2,6-Diaziadamantane: A Single-Crystal X-ray Diffraction Study and Theoretical Calculations

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The first single-crystal X-ray diffraction study of 2,6-diaziadamantane (**2**), a compound containing two diazirine functionalities, and B3LYP/6-311+G* and MP2/6-311+G* calculations relating to the interaction between carbon−nitrogen and nitrogen−nitrogen covalent bonds and electron density within the diazirine rings have been performed. In addition, the protonation of 2-aziadamantane (**1**) has been investigated. The single-crystal X-ray diffraction study of **2**, including UV/vis titrations of **1**, corroborate the theoretical conclusion that the low basicity can be attributed to a rehybridization of the nitrogen lone pairs. Moreover, the strain in diazirine is unusually small.

Introduction

3*H*-Diazirines (diazacyclopropenes) are three-membered rings, containing a carbon and two nitrogen atoms, with a N=N double bond. Since their discovery some 40 years ago,[1] these molecules have become increasingly popular carbene precursors. Their physical and chemical behavior has been the subject of numerous experimental and theoretical studies.[2] Diazirines, for instance, exhibit interesting optical[3] and chiroptical properties.[4] Although the spectroscopic properties of these molecules are well-known, only limited structural information from single-crystal X-ray diffraction has been obtained so far.[5] X-ray diffraction density maps of one chlorodiazirine had an unexpected pattern. A strong electron density maximum of the N=N bond was found *inside* the three-membered

ring.[5a,b] This result contradicted the theoretical electron density distribution obtained by ab initio calculations at the 6-31G* level of theory.[5a,b] Moreover, the reasons for differences in the refinement of an identical single-crystal X-ray structure were not discussed.[6] An explanation for the contradictory results was not offered at that time and, to our knowledge, still remains to be published.

We have investigated a series of several substituted aziadamantanes by single-crystal X-ray analysis.[7] Due to its high symmetry (222, orthorhombic space group), 2,6-diaziadamantane (**2**)[8] was chosen to address the aforementioned unresolved question by high-level theoretical calculations. The investigation of the structural properties of the supposed highly strained three-membered rings by difference electron density studies should provide rewarding insights into the nature of the chemical bonding of diazirines. The results are also expected to enhance the general understanding of the chemical behavior of these molecules such as reactivity and basicity.

The gas-phase protonation of 2-aziadamantane (**1**) yields the corresponding N-protonated diazoadamantane.[9] Therefore, the gas-phase basicity is not known. In

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(3) (a) Buterbaugh, J. S.; Toscano, J. P.; Weaver, W. L.; Gord, J. R.; Hadad, C. M.; Gustafson, T. L.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 3580. (b) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034.
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(6) While the authors state in ref 5b that "the ring does not contain a perfect twofold axis nor would this be expected," in ref 5a they assume a mirror plane containing the carbon atom and bisecting the N=N bond of the ring. This is done by imposing symmetry constraints in the multipole refinement without giving any reason for their change of mind. In addition, thermal instability and decomposition of the compound during the recording of the crystal structure were reported.
(7) Bobek, M. M. Ph.D. Dissertation, University of Vienna, Vienna, 2000.
(8) (a) Isaev, S. D.; Karpenko, N. F.; Kolyada, G. G.; Novikov, S. S.; Yurchenko, A. G. *J. Org. Chem. USSR* **1978**, *14*, 708. (b) Isaev, S. D.; Kolyada, G. G.; Novikov, S. S.; Yurchenko, A. G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1974**, 955. (c) Bobek, M. M.; Krois, D.; Brinker, U. H. *Org. Lett.* **2000**, *2*, 1999.
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SCHEME 1

1   **2**
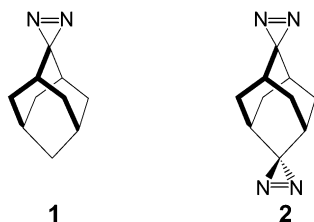
solution, however, only highly concentrated strong acids have to be used to destroy **1** by protonation.[10] Moreover, in the purification step during its preparation, **1** can easily be extracted with dichloromethane from 20% aqueous sulfuric acid.[11] This intriguing behavior led us to also investigate the protonation of **1** by UV/vis shift titrations.

