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Are 1,2-Dihydrodiazetes Aromatic? An Experimental and Computational Investigation

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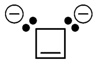
A thorough experimental and computational investigation of the aromaticity of the 1,2-dihydrodiazete ring system was carried out. The X-ray crystal structure of 1,2-dihydrodiazete **6** is reported, and the alkene-like reactivity of compound **6** is described. The compound's structure and reactivity suggest that **6** is not aromatic. This conclusion is corroborated by computational results on **6** and related compounds including homodesmotic reactions to test for aromatic stabilization, NICS calculations, and NBO calculations. Compound **6**, and 1,2-dihydrodiazetes in general, are concluded to be strained heterocycles with no indication for aromatic stabilization.

Introduction

Aromaticity continues to be an actively investigated area of chemistry.[1] The simplest criteria for aromatic compounds are that they possess cyclic conjugated π-systems containing the proper number of π-electrons (i.e., the Huckel rule). While these criteria are robust enough to predict the aromaticity of a host of neutral and charged ring systems, it is not always a clear indicator of aromaticity for more complex systems. For instance, applying these criteria to the cyclobutadienyl dianion (**1**) one would predict an aromatic compound since it contains six π-electrons akin to that of benzene and the cyclopentadienyl anion.



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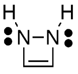

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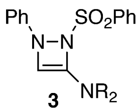
Early computational studies suggested that **1** adopted a folded structure and was therefore not aromatic.[2] More recent studies, however, suggested that the dianion is planar but adopts a structure with C_{2h} symmetry rather than the D_{4h} symmetry that would be expected for a fully delocalized aromatic structure.[3] The failure to adopt a D_{4h} structure was attributed to repulsive interaction of the negative charges within the ring. Indeed, only when two Li^+ cations were added to the model system to stabilize the charges did the ring adopt the expected D_{4h} symmetry.[3] Recently the synthesis and characterization of a cyclobutadienyl dianion substituted at each of the four carbons of the ring with anion-stabilizing trimethylsilyl groups was reported.[4] The resulting compound was planar and almost square (as determined by X-ray crystallography), suggesting that it may be aromatic.

The charge repulsion problem in the cyclobutadienyl dianion could be minimized by substituting the two adjacent negatively charged carbons of the ring by nitrogen atoms to afford a 1,2-dihydrodiazete (**2**). The 1,2-dihydrodiazetes are isoelectronic with the cyclobutadienyl dianion, but should experience considerably less charge/charge repulsion and might, therefore, exhibit aromaticity without the need for additional stabilization.

Only a few 1,2-dihydrodiazetes have been reported in the literature. The first to be reported were rather highly substituted derivatives (**3**) and their characterization did not include spectroscopic data.[5] Greene reported the syntheses of **4** (R = Me, Ph) as stable crystalline compounds.[6] Neither of these investigators discussed the possibility of aromaticity of the ring system. Warrener synthesized compound **5**, which is substituted at the nitrogens by carbomethoxy groups.[7] This compound proved to be of limited thermal stability and underwent spontaneous electrocyclic ring-opening at room temper-



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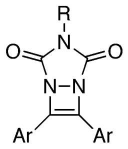

Ar = 2,6-dimethyl-4-methoxyphenyl

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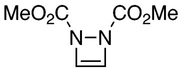

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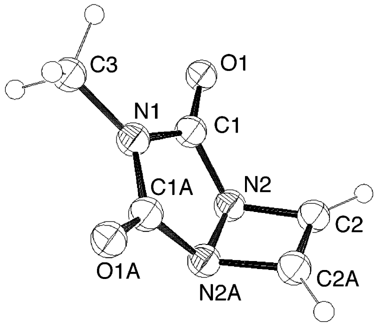
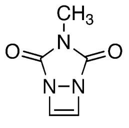


