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Aromaticity of Four-Membered-Ring 6π-Electron Systems: N_2S_2 and $Li_2C_4H_4$

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Abstract: N_2S_2 is a four-membered-ring system with 6π electrons. While earlier proposals considered N_2S_2 to be aromatic, recent electronic structure calculations claimed that N_2S_2 is a singlet diradical. Our careful reexamination does not support this assertion. N_2S_2 is closed shell and *aromatic* since it satisfies all three generally accepted criteria for aromaticity: energetic (stability), structural (planarity with equal bond lengths), and magnetic (negative nucleus-independent chemical shift due to the π electrons). These characteristics as well as the electronic structure of N_2S_2 are compared with those for an isoelectronic π system, $Li_2C_4H_4$, motivated by theoretical and recent experimental investigations that confirmed its aromaticity. However, N_2S_2 and $Li_2C_4H_4$ are both essentially 2π-electron aromatic systems with a formal N$-$S (C$-$C) bond order of 1.25 even though they both have 6π electrons. This is because four of the six π electrons occupy the nonbonding π HOMOs and only two electrons participate effectively in the aromatic stabilization. However, wave function analysis shows relatively large LUMO occupation numbers; this antibonding effect can be said to reduce the aromatic character by approximately 7% and 4% for N_2S_2 and $Li_2C_4H_4$, respectively.

Introduction

The special stability of benzene is explained satisfactorily in terms of aromaticity, which has been one of the most important concepts in chemistry for nearly two centuries.[1,2] Despite its widespread use, aromaticity is a virtual quantity; definitions either are qualitative or depend on quantitative evaluations that are not unique. Measures of "aromaticity" are based on many different criteria. The most widely accepted categories are energetic, structural, and magnetic.[2] For example, the aromatic stabilization energy (ASE) can be determined both experimentally and theoretically, but depends on the choice of reference standards.[3] Conventional aromatic molecules generally have planar ring skeletons and have equal or equalized bond lengths in contrast to the marked alternation of bond lengths in singlet

antiaromatic molecules.[2d] Characteristic magnetic properties of aromaticity include the exaltation of magnetic susceptibility, abnormal proton NMR chemical shifts, and nucleus-independent chemical shifts (NICS).[2b,c] NICS is based on the negative of the computed absolute shielding at ring centers or, better, 1 Å above.[4] Negative NICS values of significant magnitude suggest aromaticity, and positive values, antiaromaticity. The dissection of the total NICS values into separate contributions from individual localized molecular orbitals (1997; now called LMO-NICS) has been expanded recently by canonical molecular orbital decomposition methods (CMO-NICS), which identify the diatropic orbitals that actually are responsible for the aromaticity.[4b,c]

The Hückel $4n+2$ rule affords the simplest test, but aromaticity is a much more complex phenomenon than is suggested by a simple electron count.[5] "Electron-rich" systems that have too many potential π electrons, but still follow the $4n+2$ rule are a case in point. The $(NH)_3$ ring has six and the $(NH)_5$ ring 10 potential π electrons, but both are strongly nonplanar and nonaromatic. Planar six-membered rings with 10 π electrons also are not expected to be aromatic, since the "extra" four electrons would have to occupy antibonding orbitals. On the other hand, both the cyclooctatetraene dication (6 π e$^-$) and the cyclooctatetraene dianion (10 π e$^-$) are known to have planar

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(1) (a) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994. (b) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986. (c) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132−136. (d) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. v. P. *J. Org. Chem.* **2002**, *67*, 1333−1338.
(2) (a) Schleyer, P. v. R. *Chem. Rev.* **2001**, *101*, 1115−1118. (b) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301−1316. (c) Gomes, J. A. N. F.; Mallion, R. B. *Chem. Rev.* **2001**, *101*, 1349−1384. (d) Krygowski, T. M.; Cyranski, M. K. *Chem. Rev.* **2001**, *101*, 1385−1420. (e) Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317−1331. (f) Krygowski, T. M.; Cyranski, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783−1796. (g) Katritzky, A. R.; Karelson, M.; Sild, S.; Krygowski, T. M.; Jug, K. *J. Org. Chem.* **1998**, *63*, 5228−5231. (h) Krygowski, T. M.; Cyrañski, M. K.; Czarnocki, Z.; Häfelinger, G. Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783−1796.
(3) (a) Schaad, L. J.; Hess, B. A., Jr. *Chem. Rev.* **2001**, *101*, 1465−1476. (b) Slayden, S. W.; Liebman, J. F. *Chem. Rev.* **2001**, *101*, 1541−1566.
(4) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318. (b) 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. (c) Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Seifert, G.; Reviakine, R.; Weber, J. *J. Phys. Chem. A* **2003**, *107*, 6470−6475. (d) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.
(5) (a) Hückel, E. *Z. Phys.* **1931**, *70*, 204. (b) Streitweiser, A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.

Chart 1

D_{4h}	C_s	C_2
1	**2a**	**2b**

Li$_2$C$_4$H$_4$ Li$_2$C$_4$(SiMe$_3$)$_4$

3a   **3b**
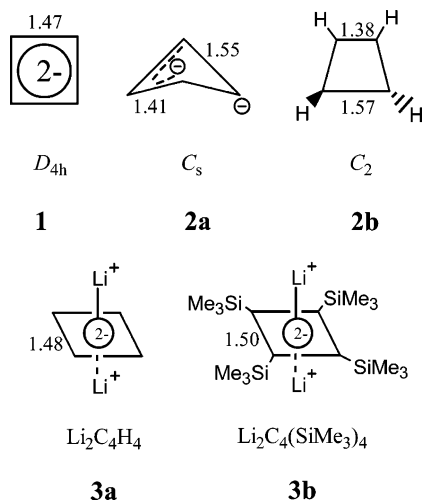
D_{8h} symmetry and are aromatic. In this system, the third π-orbital level is nonbonding. The present paper concerns the analogous situation in four-membered rings.