Experimental Section

Basicity. UV/vis shift titrations of **1** were performed in a 2 cm quartz cuvette on a Perkin-Elmer Lambda 16 spectrometer. The spectra of these experiments can be found in Supporting Information.

X-ray Structure Determination: Sample Preparation. Crystals suitable for X-ray investigation were prepared by dissolving 22 mg (0.12 mmol) of 2,6-diaziadamantane (**2**) in 3 mL of anhydrous ethanol. The solution was left standing in the dark in a glass vial capped with perforated aluminum foil to allow slow evaporation of the solvent. Within 7 days, crystals were formed.

Data Collection, Structure Analysis, and Refinement. Crystal data for **2** have been summarized previously.[12] Intensity data for **2** were obtained on a Nonius Kappa diffractometer with a CCD detector at 110 K (in detail: collection time per frame = 10 s, rotation width = 2°, detector distance = 35 mm, total number of frames = 257). Structure **2** was solved by direct methods using the program *SIR92*[13] and refined with *SHELXL97*.[14] The figures were prepared using *DIAMOND 2.1a*.[15]

Calculations. The structure of 2,6-diaziadamantane (**2**) was studied via geometry optimization at the B3LYP/6-311+G* and MP2/6-311+G* theoretical levels.[16]

Results and Discussion

Basicity. To a 5 mM solution of **1** in methanol was added concentrated sulfuric acid in small portions until a concentration of 2.9 M in sulfuric acid was achieved. A UV/vis spectrum was recorded in the range from 220 to 450 nm after each addition. The dilution-corrected spectra did not show any change during titration. Also, a
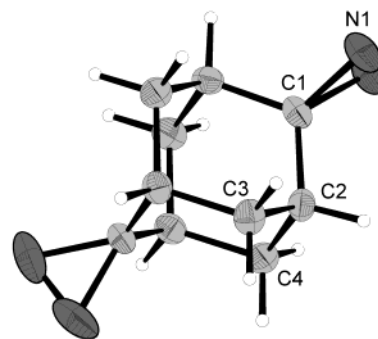

FIGURE 1. Molecular structure of 2,6-diaziadamantane (**2**) showing the atom labeling. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

titration with trifluoromethanesulfonic acid in dimethyl sulfoxide showed no spectral changes up to a concentration of 1.37 M of this very strong acid. Finally, a solution of **1** in 1,1,2-trifluoro-1,2,2-trichloroethane, a solvent that cannot be protonated, was titrated with this acid. Even in this case not the slightest spectral change was observed until addition of 1 equiv of trifluoromethanesulfonic acid,[17] which is soluble in this special solvent. For 1.4 equiv of the acid, a slight opalescence was noted.

X-ray Structure. All bond lengths and angles in bisdiazirine **2** have the values expected. This is also true for the adamantane unit where the values agree with data from the literature. The geometry of the three-membered ring (C1−N1−N1b) is not significantly influenced by the different substituents attached to the adamantane skeleton. In comparison with 12 available crystal structures in the CSD[18] containing a diazirine group, the general ring geometry is similar but not the same.

In the 12 known structures, the electron density in the diazirine unit is highly influenced by metals (6 are organometallic compounds) or by inclusion of solvent (2 of 12) and/or by strong electronegative substituents (5 structures with a chlorine atom). The hydroxy and amino substituents were shown to exert a significant distortion on the geometry of the carbene generated from the diazirine by photolysis.[5g,19] In the case of compound **2**, no such influences are present. The investigation of the geometry of the three-membered rings in diazirines is of

(10) Isaev, S. D.; Zhalnina, G. G.; Murzinova, Z. N.; Lastovenko, S. I.; Yurchenko, A. G. *J. Org. Chem. USSR* **1988**, *24*, 126.