FIGURE 1. Single-crystal X-ray crystallographic structure of 1,2-dihydrodiazete **6**. Selected bond lengths (Å): N(2)−N(2A), 1.4704(7); N(2)−C(2), 1.4631(5); C(2)−C(2A), 1.3313(9). Selected bond angles (deg): C(2)−N(2)−N(2A), 87.28(2); N(2)−C(2)−C(2A), 92.72(2). Selected torsional angles (deg): C(2)−N(2)−N(2A)−C(2A), 0.00; C(1)−N(2)−N(2A)−C(2A), 120.35(4).

ature ($t_{1/2}$[20 °C] = 6.9 h). Warrener considered the possibility of the ring's aromaticity but ultimately rejected it based on its low thermal stability, ^{1}H NMR spectroscopic data, and theoretical arguments.[7b]

We recently reported the synthesis of compound **6**, an analogue of Greene's compound **4**.[8] Compound **6** is a



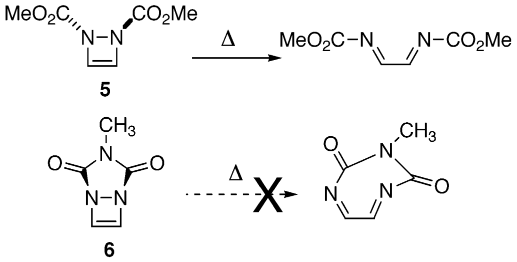
6

stable crystalline compound that lent itself to thorough structural and chemical analyses. In this paper we present our experimental work with **6** along with additional computational studies on **6** and 1,2-dihydrodiazetes in general to determine whether the 1,2-dihydrodiazete ring system exhibits any characteristics that may be attributed to aromaticity.

Results and Discussion

Experimental Studies. Compound **6** was synthesized according to our previous report.[8] Crystals suitable for single-crystal X-ray analysis were obtained upon recrystallization from hexane. Relevant bond lengths and angles are summarized in Figure 1. To our knowledge, this constitutes the first reported crystal structure of a 1,2-dihydrodiazete compound. Several features of the structure deserve comment. First, the pyramidal nature of the nitrogen atoms in the ring may be readily observed from the C1−N2−N2A−C2A torsion angle of 120.4° whereas if the nitrogen atoms were planar the torsion angle would be 180°. While the observed nitrogen pyramidality is a significant departure from the planar nitrogen atoms expected for an aromatic compound (i.e., as is found in pyrrole) it has been demonstrated in the phosphole system that the extent of pyramidality of the heteroatom is not uniquely correlated with aromaticity.[9] Therefore, judgments of aromaticity based solely on the geometry of the nitrogen atoms in the 1,2-dihydrodiazete structure may be premature. The four-membered ring is completely planar (C2A−N2A−N2−C2 torsion angle = 0°). Similarly, the C1−N2−N2A−C1A torsion angle is 0°, but the nitrogen atom (N1) of the N-Me group buckles out of the plane defined by those same atoms (e.g., N2A−N2−C1−N1 torsion angle = 7.4°). The lengths of the N−N, C−N, and C=C bonds in the 1,2-dihydrodiazete ring (i.e., 1.47, 1.46, and 1.33 Å, respectively) are very similar to other experimental values for these same types of bonds (i.e., 1.45 [N_2H_4], 1.47 [CH_3NH_2], and 1.34 Å [cyclobutene], respectively).[10] In an aromatic ring one would typically expect lengthened C=C bonds and compressed N−N and C−N bonds due to the effects of delocalization of the π-electrons. The observed bond lengths, therefore, suggest localized single and double bonds within the ring.

SCHEME 1. Results of Concerted Conrotatory Ring-Openings of Compounds 5 and 6



The thermal stability of **6** is much greater than that of the analogous 1,2-dihydrodiazete **5** reported by Warrener. While **6** survived the conditions for its synthesis which required heating at 150 °C for several hours, at 185 °C (as a solution in DMSO-d_6) it decomposed into an uncharacterized mixture of products ($t_{1/2} \approx 2.5$ h). The enhanced thermal stability of **6** relative to **5** is probably not due to the effects of aromatic stabilization since the same stabilizing effects should also be present in the more labile **5**. It is more likely (as was suggested in our previous paper)[8] that the five-membered urazole ring of **6** serves to inhibit a concerted conrotatory ring-opening process (a process that is possible for **5**, see Scheme 1) because of the inherent strain of the ring-opened product, a (1*Z*,3*E*)-cycloheptadienyl heterocyclic ring.