The cyclobutadiene dianion (C$_4$H$_4^{2-}$) has six π electrons and follows the $4n+2$ rule. But is it aromatic? Planar C$_4$H$_4^{2-}$ with D_{4h} symmetry (**1** in Chart 1) is a higher order saddle point on the potential energy surface (four imaginary frequencies). The lowest energy structure depends on the theoretical level, but has C_{2h} symmetry (**2**) (with all four carbons in a plane and only modestly bent hydrogens) at B3LYP/6-311+G(d,p).[6f,i] While aromatic stabilization of the π electrons in C$_4$H$_4^{2-}$ is outweighed by electrostatic repulsion arising from the double negative charge and the 1,3-interactions,[6,7] neither the neutral 6π-electron 1,2-dihydrodiazete (C$_2$H$_4$N$_2$)[6h] (see below) nor the highly aromatic 2π-electron cyclobutadiene dication (C$_4$H$_4^{2+}$) is planar.[6j,k] Furthermore, as first noted by Kos and Schleyer in 1980,[6e] the charge-balanced (C$_4$H$_4^{2-}$)2Li$^+$ complex has D_{4h} symmetry and a planar four-membered ring (see below). Planarity evidently is an imperfect indicator of aromaticity in these systems.

Stimulated by the indecisive early theoretical results on C$_4$H$_4^{2-}$, homo- and 1,3-heteronuclear four-membered-ring systems with 6π electrons were studied by several groups to determine if they are aromatic; the latest paper concludes that 1,2-dihydrodiazete is nonaromatic.[6i] Budzelaar et al.[6h] considered C$_2$H$_2$N$_2$H$_2$ and C$_2$H$_2$O$_2$, which are iso-π-electronic with C$_4$H$_4^{2-}$, and found both to be nonaromatic due to the strong 1,3-antibonding interactions and the differing electronegativities of C and N and of C and O. This investigation was extended by

(6) (a) Garratt, P. J.; Zahler, R. *J. Am. Chem. Soc.* **1978**, *100*, 7753−7754. (b) Hess, B. A.; Ewig, C. S.; Schaad, L. J. *J. Org. Chem.* **1985**, *50*, 5869−5871. (c) Skancke, A.; Agranat, I. *Nouv. J. Chim.* **1985**, *9*, 577. (d) Zandwijk, G. v.; Janssen, R. A. J.; Buck, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 4155−4164. (e) Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7928−7929. (f) Balci, M.; Mckee, M. L.; Schleyer., P. v. R. *J. Phys. Chem. A* **2000**, *104*, 1246−1255. (g) Sommerfeld, T. *J. Am. Chem. Soc.* **2002**, *124*, 1119−1124. (h) Budzelaar, P. H.; Cremer, D.; Wallasch, M.; Würthwein, E.-U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 6290−6299. (i) Breton, G. W.; Martin, K. L. *J. Org. Chem.* **2002**, *67*, 6699−6704. (j) Krogh-Jespersen, K.; Schleyer, P. v. R.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301−4302. (k) Bremer, M.; Schleyer, P. v. R. L. S. *J. Am. Chem. Soc.* **1989**, *111*, 1148−1150. (l) Riss, U. V.; Meyer, H. D. *J. Phys. B* **1993**, *26*, 4503. (m) Sommerfeld, T. *J. Phys. Chem. A* **2000**, *104*, 8806. (n) Sommerfeld, T.; Tarantelli, T.; Meyer, H. D.; Cederbaum, L. S. *J. Chem. Phys.* **2000**, *112*, 6635.

(7) (a) Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *21*, 132. (b) Boche. G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *21*, 133. (c) Boche, G.; Etzrodt, H.; Massa, W.; Baum, G. *Angew. Chem, Int. Ed. Engl.* **1985**, *24*, 863.

Zandwijk et al.[6d] to cyclic C$_2$H$_2$N$_2^{2-}$, N$_4^{2-}$, N$_2$H$_2$N$_2$, N$_4$H$_4^{2+}$, N$_2$H$_2$O$_2^{2+}$, N$_2$S$_2$, etc. Only, for example, N$_4^{2-}$, N$_4$H$_4^{2+}$, and N$_2$S$_2$ exhibited 6π aromaticity; the other species did not have planar minima and, hence, were considered to be nonaromatic. The role of hydrogen substituents and the related 1,3-π-repulsions as well as the strength of ring bonds were identified as factors determining the stability of planar relative to nonplanar structures.

Notably, the aromaticity of C$_4$H$_4^{2-}$ in a triple ion complex was demonstrated experimentally recently by the realization and X-ray structure determination of a stable dilithium salt of the tetrakis(trimethylsilyl)cyclobutadiene dianion (**3b**).[8] Its planar, substituted cyclobutadiene dianion moiety with equal CC bond lengths confirms the earlier theoretical predictions that Li$^+$ capping would stabilize the D_{4h} geometry (**3a**) of C$_4$H$_4^{2-}$.[6d−f] In Li$_2$C$_4$H$_4$, the two Li$^+$ countercations compensate for the dianionic electron repulsion, which leads to out-of-plane distortion of the hydrogens in C$_4$H$_4^{2-}$ itself and thus allows the aromatic potential to be fully expressed. Indeed, Sekigucki et al.[8] observed strong aromatic ring current ^{6}Li NMR shielding, which, like NICS, is an excellent aromaticity indicator. This work (along with the earlier, indecisive computational results)[6a−d] prompts the present theoretical reexamination, employing the latest methods, of the aromaticity of C$_4$H$_4^{2-}$.

C$_4$H$_4^{2-}$ (**1**), however, is unstable due to the Coulomb repulsion with respect to electron loss and therefore is a resonance state with an extremely short lifetime of 0.7 fs.[6g] Standard finite basis bound state methods must be modified to describe such resonance states correctly.[6l−n] To avoid this difficulty and to enable the use of modern electronic structure methods, neutral Li$_2$C$_4$H$_4$ (**3a**) was chosen here to unravel the aromaticity of C$_4$H$_4^{2-}$. This decision is consistent with the earlier theoretical[6d−f] and the recent experimental results.[8] We find Li$_2$C$_4$H$_4$ to be highly correlated and to have an essentially 2π-aromatic system even though it has 6π electrons.