(11) Isaev, S. D.; Yurchenko, A. G.; Stepanov, F. N.; Kolyada, G. G.; Novikov, S.S.; Karpenko, N. F. *Zh. Org. Khim.* **1973**, *9*, 724.

(12) X-ray analysis of **2** (C$_{10}$H$_{12}$N$_4$, M = 188.24). The compound crystallizes in the orthorhombic space group *Ccca* with the unit cell parameters a = 9.101(2), b = 11.634(2), c = 8.866(2) Å, $\alpha = \beta = \gamma$ = 90°, V = 938.7(3) Å^3, Z = 4, D_{calcd} = 1.332 g/cm^{-3}, μ = 0.086 mm^{-1}. Mo Kα radiation (λ = 0.71073 Å), 1295 reflections measured, 712 unique, 712 with $F = 2\sigma(F)$ gave R_1 = 0.036/wR_2 (all data) = 0.1122 in a full matrix least-squares refinement with 47 parameters. GOF on F^2 = 1.095.

(13) *SIR92: Program for Crystal Structure Solution*; Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(14) *SHELX97: Program for Crystal Structure Analysis (Release 97-2)*; Sheldrick, G. M.; Institut für Anorganische Chemie der Universität: Tammanstrasse 4, D-37077 Göttingen, Germany, 1998.

(15) *DIAMOND 2.1a: Visual Crystal Structure Information System*; Brandenburg, K.; Universität Bonn: Bonn, Germany, 1999.

(16) The calculations were carried out using Gaussian 99: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Adamo, C.; Jaramillo, J.; Cammi, R.; Pomelli, C.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 99*, Development Version, revision B; Gaussian, Inc.: Pittsburgh, PA, 2000.

(17) For reactions of diazirines with acids, see: Schmitz, E. In *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. 1, pp 90−94.

(18) CSD, Cambridge Structure Database 2000: reference codes of diazirine structures: AZCRMP, GAJRUE, GAJRUE01, GAJRUE02, PABCOK, PABCOK10, PAKWED, PARUFP, SEBHOW, VUFCUU, VUFDAB, YAVWOH.

(19) Bobek, M. M.; Brinker U. H. *J. Am. Chem. Soc.* **2000**, *122*, 7430.
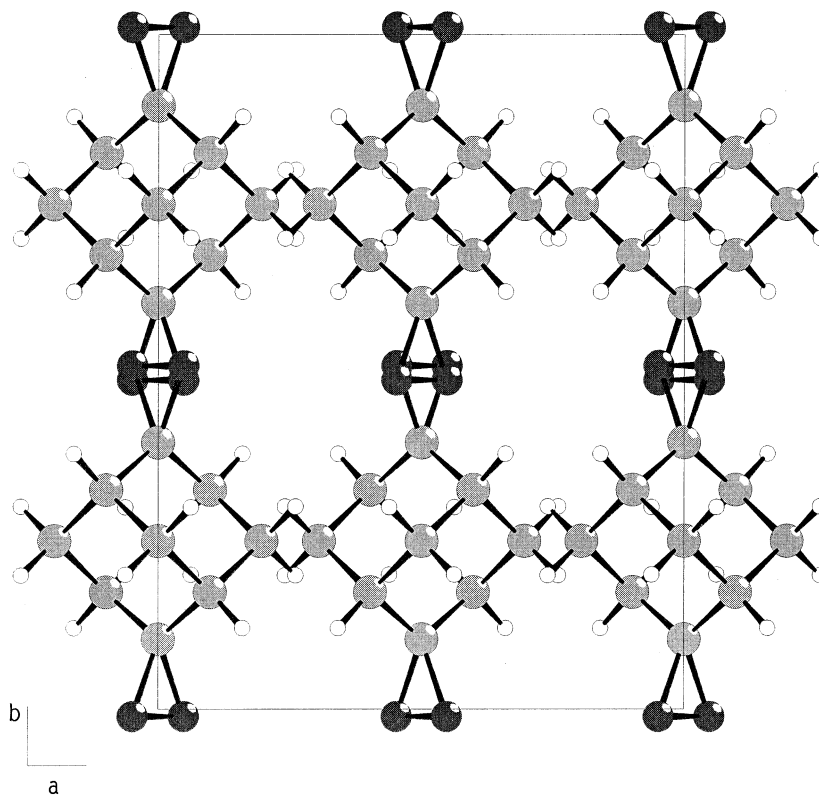
FIGURE 2. Packing mode in the unit cell of **2** along the *c*-axis.