It has been demonstrated previously that **6**, acting as a dienophile, undergoes Diels−Alder cycloadditions with cyclic and acyclic dienes to afford diazetidine products (e.g., 2,3-dimethyl-1,4-butadiene to afford **7**, Scheme 2).[8] Warrener had reported that **5** did not undergo such reactions, but this was apparently due to the low temperatures at which the reactions were attempted.[7b] Compound **6** also readily adds bromine to afford the 1,2-dibromodiazetidine **8** (Scheme 2). This compound is stable and demonstrates no tendency for spontaneous loss of HBr. The reactions of **6** may, therefore, be generally characterized simply as alkene-like. There is no evidence for resistance to reaction that disrupts the 1,2-dihydrodiazete ring system, or a tendency for regeneration of the 1,2-dihydrodiazete ring as would be expected for an aromatic system.

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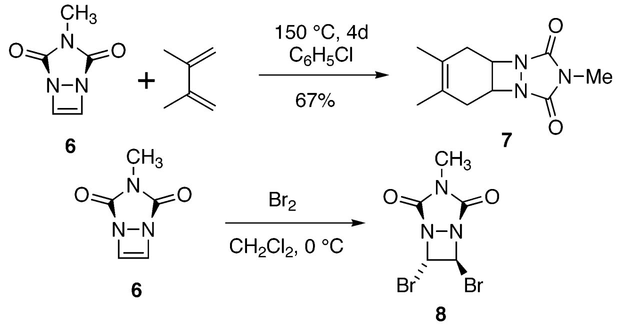
SCHEME 2. Examples of Alkene-like Reactions of Compound 6

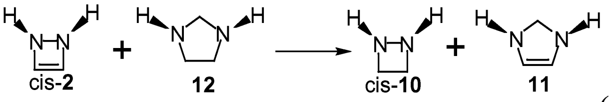


Computational Studies. (a) Computational Studies on 1,2-Dihydrodiazetes and Selected Reference Compounds. The aromaticity of the 1,2-dihydrodiazete system has been studied previously in the literature with various computational methods. Warrener performed semiempirical INDO molecular orbital calculations on the unsubstituted dihydrodiazetes *cis*- and *trans*-**2** (Chart 1).[7b] Budzelaar investigated these same species at a higher level of theory (RHF/3-21G*) along with several additional reference compounds.[11] Finally, Mo and Yanez,[12] and then Bachrach,[13] reinvestigated the series of compounds at yet a higher level of theory (RHF/6-31G*) along with several reference compounds. All of the groups arrived at essentially the same conclusion from their calculations: the 1,2-dihydrodiazete system is nonaromatic because the severe repulsions of the adjacent lone pair electrons are not adequately conterbalanced by stabilization from the π-system.

Our own geometry optimization of **6** at the RHF/6-31G* level led to a structure with an N−N bond length of 1.434 Å that was significantly shorter than that observed from X-ray crystallography (1.470 Å).[14] Reoptimization with DFT calculations at the RB3LYP/6-311+G(2d,p) level, however, resulted in a longer N−N bond (1.462 Å) with a lower overall energy ($\Delta E = 8.8$ kcal/mol) relative to the structure at the RB3LYP/6-311+G(2d,p)//RHF/6-31G* level. Other geometric data were also in better accord with the experimental structure. Similarly we obtained results identical with those of Bachrach when we optimized the geometry of *cis*-**2** at the RHF/6-31G* level.[13] Again, however, optimization at the RB3LYP/6-311+G(2d,p) level resulted in a longer N−N bond (1.482 vs 1.457 Å) with a lower overall energy ($\Delta E = 6.4$ kcal/mol) relative to the RHF/6-31G* geometry. These better descriptions of molecular geometries, and significant differences in energies, prompted us to reoptimize the geometries of several compounds of interest at this higher level of theory. Selected data from these optimizations are displayed in Chart 1.