Chart 2

4	**5**	**6**	**7**
8	**9**	**10**	**11**
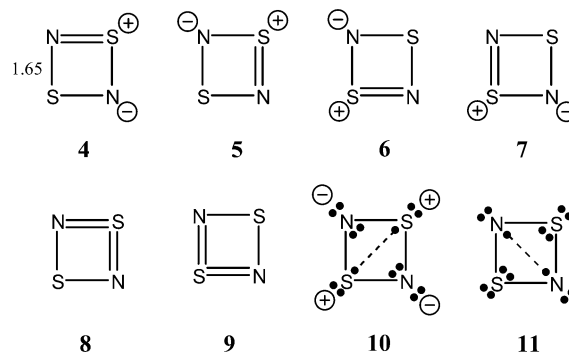
N$_2$S$_2$ (**4−11** in Chart 2) posseses a 6π-electron, four-membered ring, π-isoelectronic with C$_4$H$_4^{2-}$. Unlike the dianion, N$_2$S$_2$ is stable as an isolated entity. Two valence electrons of each nitrogen form σ bonds with two adjacent sulfur atoms, two electrons constitute a lone pair, and the remaining electron contributes to the π system. Sulfur is similar, except that it contributes two valence electrons to the total of six for the π system. The X-ray N$_2$S$_2$ structure was almost exactly square

(8) (a) Sekiguchi, A.; Matsuo, T.; Watanabe, H. *J. Am. Chem. Soc.* **2000**, *122*, 5652−5653. (b) Ishii, K. Kobayashi, N.; Matsuo, T.; Tanaka, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2001**, *123*, 5356−5357. (c) Sekiguchi, A.; Matsuo, T.; Tanaka, M. *Organometallics* **2002**, *21*, 1072−1076.

with 1.651 and 1.657 Å N–S bond lengths and 90.4° (S–N–S) and 89.6° (N–S–N) bond angles.[9] The nearest 3.58 Å S–S and 3.77 Å N–N intermolecular distances in the crystal perpendicular to the plane of the monomer are comparable to or larger than their respective van der Waals separations. In contrast, the 2.89 Å S–N intermolecular distance in the molecular plane is smaller than the corresponding 3.35 Å van der Waals separation,[10f] suggesting significant intermolecular interaction. Consequently, N_2S_2 undergoes thermal polymerization in the solid state to form the $(NS)_x$ polymer, which, remarkably, is a superconductor at very low temperatures.[9,10f]

Although the geometry and chemistry of N_2S_2 are relatively well established, there is no consensus on the best description of its electronic structure; several proposals are summarized in Chart 2. The literature includes discussions of its Hückel rule-based aromaticity,[10] resonance between **8** and **9** based on localized molecular orbital (MO) calculations, etc.[9c,11] Although resonance between zwitterionic Lewis structures (**4**–**7**) also has been considered based on an MO description,[10e] STO-6G valence bond calculations found the weight of this resonance to be smaller than the contribution from **8**. Consequently, N_2S_2 was proposed to be a singlet diradical.[12a] In agreement, the most recent calculations using the spin-coupled valence bond (SCVB) and the CISD methods also claimed singlet diradical character either of the sulfur (**10**) or of the nitrogen (**11**) atoms in N_2S_2.[12b,c]

Typically, singlet diradicals have two anti-ferromagnetically coupled unpaired electrons, each of which occupy two degenerate or nearly degenerate MOs. Because of this near degeneracy, singlet diradicals have LUMO occupation numbers close to 1, whereas closed shell molecules have near zero LUMO occupation numbers.[13] For example, dissociated singlet H_2 (a pure singlet diradical) has bonding and antibonding occupation numbers of 1 each, compared to about 1.98 and 0.02 for H_2 at equilibrium (with the 6-311++G(d,p) basis set). Note that none of the papers[12] suggesting diradical character for N_2S_2 provided molecular orbital (or natural orbital) occupation numbers. These, when properly interpreted, are one of the most direct indicators of diradical character.

Singlet–triplet energy gaps are another measure of diradical character since these usually are small for diradicals.[13] For example, H_2 at its equilibrium has huge singlet–triplet ($\sim$12.0 eV) and large HOMO–LUMO gaps. However, the singlet–triplet gap decreases as the H–H bond stretches and, like the HOMO–LUMO (or bonding–antibonding) gap, becomes zero (or exactly degenerate) at its dissociation limit.

It is necessary to investigate these factors to properly ascertain if N_2S_2 is a diradical, just as it is essential to evaluate various criteria to establish if it is aromatic. We demonstrate here that N_2S_2 has very little diradical character, but satisfies all three generally accepted criteria (structural, energetic, and magnetic criteria) for aromaticity. This conclusion that N_2S_2 and $C_4H_4^{2-}$ have similar π structures in four-membered rings is particularly illuminating. These species have been compared repeatedly in the literature,[14] but generally have been described as having different electronic structures.

This paper is organized as follows. The computational methods are described in the Theoretical Methods section below. The Results section describes the search for evidence of diradical character in N_2S_2 and then examines the three criteria for aromaticity. Structural and magnetic criteria for aromaticity for $Li_2C_4H_4$ also are compared. The Analysis section discusses the electronic structure of N_2S_2 and $Li_2C_4H_4$ in detail using an MO diagram and the orbital occupation numbers.

Theoretical Methods

Geometries were optimized using density functional theory (DFT).[15] The spin-unrestricted Kohn–Sham (KS) formalism was employed with the B3LYP[16] exchange–correlation functional and the 6-31G(d) basis.[17] This level of theory is denoted as UB3LYP/6-31G(d). The nature of the optimized structures was examined by diagonalizing the force constant matrix. Geometries were refined using the valence space optimized doubles (VOD) method with the same basis to take into account the possible diradicaloid character of the systems.[18] VOD is a relatively inexpensive coupled-cluster-based approximation to complete active space self-consistent-field (CASSCF) theory that typically allows all valence electrons to be treated as active. Both for N_2S_2 and $Li_2C_4H_4$, 22 electrons in 22 orbitals were used as the active space (designated as VOD(22,22)/6-31G(d)).