considerable interest, since the supposed highly strained rings should possess Walsh orbitals, which are expected to deviate from the linear C−N internuclear axis. First investigations of the geometric properties were done using the data of a single-crystal X-ray structure of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine.[5a,b] In this report, the authors claim to find an asymmetric electron density distribution and argue that this is to be expected.[5b] In a later publication, the authors apply symmetry constraints to the refinement of the same structure, however, without explaining the reasons for their change of mind.[5a] With a conventional refinement method[14] an electron density maximum located on the outside of the N=N bond can be detected. However, a refinement with the more accurate multipole method[20] yielded a strong electron density maximum near the N=N double bond on the *inside* of the diazirine ring. No significant electron density was found at the position where the nitrogen nonbonding lone pairs are expected. This contradicts the theoretical calculations of these authors[5a] at the 6-31G* level of theory, which predict the existence of Walsh orbitals and nitrogen lone pairs on the diazirine ring. No explanation for these inconsistencies has been offered to this point.

We report here the first X-ray diffraction study of 2,6-diaziadamantane (**2**), a compound containing two diazirine functionalities. Figure 1 shows the geometry of bisdiazirine **2**. Note that the planes of the diazirine rings are aligned perfectly perpendicular. The thermal ellipsoids of the carbon atoms are circular in all cases, whereas the thermal ellipsoids of the nitrogen atoms are

elongated. Since the single-crystal X-ray structure of **2** was recorded at 110 K and the carbon atoms show no thermal displacement, the ellipsoid form of the nitrogen atoms is not caused by vibrational movement positions of the atoms. They do not follow the axis exactly but point slightly outward from the three-membered ring.

The packing mode (Figure 2) is determined by a regular arrangement of the molecules. They fit in a orthorhombic unit cell, wherein the diazirine rings are stacked on top of each other. Weak interactions between the nitrogen atoms (Table 1) support this molecular arrangement, forming a chain like motif (N1**−N1b**... N1−N1b...N1*−N1b*). Note that the general geometry of the N1=N1b bond to N1*=N1b* in the adjacent molecule* is parallel and that the N1=N1b bond is perpendicular to N1**=N1b**.

Calculations. The structure of 2,6-diaziadamantane (**2**) was studied via geometry optimization at the B3LYP/6-311+G* and MP2/6-311+G* theoretical levels.[16] Both include correction for electron correlation, but by different methods. The calculated geometries are compared with the observed values in Table 2. There is generally good agreement, with the MP2 geometry being somewhat more satisfactory than B3LYP.[21]

For a comparison, dimethyldiazirine also was studied, and here a somewhat larger basis set, 6-311++G**, was used with MP2 in order to obtain a more accurate description of the electron density distribution. The

(20) Cameron, T. S.; Borecka, B.; Kwiatkowski, W. *J. Am. Chem. Soc.* **1994**, *116*, 1211.

(21) For multiple bonds, MP2 tends to give bond lengths that are too long but give good single-bond lengths. As an example, using 6-311+G*: ethane r(C−C), B3LYP 1.528, MP2, 1.529, obsd 1.531; ethene r(C=C), B3LYP 1.329, MP2 1.339, obsd 1.339; ethyne r(CC), B3LYP, 1.200, MP2, 1.217, obsd 1.203.

