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Geometry and Aromaticity in Highly Strained Heterocyclic Allenes: Characterization of a 2,3-Didehydro-2*H*-thiopyran

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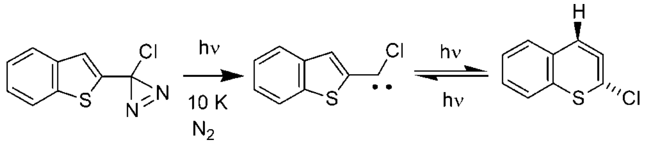
ABSTRACT



The highly strained cyclic allene 2,3-didehydro-*2H*-thiopyran was generated by irradiation of matrix-isolated 2-benzothienylchlorocarbene and characterized by IR and UV/vis spectroscopy, in situ trapping, and DFT modeling. Calculations indicate that the allenic moiety in this system, although less aromatic in character, is relatively more stable than in the corresponding oxa system. It is suggested that the thio ring system can more readily accommodate the allenic geometry.

Constraining a cumulene into a small ring can have a dramatic effect on its electronic structure as well as its stability. Depending on the ring size, forced bending at the central atom and rotation at the termini can lead to increasing amounts of diradical and/or zwitterionic character in these strained systems.[1] We have described previously the spectroscopic characterization of the highly strained heterocyclic cumulenes **1**[2] and **2**,[3] generated in low-temperature matrixes (Figure 1). Besides their theoretical attractions, these hetereoatomic analogues of the elusive cyclohexa-1,2,4-triene (i.e., “isobenzene”)[1a] have direct relevance to a variety of recently discovered synthetic routes to complex heterocycles[4] and polycyclic aromatic hydrocarbons.[5]

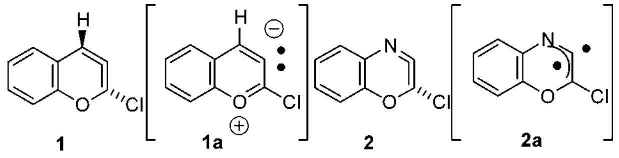


Figure 1. Heterocyclic cumulenes.[2,3]

Although spectroscopy and calculations suggested that the structure of **1** is dominated by the allenic bonding shown in Figure 1,[2] **2** gave indications of significant diradical character (e.g., **2a**).[3] Nevertheless, it remains an open question how much “aromatic” zwitterionic character (e.g., **1a**) contributes to the stabilization of these species. We now report results on the sulfur analogue of **1** which provide some insight regarding this question.

We have shown that allene **1** and ketenimine **2** can be generated by low-temperature irradiations of the corresponding 2-benzofurylchlorocarbene[2] and 2-benzoxazolylchlorocarbenes,[3] respectively. The analogous precursor for the benzothiophene system, diazirine **3**, was synthesized via

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[1] (a) Engels, B.; Schöneboom, J. C.; Münster, A. F.; Groetsch, S.; Christl, M. *J. Am. Chem. Soc.* **2002**, *124*, 287. (b) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

[2] Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **2000**, *122*, 8585.

[3] Nikitina, A.; Sheridan, R. S. *J. Am. Chem. Soc.* **2002**, *124*, 7670.

[4] (a) Wills, M. S. B.; Danheiser, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 9378. (b) Frey, L. F.; Tillyer, R. D.; Ouellet, S. G.; Reamer, R. A.; Grabowski, E. J. J.; Reider, P. J. *J. Am. Chem. Soc.* **2000**, *122*, 1215. (c) Kimball, D. B.; Weakley, T. J. R.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 13463. (d) Shirtcliff, L. D.; Weakley, T. J. R.; Haley, M. M.; Köhler, F.; Herges, R. *J. Org. Chem.* **2004**, *69*, 6979. (e) Cardenas, C.; Chamorro, E.; Notario, R. *J. Phys. Chem. A* **2005**, *109*, 4352.

[5] Berger, H.; Hopf, H.; Dix, I.; Jones, P. G. *Eur. J. Org. Chem.* **2004**, 3401 and references therein.