Singlet–triplet energy splittings were calculated using a recently developed spin-flip time-dependent DFT method with the Tamm–Dancoff approximation (SF-TDDFT/TDA) using the 6-31G(d) basis.[19] In the spin-flip (SF) model, closed and open shell singlet states as well as an $M_s = 0$ triplet state are described by excitations from an $M_s = 1$ triplet reference state. In the SF-TDDFT/TDA method, dynamical correlation is recovered through time-dependent density functional theory (TDDFT) in the Tamm–Dancoff approximation (TDA),[19a] and nondynamical correlation is recovered by the spin-flip excitation part (SF). Full details as well as application to several diradical systems can be found in refs 19. Following ref 19b, we used SF-TDDFT/TDA

(9) (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984. (b) MacDiarmid, A. G.; Mikulski, C. M.; Russo, P. J.; Saran, M. S.; Garito, A. F.; Heeger, A. J. *J. Chem. Soc. Chem. Commun.* **1975**, 478. (c) Mikulski, C. M.; Russo, P. J.; Saran, M. S. MacDiarmid, A. G.; Garito, A. F.; Heeger, A. F. *J. Am. Chem. Soc.* **1975**, 97, 6358–6363. (d) A marginal inequality in the X-ray bond lengths (1.651 and 1.657 Å) is probably due to some crystal field environment (and is not from its internal electronic structure) like benzene in crystal.

(10) (a) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 444–452. (b) Karpfen, A.; Schuster, P.; Petkov, J.; Lischka, H. *J. Chem. Phys.* **1978**, 68, 3884. (c) Jolly, W. L. *Sulfur Research Trends*; Advances in Chemistry Series No. 110; American Chemical Society: Washington, DC, 1972. (d) Adkins, R. R.; Turner, A. G. *J. Am. Chem. Soc.* **1978**, 100, 1383–1387. (e) Patton R. L.; Raymond, K. N. *Inorg. Chem.* **1969**, 8, 2426–2431. (f) Cohen, M. C.; Garito, A. F.; Heeger, A. J.; MacDiarmid, A. G.; Mikulski, C. M.; Saran, M. S.; Kleppinger, J. *J. Am. Chem. Soc.* **1976**, 98, 3844–3848. (g) Herler, S.; Mayer, P.; Noth, H.; Schulz, A.; Suter, X.; Vogt, M. *Angew. Chem., Int. Ed.* **2001**, 40, 3173–3175. (h) Kessenich, E.; Polborn, K.; Schulz, A. *Inorg. Chem.* **2001**, 40, 1102–1109.

(11) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Edgell, R. G.; Evans, R. *Inorg. Chem.* **1980**, 19, 1307–1314.

(12) (a) Skrezenek, F. L.; Harcourt, R. D. *J. Am. Chem. Soc.* **1984**, 106, 3934–3936. (b) Gerratt, J.; McNicholas, S. J.; Karadakov, P. B.; Sironi, M.; Raimondi, M.; Cooper, D. L. *J. Am. Chem. Soc.* **1996**, 118, 6472–6476. (c) Harcourt, R. D.; Klapotke, T. M.; Schulz, A.; Wolynec, P. *J. Phys. Chem. A* **1998**, 102, 1850–1853.

(13) (a) Flynn, C.; Michl, J. *J. Am. Chem. Soc.* **1974**, 96, 3280–3288. (b) Dohnert, D.; Koutecky, J. *J. Am. Chem. Soc.* **1980**, 102, 1789–1796. (c) Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, 26, 170–189. (d) Seierstad, M.; Kinsinger, C. R.; Cramer, C. J. *Angew. Chem., Int. Ed.* **2002**, 41, 3894–3896 (e) Jung, Y.; Head-Gordon, M. *ChemPhysChem* **2003**, 4, 522–525. (f) Head-Gordon, M. *Chem. Phys. Lett.* **2003**, 372, 508–511.

(14) (a) Chivers, T. *Acc. Chem. Res.* **1984**, 17, 166–171. (b) Chivers, T. *Chem. Rev.* **1985**, 85, 345–365. Also the references therein.

(15) Parr, R. G.; Yang, W. *Density Functional Theory*; Oxford University Press, 1989.

(16) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.

(17) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, 56, 2257–2261. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, 77, 3654–3665.

(18) (a) Krylov, A. I.; Sherrill, C. D. *J. Chem. Phys.* **2002**, 116, 3194–3203. (b) Shao, Y.; Krylov, A.; Head-Gordon, M. *J. Chem. Phys.* **2003**, 118, 4807. (c) Hirata, S.; Head-Gordon, M. *Chem. Phys. Lett.* **1999**, 302, 375–382.

(19) (a) Fetter, A. L.; Walecka, J. D. *Quantum Theory of Many-Particle Systems*; McGraw-Hill: New York, 1971. (b) Krylov, A. I.; Sherrill, C. D.; Byrd, E. F. C.; Head-Grodon, M. *J. Chem. Phys.* **1998**, 109, 10669–10678.

with a 50/50 functional (50% Hartree−Fock + 8% Slater + 42% Becke for exchange functional, and 19% VWN + 81% LYP for correlation functional). As shown in ref 19b, this gives the best singlet−triplet splittings compared to experiment. Electronic energies reported here are not corrected for zero-point energies.

We analyzed the VOD correlation amplitudes and orbital occupation numbers[18] to understand the effect of electron correlation on the electronic structures of N_2S_2 and $Li_2C_4H_4$, For comparison, we also performed complete active space self-consistent-field (CASSCF)[20] calculations including six π electrons in four π orbitals, denoted by CASSCF(6,4)/6-31G(d). As a magnetic measure of aromaticity, NICS values[4] were computed using the gauge-including atomic orbitals method (GIAO)[4d] at the PW91/IGLO-III//VOD(22,22)/6-31G(d) level. Dissected CMO-NICS analysis separated the π canonical MO contributions to the magnetic shielding from all other contributions.[4c] A pure density functional (i.e., no exact exchange) permits the NICS contributions from individual orbitals to be assigned unambiguously.[4c]

All calculations were carried out with the Q-CHEM electronic structure program,[21] except for the CASSCF calculations, which employed GAMESS,[22] and NICS, which used GAUSSIAN 98,[23a] and MAG-Respect.[23b]

Results

Structure of N_2S_2. The geometry of N_2S_2 was optimized with D_{2h} symmetry at the UB3LYP/6-31G(d) level of theory. The N−S bond length was 1.666 Å and the N−S−N angle 90.2° (∠S−N−S is 89.8°). An X-ray structure is similar.[9] *No spin symmetry broken unrestricted solution* was found. Stability analysis confirmed that the spin-restricted SCF solution is indeed a minimum in orbital space.[24] This implies that the molecule does not have much diradical character, since singlet diradicals usually possess spin-unrestricted solutions with significant "spin contamination".[25] A vibrational frequency calculation confirmed that square planar N_2S_2 is a true minimum, showing the stability of the compound. An X-ray structure of N_2S_2 (as well as our optimized geometry) already manifests the structural criterion for aromaticity: it is planar and all four N−S bond lengths are equal (1.654 Å; between those of a single N−S (1.74 Å) and a double N=S (1.54 Å) bond).[9d,10h] The VOD(22,22)/6-31G(d)-optimized N−S bond length was 1.669 Å, very close to the X-ray value.