TABLE 1. Bond Lengths/Interaction Distances (Å) and Bond Angles/Interaction Angles (deg) of the Crystal Structure of 2 (Esds, are in Parentheses)

atoms involved (symmetry)	bond lengths	atoms involved (symmetry)	bond angle
adamantane			
C1(i)−C2(i)	1.505(1)	C1(i)−C2(i)−C3(i)	108.08(6)
C2(i)−C3(i)	1.537(1)	C1(i)−C2(i)−C4(i)	108.02(6)
C2(i)−C4(i)	1.537(1)	C4(i)−C2(i)−C3(i)	109.98(7)
diazirine ring			
N1(i)−C1(i)	1.473(1)	N1(i)−C1(i)−C2(i)	119.56(6)
N1b(ii)−C1(i)	1.473(1)	N1b−C1(i)−N1(i)	49.83(10)
N1b(ii)−N1(i)	1.241(2)	N1b(ii)−N1(i)−C1(i)	65.09(5)

intermolecular interaction[a]	interaction distance	atoms[a] involved (symmetry)	interaction angle
N1...N1*(iii)	3.671(3)	N1(i)...N1*(iii)−N1b* (iv)	121.04(6)
N1...N1**(v)	3.682(3)	N1(i)...N1**(v)−N1b**(vi)	134.87(6)
(i) x, y, z	(ii) 0.5 − x, 0.5 + y, 0.5 − z	(iii) −x, −y, −z (1 1 0)	(iv) 0.5 + x, 0.5 − y, 0.5 − z
(v) −x, 0.5 − y, z (1 0 0)	(vi) 0.5 + x, −y, 0.5 − z		

[a] Different molecules are indicated with * and **. The atom codes N1 and N2 indicate the two nitrogen atoms of the diazirine group in one molecule.

TABLE 2. Comparison of Calculated and Observed Structures of 2,6-Diaziadamantane (2) in Å

parameter	B3LYP/6-311+G*	MP2/6-311+G*	obsd
N1−N2	1.230	1.262	1.241
C3−N1	1.476	1.480	1.473
C3−C4	1.517	1.508	1.505
C4−C5	1.547	1.540	1.537
C3−N2−N1	65.4	64.8	65.1
N1−C3−N2	49.4	50.5	49.8
N1−C3−C4	119.9	119.4	119.6

TABLE 3. Calculated Structure of Dimethyldiazirine

parameter	MP2/6-311++G**
N1−N2	1.259 Å
C3−N1	1.482 Å
C3−C4	1.503 Å
C3−N1−N2	64.9°
N1−C3−N2	50.3°

geometry is given in Table 3, and it is not much different than that for diaziadamantane **2**.

The MP2 deformation density in the plane of the three-membered ring was calculated for both compounds[22] and shown in Figure 3. The outer contour value is 1.0×10^{-2} e/au^3 and increases by a factor of 2 for each subsequent contour. The B3LYP and MP2 deformation densities for diaziadamantane **2** are similar, and the MP2 deformation density for dimethyldiazirine is quite similar to that for 2,6-diaziadamantane (**2**). In each case, the density outside the C−N line shows that the bonds are bent, just as they are in cyclopropane.[23] The deformation density for the N=N bond and for the lone pairs at the nitrogens is seen in Figure 3.

To better characterize the bonds in these molecules, the Fulton bond indices[24] (closely related to the bond

orders, but generally somewhat smaller in magnitude) were calculated for the bonds in dimethyldiazirine. The values are 1.609 for the N=N bond, 0.732 for the N−C bond, and 0.855 for the C−C bond. It is clear that the N−N bond is properly considered as a double bond.