The calculated N−N bond length of **6** (1.462 Å), which is in reasonable accord with that afforded by the X-ray crystal structure, is equivalent to the calculated N−N bond of the nonaromatic saturated diazetidine **9** (1.460 Å), and much longer than the N═N double bond (1.259 Å) found in 3,4-dihydrodiazete **16**. The calculated C−N single bond (1.451 Å) of **6** is similar to the C−N single bonds found in the nonaromatic compounds **11** (1.430 Å) and azetidine **14** (1.428 Å), but much longer than the C−N bonds of pyrrole (1.372) and the C═N double bond found in 1,4-dihydrodiazete **15** (1.289 Å). The C═C bond of **6** is of typical length and compares well to the calculated values for both of the nonaromatic compounds **11** and **14**. Similar conclusions may be drawn from the optimized structures of *cis*- and *trans*-**2**. The computed geometries reinforce the conclusions drawn from the X-ray crystal structure data that there are conventional single and double bonds in the structure of **6** (and **2**), with no apparent structural evidence for the effects of aromaticity.

Homodesmotic reactions to test for the presence of aromatic stabilization of the 1,2-dihydrodiazete ring system are provided in eqs 1 and 2. More conventional comparisons of the system with open-chain reference compounds have been reported earlier and suggested little or no aromatic stabilization.[11] We chose the series of reference compounds in eqs 1 and 2 to determine if any stabilization of the 1,2-dihydrodiazete ring system was observed above and beyond that expected through resonance interaction of the nitrogen lone pairs with the C═C bond. The equations effectively measure the change in energy upon moving the C═C bond from the potentially aromatic 1,2-dihydrodiazete ring to the nonaromatic **11**. Both the cis- and trans-isomers are investigated since the cis-isomer, although less stable than *trans*-**2** ($\Delta E = 4.2$ kcal/mol), is a more suitable model for compound **6**. In each case, the cis-isomers of **11** and **12** were the more stable stereoisomer. We calculated $\Delta E = -3.4$ kcal/mol for eq 1 and $\Delta E = -3.0$ kcal/mol for eq 2. However, there is a difference in strain energies when the double bond is in the four-membered ring versus the



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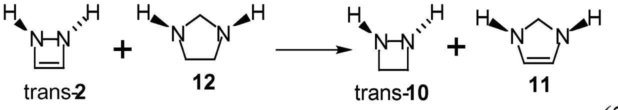

(2)

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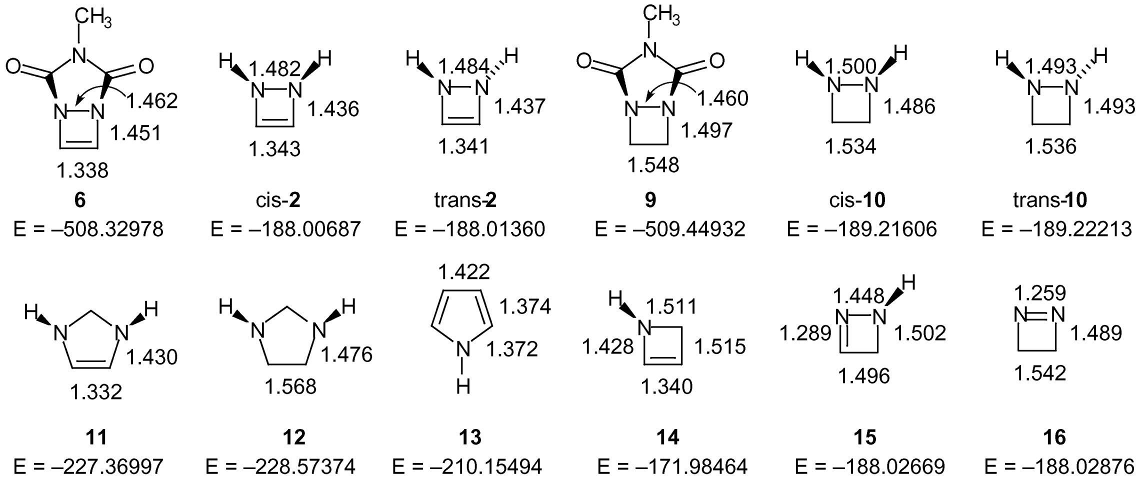
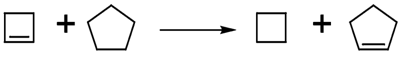
CHART 1. Optimized Geometries[a] of 1,2-Dihydrodiazetes and Reference Compounds at RB3LYP/6-311+G(2d,p)[14]