Structure of $Li_2C_4H_4$. Following Kos and Schleyer,[6e] computed $Li_2C_4H_4$ (**3a**) structures have been reported several times.[6d−f] We have confirmed these results and have computed the structure of Sekiguchi's experimentally characterized Li_2C_4-$(SiMe_3)_4$ (**3b**)[8] for comparison.

The B3LYP/6-31G(d)-optimized C−C bond lengths for D_{4h} $Li_2C_4H_4$ (**3a**) were 1.475 and 1.495 Å (an average of 1.500, 1.498, 1.495, 1.498 Å) for the lower symmetry $Li_2C_4(SiMe_3)_4$ (**3b**). The experimental value for the latter, 1.495 Å (an average of 1.496, 1.507, 1.485, and 1.493 Å), is identical.[8] The bulky silyl groups evidently expand the **3b** ring relative to **3a**.

$Li_2C_4H_4$ and $Li_2C_4(SiMe_3)_4$ exhibit the structural signature of aromatic molecules. Both species are planar, and their essentially equal C−C bond lengths (1.48−1.50 Å) are between typical CC single (1.54 Å) and double (1.34 Å) bonds. Note that their lengths are closer to a C−C single bond.

Singlet−Triplet Gap for N_2S_2. The B3LYP/6-31G(d)-computed HOMO−LUMO gap for N_2S_2, 5.2 eV, is much larger than the ∼2−3 eV gaps of diradicaloid species of comparable size.[13b] Relatively large HOMO−LUMO gaps indicate stable closed shell rather than diradicaloid character. The singlet was 3.6 eV more stable than the triplet, computed vertically on the singlet geometry at the SF-TDDFT/TDA/6-31G(d) level. This is somewhat larger than the SCVB ST gap (2.0 eV),[12b] but is close to the 3.4 eV based on configuration interaction (CI) calculations.[26] The 3.6 eV singlet−triplet gap in N_2S_2 is not much smaller than that of benzene at the same level (4.4 eV). In contrast, diradicals usually have much smaller singlet−triplet gaps (usually less than 1 eV). This provides further evidence that N_2S_2 is a relatively stable closed shell molecule.

To summarize, the lack of a spin-unrestricted DFT solution and the moderately large HOMO−LUMO and singlet−triplet gaps all suggest that N_2S_2 does *not* have significant diradical character. The LUMO occupation number of N_2S_2 as a measure of diradical character confirms this conclusion and will be presented in the analysis section below.

Aromatic Stabilization Energies (ASE). ASE is defined as the extra stabilization energy exceeding that exhibited by reference molecules, which are conjugated, but lack cyclic electron delocalization. Advances have been made in ASE evaluation methods recently.[27] Strain energy corrections are particularly important for the four-membered-ring compounds considered here. Hence, acyclic reference molecules are unsuitable.

Thus, a surprisingly large 29.2 kcal/mol ASE for $Li_2C_4H_4$ can be evaluated at the B3LYP/6-311+G(d,p)//B3LYP/6-311+G-(d,p)+ZPE level by means of the homodesmotic and strain-corrected eq 1 (involving the global minima of each compound):
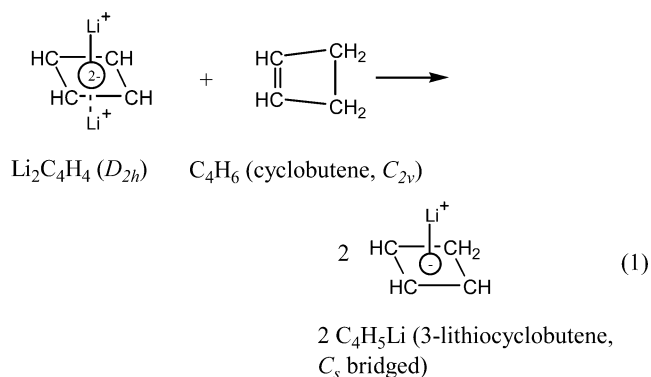
(20) Schmidt, M.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233−266.
(21) Kong, J.; White, C. A.; Krylov, A. I.; Sherrill, D.; Adamson, R. D.; Furlani, T. R.; Lee, M. S.; Lee, A. M.; Gwaltney, S. R.; Adams, T. R.; Ochsenfeld, C.; Gilbert, A. T. B.; Kedziora, G. S.; Rassolov, V. A.; Maurice, D. R.; Nair, N.; Shao, Y. H.; Besley, N. A.; Maslen, P. E.; Dombroski, J. P.; Daschel, H.; Zhang, W. M.; Korambath, P.; Baker, J.; Byrd, E. F. C.; Van Voorhis, T.; Oumi, M.; Hirata, S.; Hsu, C. P.; Ishikawa, N.; Florian, J.; Warshel, A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *J. Comput. Chem.* **2000**, *21*, 1532−1548.
(22) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.
(23) (a) 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.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; 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 98*; Gaussian Inc.: Pittsburgh, PA, 1998. (b) Malkin, V. G.; Malkina, O.; Reviakine, R.; Schimmelpfennig, B.; Arbrouznikon, A.; Kaupp, M. *MAG-ReSpect 1.0*; 2001.
(24) Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1977**, *66*, 3045−3050.
(25) Hrovat, D. A.; Duncan, J. A.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *112*, 169−175.

$Li_2C_4H_4$ (D_{2h}) C_4H_6 (cyclobutene, C_{2v})

$2\ C_4H_5Li$ (3-lithiocyclobutene, C_s bridged)

Table 1. Comparison of N_2S_2, $Li_2C_4H_4$, and Benzene Using the NICS Values, N−S (or C−C) Bond Lengths, Formal Bond Orders, and Aromatic Stabilization Energies (ASE)

|	N_2S_2	$Li_2C_4H_4$	benzene
π NICS (ppm)	−26.2	−30.5	−25.4[b]
N−S (or C−C) bond length (Å)	1.669	1.491	1.397[b]
formal bond order	1.25	1.25	1.5
ASE (kcal/mol)	6.5[d] (−0.7)[e]	29.2	33[c]

[a] Geometries optimized at the VOD(22,22)/6-31G(d) level are used in comparison. The π NICS values are calculated at the GIAO-PW91/IGLO-III level using the above geometries (see also Table 2). Data for benzene are from ref 4c and ref 27. [b] Ref 4c. [c] Ref 27. [d] Using eq 3. [e] Using eq 2.