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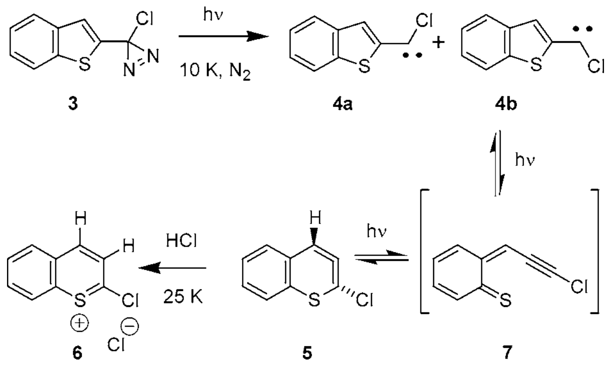
conventional Graham oxidation of the corresponding amidine.[6,7] Photolysis of **3** in N$_2$ matrixes at 10 K produced three major products which could be distinguished in the IR spectrum, whose relative amounts depended on wavelength and duration of irradiation (Scheme 1).[8] Calculations, comparisons to previous investigations on related systems, and subsequent chemistry indicate that the three products are the *anti*-**4a** and *syn*-**4b** chlorocarbenes and allene **5**. For example, irradiating diazirine **3** at 334 nm very slowly produced mainly a mixture of **4a** and **4b**. Comparison to B3LYP/6-31G** calculations suggests that a modest excess of **4a** (stereochemistry assigned tentatively), with a strong band at 1156 cm^{-1}, was formed compared to **4b**, with a similar characteristic 1130 cm^{-1} absorption.[9] UV/vis absorptions at 355 and 415 nm appeared concurrently with **4**. Continued irradiation at this wavelength caused IR absorptions assignable to **5** to appear, dominated by a strong 907 cm^{-1} band, along with UV/vis absorptions at 310 and 424 nm (Figure S1 in the Supporting Information). Alternatively, photolysis at 366 nm completely destroyed diazirine **3** in a few hours, producing mainly allene **5**, with lesser amounts of **4a**,**b** in the IR spectrum.

Scheme 1. Low-Temperature Transformations



Allene **5** and carbene **4** could be interconverted photochemically. Hence, for example, irradiation of a matrix containing **5** at 302 nm slowly converted the allene to **4** (Figure 2); conversion was nearly complete in the IR spectrum after ca. 50 h. Conversely, 366 nm rapidly converted carbene **4** to **5**. Although the corresponding didehydropyran **1** was observed to rearrange to a benzocyclobutadiene on prolonged irradiation,[2] we detected no other products after repeated interconversions of **4** and **5**, irrespective of wavelength or duration of irradiation.

We have shown that ring-opened quinomethide species intercede in the interconversions of the benzofurylchloro- and benzoxazoylchlorocarbenes with **1** and **2**, respectively.[2,3] In the present case, however, we have only scant direct evidence for the intermediacy of the thioquinomethide **7** in the interconversion of **4** and **5**. In limited experiments, a band at 2157 cm^{-1} appeared transiently in the IR spectra during irradiations of matrix isolated diazirine **3**. We have found strong absorptions in this region to be characteristic of chloroacetylenes such as **7**. Although direct 1,2-shifts cannot be ruled out, analogy to **1** and **2** would nevertheless suggest that a particularly photolabile ring-opened **7** is likewise an intermediate in the transformations between **4** and **5**. Irradiation at, e.g., 366 nm, where carbene **4** absorbs more strongly, favors formation of **5** in the photoequilibrium. Conversely, at shorter wavelengths around 300 nm, **5** absorbs more strongly than **4**, and the system is driven toward carbene.