[a] All distances are in Å and all energies are in au (complete Cartesian coordinates for all computed structures are available as Supporting Information).

five-membered ring (eq 3). By using Benson's group



(3)

strain energies,[15] it can be estimated that this difference in strain (for the reaction as written) is approximately −4.0 kcal/mol. Including this in the above analysis suggests a corrected ΔE for eqs 1 and 2 of +0.6 and 1.0 kcal/mol, respectively. This suggests that there is essentially *no additional stabilization of the 1,2-dihydrodiazete ring system relative to the nonaromatic* ***11***.

There are three double-bond positional isomers for the dihydrodiazete system (Chart 1): 1,2-dihydrodiazete (*trans*-**2**), 1,4-dihydrodiazete (**15**), and 3,4-dihydrodiazete (**16**). The calculated relative energies of the isomers fall in the order **2** (0.0) > **15** (−8.21) > **16** (−9.51 kcal/mol). Thus the "potentially" aromatic **2** is less stable than either of the other possible nonaromatic isomers! This ordering parallels what is predicted for the relative energies based on simple standard bond energy calculations for each of the isomers, further suggesting that there are no special stabilizing (or destabilizing) forces present in any one particular isomer.

Two pertinent stationary points at higher energy relative to **2** were located and analyzed (Figure 2). The first structure, **SP1**, corresponds to a structure with a single planar nitrogen atom in the ring and serves as a transition state (a single imaginary frequency) for interconversion of *cis*-**2** to *trans*-**2**. This transition state lies 10.4 kcal/mol higher in energy than *trans*-**2** in reasonable agreement with the same prediction by Mo and Yanez (12.9 kcal/mol at MP2/6-31G*//RHF/6-31G*).[12]

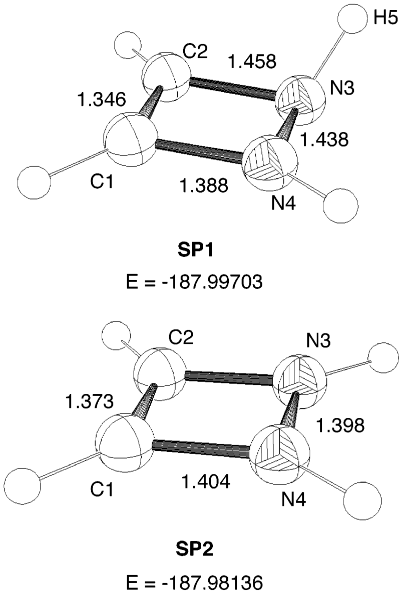


FIGURE 2. Stationary points **SP1** and **SP2** calculated at the RB3LYP/6-311+G(2d,p) level. Selected geometrical data for **SP1**: N(3)−C(2)−C(1), 91.3°; C(2)−C(1)−N(4), 91.8°; C(1)−N(4)−N(3), 90.9°; C(2)−N(3)−N(4), 85.8°; N(3)−C(2)−C(1)−N(4), 2.7°; H(5)−N(3)−C(2)−(C1), −112.8°. Selected geometrical data for **SP2**: N(3)−C(2)−C(1), 90.5°; C(1)−N(4)−N(3), 89.5°; N(4)−C(1)−C(2)−N(3), 0.0°.