To gain information concerning the relatively low basicity of diaziadamantane **1**, we have examined the diazacycloalkenes with three-, four-, five-, and six-membered rings via B3LYP/6-311+G* and MP2/6-311+G* geometry optimizations. The energies are given in Table 4. The relative acidities of the conjugate acids could be estimated from proton-transfer energies to ammonia: The energy changes are given in Table 5, and include the open-chain *cis*-1,2-dimethyldiimide. As the ring size increases, the proton transfer energy becomes less exothermic and, finally, endothermic. Diazirines give the largest exothermic reaction, indicating its low basicity with respect to ammonia. It should be noted that ammonia itself is a very weak base in the gas phase because the ammonium ion, with its small size, has a high electrostatic energy. The B3LYP/6-311+G* energy of protonated **2** also was calculated, and it was found to be somewhat more basic than diazirine in the gas phase, which is expected because of its larger size.

The strain in the diazacycloalkenes also was of interest. With the cycloalkenes, an unstrained model may be obtained by starting with cyclohexene (assumed unstrained) and subtracting the energy of enough CH_2 group energies to give a model of an "unstrained" cycloalkene.[25] The difference between the energy of this model and the calculated total energy gives the strain energy. The CH_2 group energies were taken as one-sixth of the calculated energy of cyclohexane. The values thus calculated are in good agreement with those derived from experimental data. This method also was applied to the diazacycloalkenes. If diazacyclohexene is taken as the unstrained model, diazacyclopentene is calculated to have a negative strain energy. Therefore, in this case diazacyclopentene was taken as the unstrained model, and the "unstrained" model energies for the other diazacycloalkenes were derived from it by adding or subtracting the

(22) Deformation densities were calculated using the CASGEN programs written by Paul R. Rablen (Ph.D. Thesis, Yale University, New Haven, CT, 1994).

(23) Coulson, C. A.; Moffitt, W. *Philos. Mag.* **1949**, *40*, 1.

(24) Fulton, R. L.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 7530. The bond indices give the covalent part of the bond order, which is less than the bond order for polar molecules. The values were calculated using a program written by Todd A. Keith, Semichem, Inc. (Shawnee Mission, KS).

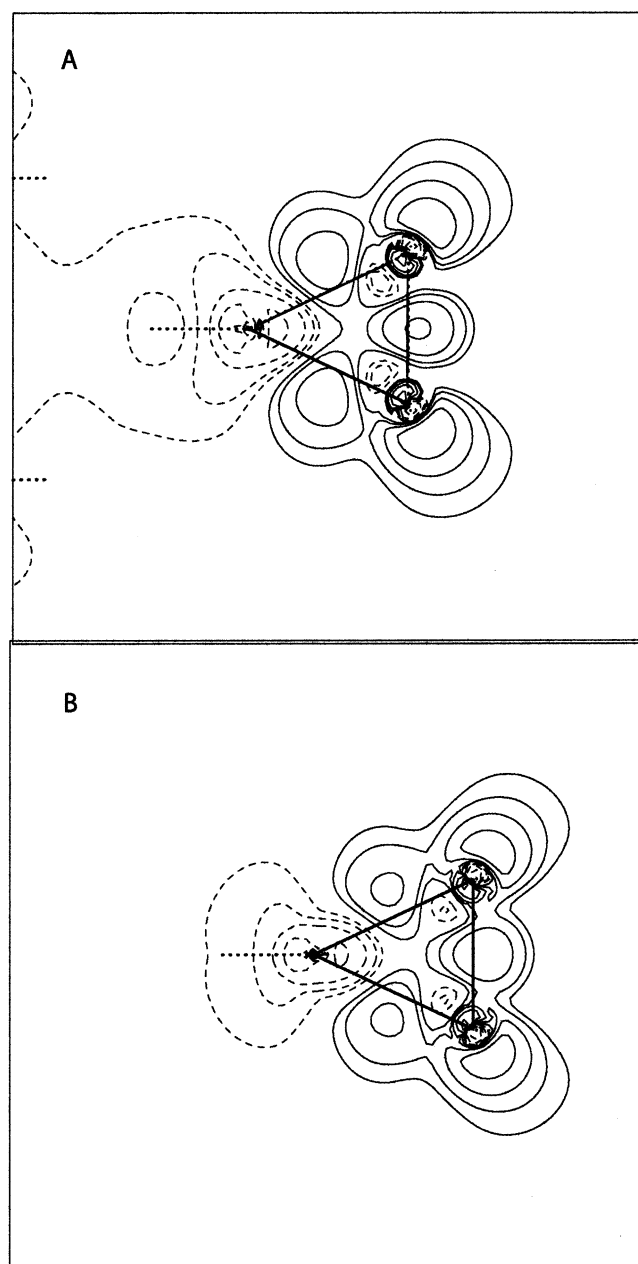(25) Dudev, T.; Lim, C. *J. Am. Chem. Soc.* **1998**, *120*, 4450.