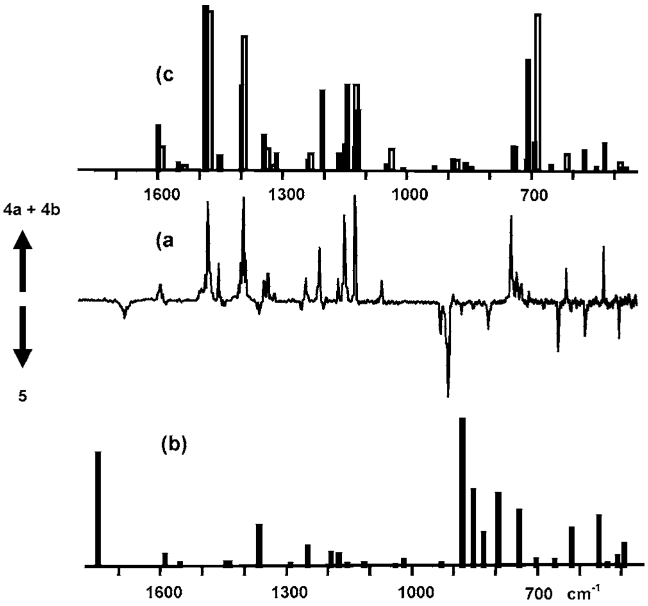


Figure 2. (a) IR difference spectra (arbitrary absorbance units) showing bleaching of allene **5** ("down bands") on 3 h irradiation at 302 nm (carbenes **4a**,**b** "up bands"). (b) B3LYP/6-31G**-calculated IR spectrum for allene **5**. (c) B3LYP/6-31G**-calculated IR spectra for carbenes **4a** (open bars) and **4b** (filled bars). All calculated frequencies are scaled by a factor of 0.97.

The observation of two conformational isomers of carbene **4**, with different spectral and photochemical characteristics, parallels other heteroarylcarbenes reported from our group.[2,3,10,11] TD-B3LYP/6-31+G** (time-dependent DFT) calculations predict absorptions (and corresponding transition moments) at 802 (0.001), 424 (0.04), and 332 (0.43) nm for **4a** and 746 (0.001), 413 (0.03), and 327 (0.42) nm for **4b**. Although only a very broad and weak long-wavelength absorption centered around 700 nm could just be discerned in the baseline accompanying the presence of carbene **4** in the IR spectrum, prominent bands at 415 and 355 nm were clearly assignable to the carbene. As the calculations would suggest, however, the two conformers of carbene could not be distinguished in the UV/vis spectra. Interestingly, short-

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(6) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(7) Synthetic and other experimental details are described in the Supporting Information.

(8) For a general description of the matrix isolation instrumentation, see: Zuev, P. S.; Sheridan, R. S. *J. Am. Chem. Soc.* **2004**, *126*, 12220 and references therein.

(9) Details of the calculations, and theoretically predicted spectra, are given in the Supporting Information.

(10) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233.

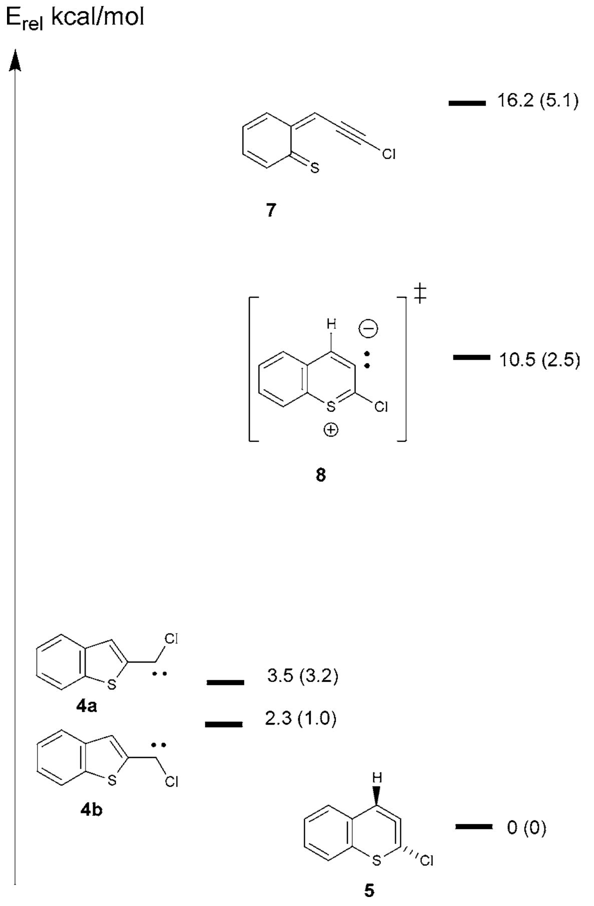
(11) Khasanova, T.; Sheridan, R. S. *Org. Lett.* **1999**, *1*, 1091.

term irradiations of allene **5** initially appeared to favor formation of the isomer we have tentatively assigned as *syn*-**4b**, consistent with a stereoelectronically controlled anti-addition ring-closure of **7**.[10] After several hours of irradiation, however, the carbene isomers appear to undergo photo-equilibration.