This charge-balanced equation employs four-membered-ring compounds to equalize angle strain reasonably well and compares two conjugated, allyl-type cyclobutenyl anion systems with the cyclically delocalized cyclobutadienyl dianion ion. The resulting ASE is comparable to the best estimates for the benzene value (33 kcal/mol).[27]

The ASE evaluation of N_2S_2 is not as straightforward since suitable four-membered-ring reference compounds comprised only of nitrogen and sulfur atoms are not possible. Acyclic −SNSN− systems do not afford satisfactory comparisons. However, one can employ reference rings for this purpose, where CH_2 groups replace S or N atoms, as in isodesmic eq 2. Surprisingly, this is nearly thermoneutral at B3LYP/6-311+G-(d,p). In fact, it is endothermic by 0.7 kcal/mol. In eq 2, all species are minima in the point groups given.

$$N_2S_2 \;+\; 1/2 \qquad\qquad (2)$$

$$D_{2h} \qquad\qquad D_{2d}$$
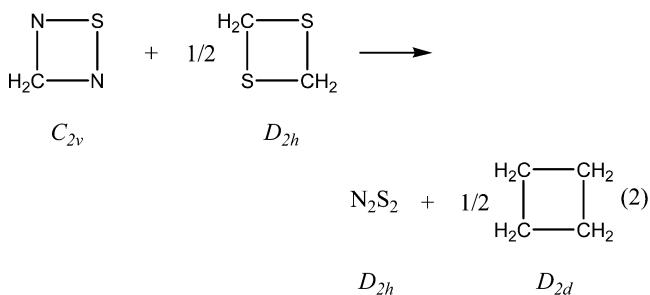
We also examined an alterative ASE evaluation. Noting that resonance structures **4**−**7** describe N_2S_2, one of these was used to calculate an ASE for N_2S_2 based on the following eq 3:

$$(3)$$
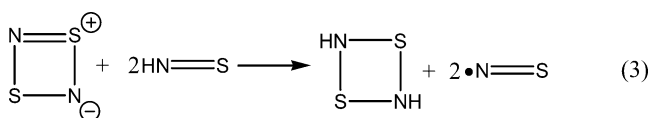
While this reaction is neither homodesmotic nor isodesmic, it should provide at least a rough estimate of the N_2S_2 ASE, since the two delocalized electrons in N_2S_2 are localized in the two NH bonds in $H_2N_2S_2$, and thus it gives the net stabilization effect due to the delocalization in N_2S_2. Additionally, ring strain effects are roughly the same in reactants and products. Every species was fully optimized at the B3LYP/6-311+G(d,p) level. Reaction 3 yielded an ASE of only 6.5 kcal/mol, also suggesting that N_2S_2 is weakly aromatic. By contrast, benzene has an ASE of ca. 33 cal/mol (Table 1).[27] It is also conceivable to combine the two radical species (2NS) in the product side and use SN−

(26) Jafri, J. A.; Newton, M. D.; Pakkanen, T. A.; Whitten, J. A. *J. Chem. Phys.* **1977**, *66*, 5167−5172.
(27) Schleyer, P. v. R.; Puhlhofer, F. *Org. Lett.* **2002**, *4*, 2873−2876.

Table 2. Dissected Canonical Orbital-Based NICS Analyses (CMO-NICS) at the GIAO-PW91/IGLO-III//VOD(22,22)/6-31G(d) Level (in ppm)

	N_2S_2	$Li_2C_4H_4$
NICS (total)	+5.6	−19.6
$1b_{2g}$ ($1e_{2g}$)[a]	−2.0	−3.9
$1b_{3g}$ ($1e_{2g}$)[a]	−0.8	−3.9
$1b_{1u}$ ($1a_{2u}$)[a]	−23.4	−22.7
all others	+31.8	+10.9

[a] Orbital symmetries in parentheses are for $Li_2C_4H_4$.

NS instead of 2NS for calculating an ASE. This yielded an ASE of 3.3 kcal/mol, about half of the 6.5 kcal/mol (eq 3).

When acyclic N−S reference molecules, such as HN=S−N−S−NH$_2$ or HN=S−N−SH, instead of $H_2N_2S_2$ are used, the reaction energies actually are negative, most likely due to the relief of ring strain. This reflects the known spontaneous opening of N_2S_2 at high enough temperatures with the formation of the metallic polymer, $(NS)_x$.

NICS. Both N_2S_2 and $Li_2C_4H_4$ satisfy the NICS magnetic criterion for aromaticity. However, the behavior of N_2S_2 is not straightforward, and detailed CMO analysis of the individual contributions of the individual orbitals to the total NICS is required before this conclusion can be reached. Table 2 tabulates the NICS results obtained at the GIAO-PW91/IGLO-III//VOD-(22,22)/6-31G(d) level[4] (this spin-restricted level of theory is stable to unrestricting the orbitals).

The total NICS(0) shows a marked contrast between N_2S_2 and $Li_2C_4H_4$: the +5.6 value for N_2S_2 is positive (suggesting antiaromaticity), but the −19.6 for $Li_2C_4H_4$ is large and negative (confirming its aromaticity). In contrast, the individual π-orbital contributions to the total NICS(0) values are very similar for N_2S_2 and $Li_2C_4H_4$. The lowest occupied π orbital shows a strong diatropic (negative) NICS contribution (−23.4 ppm for N_2S_2 and −22.7 ppm for $Li_2C_4H_4$), while the contributions of the two higher π orbitals are only very modest (−2.0 ppm, −0.8 ppm for N_2S_2 and −3.9 ppm (degenerate) for $Li_2C_4H_4$). For comparison, the individual CMO-NICS values for benzene behave similarly, although the difference between the lowest π orbital and the degenerate pair of π orbitals is smaller (a factor of 3).[4c] The qualitative difference in total NICS values of N_2S_2 and $Li_2C_4H_4$ arises almost entirely from the very different σ contributions (Table 2), which are not relevant for aromaticity.