FIGURE 3. Deformation density plots for **2** (A) and dimethyldiazirine (B).

requisite number of CH_2 group energies. The strain energies thus derived are given in Table 6.

This procedure may be critized because it does not take into account the difference between a CH_2 group attached to a carbon and that group attached to nitrogen. Despite this caveat, it is clear that the strain in diazirine is unusually small.

A related observation has been made by Bach and Dmitrenko,[26] who found that the cyclic three-membered ring peroxide (dioxirane) is unusually stable. The origin of the stabilization of three-membered rings with two heteroatoms is at present not clear.

Figure 4 shows deformation density plots for the four diazacycloalkenes. The outer electron density contour has the value 1.0×10^{-2} e/au^3, and it increases by a factor of

TABLE 4. Calculated Energies (Hartrees)

compd	B3LYP^a	MP2^a	Hcorr^b
diazacyclopropene	−148.75839	−148.34790	0.03735
diazacyclobutene	−188.07832	−187.51983	0.06752
diazacyclopentene	−227.44090	−226.74215	0.09842
diazacyclohexene	−266.75291	−265.91165	0.12827
2,6-diaziadamantane (**2**)	−607.29203		0.22540
MeNNMe	−189.30847	−188.71300	0.09000
NH$_3$	−56.57282	−56.38609	0.03848
Hdiazacyclopropene$^+$	−149.02918	−148.61101	0.04994
Hdiazacyclobutene$^+$	−188.40961	−187.84385	0.08114
Hdiazacyclopentene$^+$	−227.78485	−227.07834	0.11257
Hdiazacyclohexene$^+$	−267.11223	−266.26333	0.14265
H2,6-diaziadamantane$^+$	−607.59074		0.28698
HMeNNMe$^+$	−189.65940	−189.05691	0.10461
NH$_4^+$	−56.91170	−56.71678	0.05409
cyclopropene	−116.64605	−116.24734	0.05990
cyclobutene	−156.00765	−155.46763	0.09097
cyclopentene	−195.37039	−194.69147	0.12211
cyclohexene	−234.69962	−233.87995	0.15251
cis-2-butene	−157.26086	−156.68414	0.11431
cyclohexane	−235.92984	−235.08226	0.17695

^{a} 6-311+G* basis set total energies. ^{b} Zero-point energy and enthalpy change on going to 298 K.

SCHEME 2

TABLE 5. Energies of Isodesmic Reactions

	proton transfers to ammonia (kcal/mol)	
compd	B3LYP	MP2
Hdiazacyclopropene$^+$	−40.8	−40.5
Hdiazacyclobutene$^+$	−3.5	−2.9
Hdiazacyclopentene$^+$	4.1	4.4
Hdiazacyclohexene$^+$	13.6	13.9
HMeNNMe$^+$	8.2	8.9
H2,6-diaziadamantane$^+$	−27.2	

TABLE 6. Calculated Strain Energies

compd	B3LYP	MP2	obsd^a
cyclopropene	53.0	54.2	52.6
cyclobutene	28.9	30.8	28.8
cyclopentene	4.2	4.5	4.4
cyclohexene	[0.0]	[0.0]	[0.0]
diazacyclopropene	23.3	19.8	
diazacyclobutene	24.8	25.5	
diazacyclopentene	[0.0]	[0.0]	
diazacyclohexene	6.3	7.1	

^{a} Experimental data were taken from: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970.