The second structure, **SP2**, corresponds to a fully planar structure, and could be obtained computationally either through a search for the transition state corresponding to double nitrogen inversion to convert *cis*-**2** to its mirror image or via geometry minimization of a structure constrained to be planar. In each case, the structure that was afforded displayed two imaginary frequencies. One of these vibrational modes led to *trans*-**2** and the other to *cis*-**2**. We were unable to locate a planar species characterized by a single imaginary frequency. The energy of **SP2** is 20.2 kcal/mol higher in energy than *trans*-**2** and 9.8 kcal/mol higher in energy than **SP1**. Although the predicted bond lengths for **SP2** (Figure 2) are more consistent with what would be expected for a structure experiencing delocalization of the π-electrons

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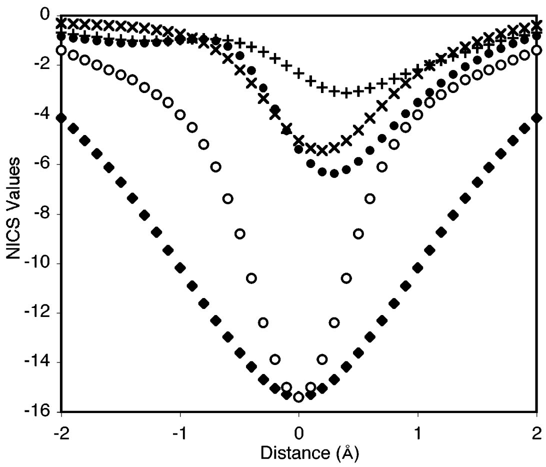

FIGURE 3. Computed NICS values for *cis*-**2** (●), **13** (♦), **PS2** (○), **11** (×), and **14** (+).

(i.e., contracted N−N and C−N bonds, and a somewhat extended C=C bond), its high energy relative to **2** and **SP1** precludes suggestions of aromaticity in the ring (also see the NICS and NBO analysis of **SP2** below).

(b) Nucleus-Independent Chemical Shift (NICS) Calculations. Nucleus-independent chemical shift (NICS) calculations provide a probe for the magnetic properties of aromatic compounds.[1,16] The magnetic shielding at the center of a ring system is determined by calculating the chemical shift of "ghost" atoms. By convention, the NICS value is defined as the negative of the computed isotropic shielding value. Large negative values indicate aromaticity, large positive values antiaromaticity, and near-zero values nonaromatic rings. For small rings especially, local contributions from σ bonds can seriously affect the magnitude of the NICS values in the plane of the ring.[17] It is, therefore, good practice to observe the effect of NICS values at regular intervals along a line running through the center of the ring and perpendicular to the plane defined by the ring atoms.[17,18] Figure 3 shows such a plot of NICS values calculated for several compounds with the GIAO method and with a RHF/6-311+G** basis set. For unsymmetrical rings, positive distance values are taken as being on the side syn to the nitrogen atom lone pairs. It is obvious that the NICS values for all of the 1,2-dihydrodiazetes and reference compounds are significantly less negative than that of the aromatic reference compound pyrrole. Indeed, on the sides of the ring syn to the lone pair electrons, all of the NICS values ultimately coalesce to a narrow range at about 1.0 Å above the rings (where local bond effects should be minimal)[17] *whether the compound could be aromatic* (i.e., *cis*-**2**) *or not* (i.e., **11** and **14**). Interestingly, the planar species **SP2** displays an NICS value in the plane of the ring equivalent to that of pyrrole (−15). However, these values drop off precipitously such that at 1.0 Å above the ring the NICS value (−4.0) is comparable to that of *cis*-**2** (−3.5) and considerably less negative than that of pyrrole (−10.2). The large value in the plane of the ring must therefore be attributed to local effects. This magnetic criterion of aromaticity, therefore, suggests that there is no significant aromatic character to the 1,2-dihydrodiazete ring systems.