In conclusion, the π-orbital systems of both N_2S_2 and $Li_2C_4H_4$ are strongly diatropic (aromatic). The large negative total π NICS values for these two molecules, comparable to benzene (see Table 1), are due in part to the smaller ring size.[4c]

Analysis of Electronic Structure

We have shown above that N_2S_2 does not have significant diradical character. However, it is aromatic since the three generally accepted criteria for aromaticity (structural, energetic, and magnetic) are satisfied. Similar conclusions have been reached for $Li_2C_4H_4$ already, in agreement with our computations. We now discuss the electronic structure of N_2S_2 and $Li_2C_4H_4$ in more detail.

Applying Hückel theory, the six π electrons in four π orbitals in N_2S_2 (as in $Li_2C_4H_4$) give the MO diagram shown in Figure 1. The $1b_{1u}$, $1b_{3g}$, $1b_{2g}$, and $2b_{1u}$ MOs have 0, 1, 1, and 2 nodal planes perpendicular to the ring plane, respectively. The computed MOs (Figure 2) are similar to the illustrations in
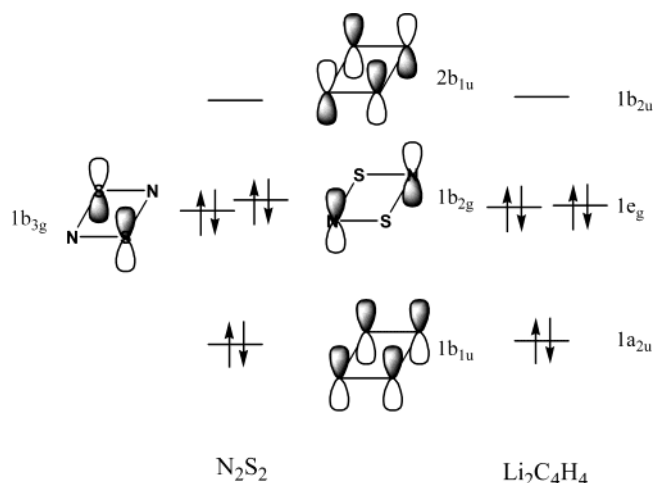
Figure 1. Molecular orbital (MO) diagrams for six π electrons in N_2S_2 and $Li_2C_4H_4$ using Hückel MO theory. Two π electrons occupying $1b_{1u}$ for N_2S_2 and $1a_{2u}$ for $Li_2C_4H_4$ are delocalized over the entire ring structure, and the other four electrons are essentially nonbonding electrons.

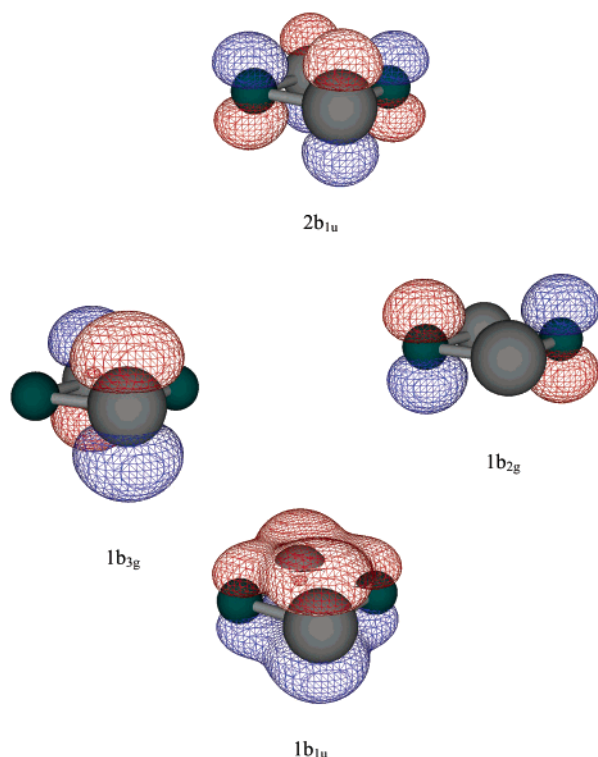**Figure 2.** Calculated π-symmetry molecular orbitals occupied by six π electrons in N_2S_2. A bigger ball indicates sulfur, and a smaller ball nitrogen. $Li_2C_4H_4$ has essentially similar orbitals, except that the two nonbonding orbitals are denegerate by symmetry.

Figure 1. The nodal plane between the two S atoms in the $1b_{3g}$ MO precludes a bonding interaction between these atoms, as

Gerratt et al. have pointed out.[12b] However, our results in the previous section contradict their overall conclusion that N_2S_2 is a singlet diradical.

The $1b_{3g}$ and $1b_{2g}$ nodal planes result in nonbonding MOs.[10e] Hence, the four π electrons occupying these orbitals, each with one nodal plane, are nonbonding. Note that these nonbonding electrons remain paired and do not exhibit diradical character.

The other two π electrons in N_2S_2 occupy the lowest energy $1b_{1u}$ bonding orbital (see Figure 1). The delocalization of these two π electrons ($1b_{1u}$) results in the aromatic characteristics, i.e., planarity, stability, and the negative CMO-NICS $1b_{1u}$ value. Despite the presence of six π electrons in the electron structure, only two of these electrons participate in bonding (the other four π electrons are nonbonding). Hence, N_2S_2 *should be regarded as a 2π-electron aromatic system*,[10e,f] and the formal N−S bond order in N_2S_2 is 1.25 (rather than 1.75, based on a 6π-electron system averaged over four bonds). In agreement, the Wiberg bond index is 1.212 (B3LYP/6-311+G(d)) and the estimated bond order is 1.3 based on a bond length−bond order correlation.[10e] While the formal charges are N(+) and S(−), as depicted by the resonance contributors **4**−**7** in Chart 1, these do agree with the greater electronegativity of nitrogen (3.0) than sulfur (2.8). The natural charges are 0.856, positive for S and negative for N. The Mulliken charges are smaller (0.444), but have the same signs (S+, N−).

