K, taking into account the ZPE correction.
[b] The value agrees with the data published earlier[4,5] for the **2** + **5** reaction.
[c] The value agrees with the data published earlier[4] for the **2** + **6** reaction.

It should be noted that 3- or 4-substituted pyrazolines can in principle be formed from monosubstituted unsaturated compounds depending on the relative orientation of the diazo compound and olefin. Earlier calculations[5] at the B3LYP/6-31G(d) level demonstrated that the energy barrier to the **2** + **6** reaction giving rise to 4-substituted pyrazoline is 2.93 kcal mol^{-1} higher than that for 3-substituted pyrazoline. Our calculations demonstrated that 3-substituted pyrazoline would also be produced more readily in the **1** + **6** reaction, and the difference in the energy barriers responsible for the regioselectivity of the reaction is 1.8 kcal mol^{-1}. These data are consistent with the results of our experimental studies of the reactions of diazocyclopropane.[7–9] Hence, hereafter we consider only the processes giving rise to the most probable cycloadducts, *viz.*, 3-substituted pyrazolines.

Transition state structure. When studying 1,3-dipolar cycloaddition reactions, we assumed that they proceed by a synchronous mechanism to give a five-membered cyclic transition state (Fig. 2).

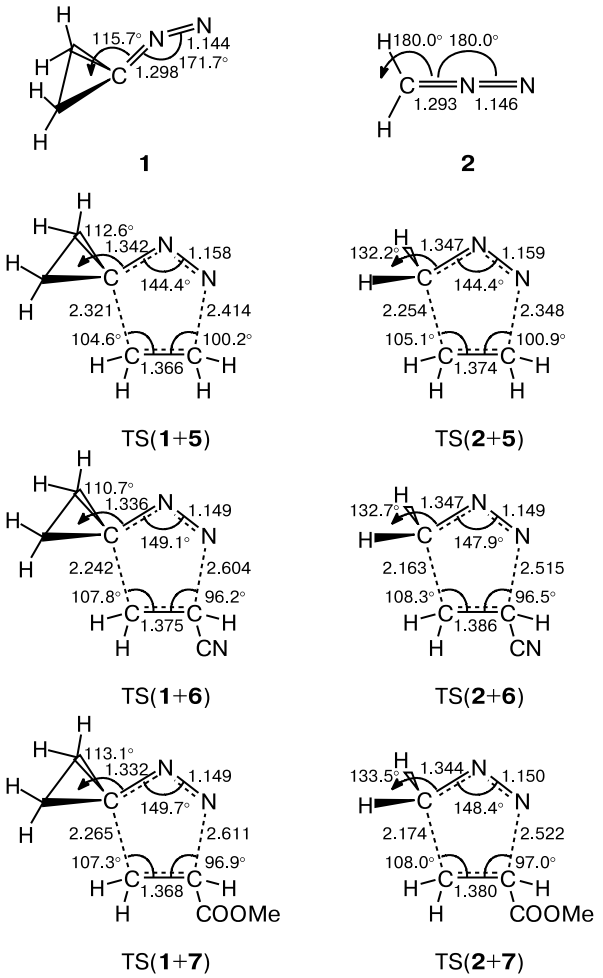

Fig. 2. Structures of diazo compounds **1** and **2** and the transitions states (TS) of their addition to ethylene, acrylonitrile, and methyl acrylate (B3LYP/6-31G(d)).

A comparison of the structures of free molecules **1** and **2** with the structure of the transition state of cycloaddition shows that the geometry of diazocyclopropane (**1**) changes only slightly. The torsion angle between the plane of the cyclopropane ring and the C=N fragment in **1** increases by 1.5—2°, and the C=N=N angle changes from 171.7 to 149.7—144.4°. The changes in the geometry of the planar diazomethane molecule (**2**) containing the linear C=N=N fragment are more substantial, and the torsion angle changes by almost 50°.