(c) Natural Bond Orbital Analyses. Finally, we conducted Natural Bond Orbital (NBO) analyses on several of the 1,2-dihydrodiazetes and reference compounds.[14c] NBO analysis provides a means of investigating the extent of electron delocalization within a given structure.[19] Electron delocalization is indicated by depletion of electron density in traditional "Lewis-type" bonding orbitals with simultaneous occupancy of antibonding, or "non-Lewis" orbitals. The higher the percentage occupancy of "non-Lewis" orbitals, the greater the extent of delocalization.[19] In addition, NBO analysis provides a means for determining the bond order for each of the bonds within a given structure. Pyrrole exhibited 2.42% occupancy of "non-Lewis" orbitals relative to the 2.94% of fully delocalized benzene. In addition, the C=C bonds of pyrrole had a decreased bond order of 1.56, while increased bond orders for the C−N bonds (1.19) and the C−C bond (1.32) were observed reflecting the "bond equalizing" effects of electron delocalization within the π-system. In contrast, *cis*- and *trans*-**2** exhibited considerably less occupancy of the "non-Lewis" orbitals (1.22% and 1.17%, respectively) and the bond orders were more consistent with localized bonds: N−N, 1.01; N−C, 1.06; and C=C, 1.76. Furthermore, these values were very similar to the values for the nonaromatic **11** which had occupancy of "non-Lewis" orbitals of 1.15% and bond orders of 1.04 for N−C and 1.82 for C=C. The planar **SP2** species exhibited slightly higher occupancy of non-Lewis orbitals (1.81%) relative to its nonplanar counterparts but still considerably less than that of pyrrole.

Conclusions

A cyclic π-electron system is typically considered aromatic if it exhibits specific properties common of all aromatic species:[1b] (i) delocalization of the π-electrons, (ii) enhanced stability of the system relative to suitable conjugated unsaturated analogues, (iii) bond lengths intermediate between single and double bonds, (iv) exhibition of a diatropic π-ring current in the presence of an external magnetic field, and (v) expression of a tendency in its reactions toward retaining its π-electron structure. While these properties are not always equally expressed in all aromatic compounds, compounds should be characterized as truly aromatic only upon meeting all of the criteria.[1b]

Detailed assessment according to the each of these criteria revealed that 1,2-dihydrodiazetes are simply strained, nonaromatic heterocycles that do not benefit from aromatic stabilization. NBO analysis suggested no π-electron delocalization in **2** beyond typical lone-pair/C=C double bond resonance. Appropriate homodesmotic reactions indicated no enhanced stability of **2** relative to the nonaromatic reference compound **11**. Furthermore, the greater stability of **6** in relation to Warrener's 1,2-dihydrodiazete **5** was attributed to kinetic stabilization

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(16) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.

(17) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465−2468.

(18) See, for example: Delamere, C.; Jakins, C.; Lewars, E. *Can. J. Chem.* **2001**, *79*, 1492−1504.

(19) (a) Bean, G. P. *J. Org. Chem.* **1998**, *63*, 2497−2506. (b) Sadlej-Sosnowska, N. *J. Org. Chem.* **2001**, *66*, 8737−8743.

relative to a conrotatory ring-opening process rather than special π-stabilization. The X-ray crystal structure, computed minimized geometries, and NBO bond orders all suggested traditional localized bonds within the rings of **6** and/or **2**. The search for a diatropic π ring-current utilizing NICS calculations did not indicate aromaticity. Finally, compound **6** underwent reactions typical of alkenes (i.e., bromination, Diels−Alder reactions), and compound **8** expressed no tendency to regain the π-structure of **6** via spontaneous dehydrobromination.

The usefulness of **6** as an intermediate for the synthesis of other strained heterocycles has already been reported.[8] We intend to further demonstrate its usefulness in this way in future publications.