two for each successive contour. When comparing the three-membered ring with the others, its lone pairs are contracted with respect to the higher homologues. The highest contour in diazirine is at 8×10^{-2} au^{-3}, whereas the others have a highest contour at 16×10^{-2} au^{-3}. Clearly, in diazirine, its lone pairs are contracted with respect to the four-, five-, and six-membered systems. Thus, it resembles cyclopropene where the hydrogens are attached to the double-bonded carbons using an orbital with high s character. This is seen experimentally in their

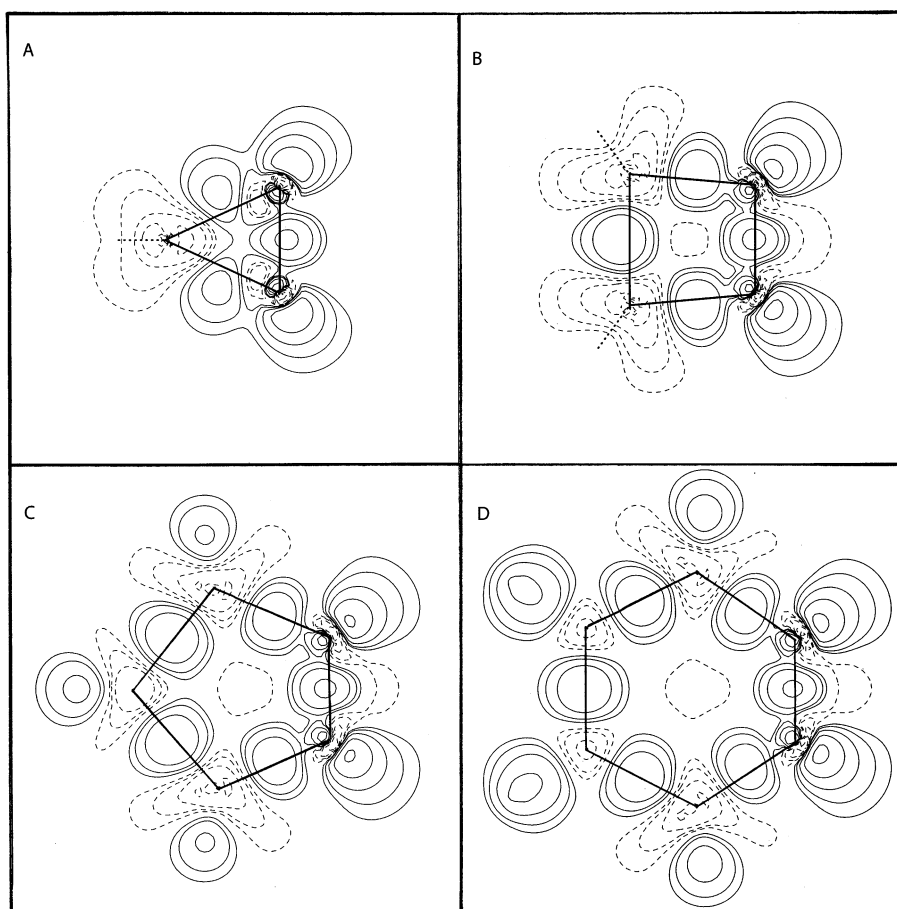(26) Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2002**, *67*, 2588.

FIGURE 4. Deformation density plots for diazirine (A), 1,2-diazacyclobutene (B), 1,2-diazacyclopentene (C), and 1,2-diaza-cyclohexene (D).

high acidity for C−H bonds, approaching that for an acetylene.

Supporting Information Available: Spectral data of UV/vis shift titrations of **1**. This material is available free of charge via the Internet at http://pubs.acs.org. A list of atomic coordinates and thermal components of the atoms can be obtained by request from T.H.B. or G.G. The Cambridge Crystallographic Data Center administers the supplemen-tary crystallographic data for this paper: deposition number CCDC 185031. These data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). This material is available free of charge via the Internet at http://pubs.acs.org.

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