Analysis of the structures of the transition state of the cycloaddition reactions of diazocyclopropane (**1**) and diazomethane (**2**) demonstrated that the bonds formed in the reaction of **1** are longer by 0.07—0.08 Å. A comparison of the transition states of the reactions of **1** and **2** shows that the structure of the diazo group is most substantially affected by ethylene, whereas the geometry changes to a lesser extent in the reactions with acrylonitrile and methyl acrylate. This observation agrees well with the fact that the addition of diazo compounds to acrylonitrile and methyl acrylate occurs more easily than the addition to ethylene.

Energy parameters. An estimation of the thermal effect (see Table 3) suggests that the reaction with ethylene is slightly more exothermic than the reactions with substituted alkenes. In turn, a comparison of **1** and **2** demonstrates that the reactions with diazocyclopropane (**1**) are characterized by a larger thermal effect. It should be noted that the thermodynamic parameters calculated by different methods (B3LYP or the modified G2 scheme) differ insignificantly.

The activation energies calculated at the B3LYP/6-31G(d) level agree well with the data obtained earlier for the reactions of **2** with ethylene[4,5] and acrylonitrile.[4] The published data[5] and the results of our study (see Table 3) demonstrate that the activation barriers to the 1,3-dipolar cycloaddition reactions of diazo compounds to unsaturated compounds decrease substantially on going from ethylene to compounds containing electron-withdrawing substituents at the double bond (acrylonitrile or methyl acrylate). For example, the activation energy ΔE_0 of the reaction of diazomethane (**2**) with ethylene (taking into account the ZPE correction) is 16.6 kcal mol^{-1}, whereas the activation energies of the reactions with acrylonitrile (**6**) and methyl acrylate (**7**) decrease to 12.6 and 11.9 kcal mol^{-1}, respectively. The activation energies estimated by the more precise G2 method are 15.3, 11.2, and 9.1 kcal mol^{-1}, respectively.

As demonstrated above, diazocyclopropane (**1**) is more reactive in 1,3-dipolar cycloaddition reactions than diazomethane (**2**), which is attributable to the fact that the formation of the transition state of compound **1** requires smaller structural changes. For the reactions of diazocyclopropane (**1**) with unsaturated compounds **5**, **6**, and **7**, the activation energies ΔE_0 are 8.9, 4.7,

and 4.4 kcal mol^{-1} (B3LYP method) or 6.2, 1.8, and 0.3 kcal mol^{-1} (G2 method), respectively.

The calculated data provide an explanation for the absence of the addition products of diazocyclopropane (**1**) to substrates containing the inactivated C=C bond, for example, to ethylene.[7] Due to the low dissociation energy, the lifetime of compound **1** is very short even at low temperature. Hence it can be involved only in reactions, which proceed more rapidly than decomposition of **1** into nitrogen and cyclopropylidene. The very low activation energies of the reactions of **1** with acrylonitrile (**6**) and methyl acrylate (**7**) allow one to synthesize the corresponding cycloaddition products in preparative yields.[9]

* * *

Our calculations showed that diazocyclopropane (**1**), unlike the simplest diazoalkanes, is characterized by an unusual geometry. The C=N=N angle is 171.7°, and the C=N bond forms an angle of 115.7° with the plane of the cyclopropane ring. The electron density of the highest occupied molecular orbital is redistributed and localized on the carbon atom bearing the diazo group. As a consequence, on the one hand, the 1,3-dipolar cycloaddition of diazocyclopropane (**1**) at the C=C bonds activated by electron-withdrawing substituents is facilitated, and, on the other hand, dissociation accompanied by the C=N bond cleavage is much less endothermic compared to the reactions of diazomethane (**2**), 2-diazopropane (**3**), or diazocyclobutane (**4**). These data explain, first, high yields of products of 1,3-dipolar addition of diazocyclopropane (**1**) to a series of unsaturated substrates and, second, instability of this diazo compound.

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