Experimental Section

Computational Methods. Computations were carried out with the Gaussian 98W suite of programs.[14] All structures and accompanying energies were computed at the RB3LYP/6-311+G(2d,p) level unless otherwise specified. All points were characterized by the calculation of the vibrational frequencies at the same computational level. All energies reported include the zero-point corrections (scaled by a factor of 0.9614). NBO analyses were carried out from within Gaussian. NICS calculations were carried out as described previously utilizing the GIAO method and RHF/6-311+G** basis set.[16−18]

3-Methyl-1,3,5-triazabicyclo[3.2.0]hept-6-ene-2,4-dione (6).[8] Compound **6** was synthesized as described earlier.[8] Recrystallization of **6** was executed via slow cooling of an initially saturated boiling solution in hexane. Initially fine needles crystallized, but upon prolonged standing in solution at 10 °C, the crystals obtained a suitable diameter. The crystals were isolated via filtration and then analyzed via X-ray diffraction.

6,7-Dibromo-3-methyl-1,3,5-triazabicyclo[3.2.0]heptane-2,4-dione (**8**). To a stirring solution of **6** (23 mg, 0.16 mmol) in 2 mL of CH_2Cl_2 at 0 °C was added a solution of Br_2 (48 mg, 0.3 mmol, 1.8 equiv) in 0.5 mL of CH_2Cl_2, dropwise. The resulting orange solution was stirred for 1 h and then warmed to room temperature. The solution was diluted with 20 mL of CH_2Cl_2, washed with 5 mL of 5% $NaHSO_3$, dried over Na_2SO_4, filtered, and concentrated to afford 39.8 mg (81% yield) of **8**: mp 113.5−114.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.20 (s, 2H), 3.15 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 158.9, 67.0, 26.8.

X-ray Single-Crystal Structure Determination of Compound 6 at 150(2) K. Crystal Data: $C_5H_5N_3O_2$, $M_r = 139.12$, monoclinic, space group $P2_1/m$, $a = 3.7770(1)$ Å, $b = 9.4807(2)$ Å, $c = 8.2024(2)$ Å, $\beta = 98.348(1)°$, $V = 290.60(2)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.590$ Mg/m^3, $F_{000} = 144$, wavelength (λ) = 0.71073 Å, absorption coefficient (μ) = 0.127 mm^{-1}. **Data Collection and Reduction**: crystal size = 0.50 × 0.35 × 0.25 mm^3; θ range = 2.51−53.11°; index ranges = $-7 \leq h \leq 8$, $-21 \leq k \leq 21$, $-18 \leq l \leq 18$; reflections collected = 14 927; independent reflections = 3501 [$R_{\mathrm{int}} = 0.0270$]; refinement method = full-matrix least-squares on F^2; data/restraints/parameters = 3490/0/61; final R index is $R1 = 0.0318$ [$I > 4\sigma(I)$]; R indices (all data) are $R1 = 0.0607$, $wR2 = 0.0848$, GOF on $F^2 = 0.686$; largest difference peak = 0.54 eÅ^{-3}; deepest difference hole = −0.24 eÅ^{-3}. **Measurement, Computing, and Graphics**: SMART 1K CCD (Bruker, 2000); cell refinement, SMART; data reduction, SAINT-Plus (Bruker, 2000); program(s) used to solve structure, *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure, SHELX97 (Sheldrick, 1997); molecular graphics, SHELXTL97 (Sheldrick, 1997); software used to prepare material for publication, SHELXTL97.[20]

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Supporting Information Available: Crystallographic information file (CIF) for **6**; Cartesian coordinates, total energies, and computed zero point corrections for all of the calculated structures; and ^{13}C NMR spectrum of **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] (a) *SMART* (Version 5.060) and *SMART-Plus* (Version 6.02); Bruker AXS, Inc: Madison, WI, 2000. (b) Sheldrick, G. M. *SHELXTL DOS/Windows/NT*, Version 5.1; Bruker AXS, Inc: Madison, WI, 1997. (c) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.