Similarly, the isoelectronic $Li_2C_4H_4$ also has a 2π-electron (rather than a 6π) aromatic system. The higher symmetry (D_{4h}) of $Li_2C_4H_4$, compared to D_{2h} for N_2S_2, results in the different orbital symmetry designations for the π orbitals shown in Figure 1. In particular, the two nonbonding π orbitals of $Li_2C_4H_4$ are degenerate. Note that the average C−C X-ray bond length for **3b** (also computed for **3a**), 1.495 Å, approaches the typical C−C single bond length (1.53 Å) and is much longer than the 1.40 Å distance in benzene. The formal CC bond orders of 1.25 for $Li_2C_4H_4$ (based on 2π electrons) vs 1.5 for benzene are consistent with these bond length differences (Table 1). The CC Wiberg bond index for $Li_2C_4H_4$ is 1.234.

What is the nature of the strong electron correlations in N_2S_2 and $Li_2C_4H_4$? Analysis of their valence space optimized doubles (VOD) wave functions gave the occupation numbers for the relevant π-symmetry orbitals summarized in Table 3. The LUMO occupation number for N_2S_2, $n(2b_{1u}) = 0.12$ e$^-$, is relatively large compared to normal closed shell molecules ($\sim$0.03 e$^-$).[13] Similarly, the $Li_2C_4H_4$ $n(1b_{2u})$ occupation number is 0.06 e$^-$, which also is somewhat larger than usual.

For comparison, a comparable VOD(30,30)/6-31G(d) computation on benzene yields occupation numbers of 0.08, 0.08, and 0.04 e$^-$ for the three antibonding π orbitals with 2, 2, and 3 perpendicular nodal planes, respectively. The total of 0.20 electron in the benzene antibonding π orbitals does *not* translate

Table 3. Occupation Numbers of Relevant π Orbitals for N_2S_2 and $Li_2C_4H_4$

	N_2S_2		$Li_2C_4H_4^a$	
	VOD (22,22)[b]	CASSCF (6,4)[c]	VOD (22,22)	CASSCF (6,4)
$2b_{1u}$ ($1b_{2u}$)[a]	0.12	0.20	0.06	0.06
$1b_{2g}$ ($1e_{2g}$)	1.92	1.81	1.96	0.97
$1b_{3g}$ ($1e_{2g}$)	1.95	1.99	1.96	0.97
$1b_{1u}$ ($1a_{2u}$)	$\sim$1.97	2.00	$\sim$1.98	2.00

[a] Orbital labels in parentheses are for $Li_2C_4H_4$. [b] Full valence space optimized doubles (VOD) calculation using 22 valence electrons in 22 active orbitals. [c] Complete active space SCF (CASSCF) calculation using six π electrons in four active π orbitals, namely, $1b_{1u}$, $1b_{3g}$, $1b_{2g}$, and $2b_{1u}$.

directly into 20% diradical character since six electrons correlate in six orbitals, rather than two electrons in two orbitals as in diradicals. Likewise, the LUMO occupation numbers of 0.12 and 0.06 e$^-$ for N_2S_2 and $Li_2C_4H_4$ also indicate quite strong nonbonding to antibonding correlations, but these are not directly associated with 12% and 6% diradical character, respectively.

There would be true two-electron aromatic character in N_2S_2 when $n(1b_{1u}) = 2$ e$^-$ and $n(2b_{1u}) = 0$. In contrast, there would be no aromaticity at all if $n(1b_{1u}) = n(2b_{1u})$, since the former is fully bonding and the latter is antibonding between each pair of atoms. Therefore, our computed $n(1b_{1u}) = 1.97$ e$^-$ and $n(2b_{1u}) = 0.12$ e$^-$ values suggest that N_2S_2 has approximately 93% two-electron aromatic character. Similarly, the two-electron aromatic character of $Li_2C_4H_4$ is approximately 96%, since the occupations are 1.98 e$^-$ for the delocalized and 0.06 e$^-$ for the antibonding orbitals.

CASSCF computations, which included six π electrons in the four π orbitals depicted in Figure 1 as the active space, yielded similar results but overemphasized electron correlation slightly compared to VOD. (Note the $2b_{1u}$ and $1b_{2u}$ orbital occupation numbers for N_2S_2 and $Li_2C_4H_4$, respectively, in Table 3.) This is due primarily to the smaller active space employed in CASSCF compared to VOD. As a result, we infer that N_2S_2 and $Li_2C_4H_4$ have approximately 90% and 97% two-electron aromatic character, respectively, at the CASSCF(6,4) level.

Conclusions

We have reexamined the claimed diradical character of N_2S_2 carefully.[12] The lack of a spin-unrestricted DFT solution as well as moderately large HOMO−LUMO and singlet−triplet gaps all suggest that the diradical character of N_2S_2 is not significant. Instead, N_2S_2 is aromatic based on its structure (a planar four-membered ring with equal N−S bond lengths, which are intermediate between a single and a double bond), and its negative π CMO-NICS value (−26.2 ppm) is dominated by the lowest π orbital. However, the aromatic stabilization energy is small at best (our largest ASE estimate is 6.5 kcal/mol). While the aromaticity of N_2S_2 is consistent with the Hückel $4n+2$ rule since it has six π electrons, the higher, degenerate set of π orbitals (which are qualitatively similar to those deduced from Hückel MO theory) do not contribute significantly to the bonding. This suggests that N_2S_2 is essentially a 2π-electron aromatic system with N−S bond order near the formal value of 1.25.

The isoelectronic π system, $Li_2C_4H_4$, a derivative of which was just confirmed experimentally to be aromatic, also is a 2π-electron aromatic system with a C−C bond order near 1.25 despite its total of 6π electrons. The π CMO-NICS value is quite similar to that computed for N_2S_2, the CC bond lengths are equal, and our ASE estimate is quite large, 29.2 kcal/mol.

Analysis of correlated wave functions shows that N_2S_2 and $Li_2C_4H_4$ do exhibit quite strong correlations involving excitations from the nonbonding π to the antibonding π orbitals. The aromaticity of N_2S_2 and $Li_2C_4H_4$ is reduced slightly as a consequence, to approximately 93% and 96% two-electron aromatic character, respectively, at the VOD(22,22)/6-31G(d) level. However, the overall occupation of the antibonding π level is lower in both molecules than the total occupation of the three antibonding π levels in benzene.

Supporting Information Available: Optimized geometries and energies for all molecular species considered in this paper (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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