One of the striking observations we made previously was that **1** could be protonated at cryogenic temperatures to give a stable benzopyrilium/Cl^- ion pair.[2] Similarly, warming a 2% HCl-doped N_2 matrix containing **5** to 25−31 K caused the allene IR bands to disappear, and those of thiopyrylium salt **6** to grow concurrently. B3LYP calculations gave an excellent fit to the experimental IR spectrum of **6** (Figure S2 in the Supporting Information). There were no indications in the IR spectrum for collapse of the ion pair to a neutral trapping product.

It is instructive to compare the sulfur containing allene **5** to the corresponding didehydropyran **1**. Scheme 2 shows calculated relative energies for intermediates **4a**,**b**, **5**, and **6**, as well as the planar transition state, **8**, for enantiomerization of allene **5**. Corresponding energies for the oxo systems, relative to didehydropyran **1**, are given in parentheses. The apparent stabilization of the thio allene relative to ring opening (**7**) and planarization (**8**) is particularly striking, in comparison to the oxo intermediates.

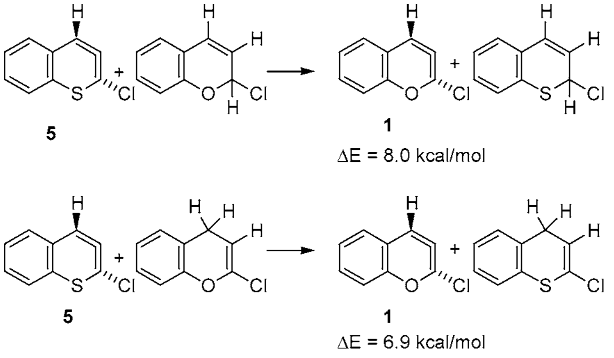
Scheme 2. Relative B3LYP/6-31G** Energies in kcal/mol (Uncorrected)[a]



[a] Values for oxo derivatives are shown in parentheses.[2]

For a more direct comparison of the relative stabilities of the allenic structures in **1** and **5**, we examined the isodesmic reactions shown in Scheme 3, with energies calculated at the B3LYP/6-31G** level. The calculational results clearly support the notion that the cumulene moiety is more stable in the thio than in the oxo ring system. At least two factors contributing to this difference might be envisioned. Aromatic stabilization from some contribution of a zwitterionic structure analogous to **8** might be greater in **5** than in **1**. Alternatively, or perhaps additionally, the longer C−S bonds and smaller C−S−C angle in **5** might accommodate a more allene-like structure with less strain.

Scheme 3. Isodesmic Reactions To Compare **5** and **1**



To compare aromatic character, we carried out calculations of nucleus-independent chemical shifts (NICS) on **1** and **5**, as well as related systems **6**, **8**, and their oxo analogues. Schleyer and co-workers[12] have shown that NICS values offer a convenient qualitative measure of relative aromaticity. The "NICS(1)" values were computed at the GIAO/HF/6-31+G* (gauge-independent atomic orbital method) level at points 1 Å above and below the geometric centers of the heteroatomic rings. As expected, the aromatic characters of planar systems **6** and **8** are reflected in moderately negative NICS(1) values of −8.8 and −8.4 ppm, respectively. Similarly, the planar analogue of **1** and protonated **1** have values of −7.9 and −7.2 ppm. Corresponding values of −6.6 and −5.7 ppm were calculated 1 Å from the geometric center of the didehydropyran ring of **1**, syn and anti to Cl, suggesting still significant aromaticity in that ring despite deviation from planarity. However, analogous values of −5.0 and −4.9 ppm for thio allene **5** indicate significantly less aromatic character compared to **6** and **8**.

On the other hand, calculations indicate that **5** is somewhat more deformed from planarity than is **1**, with a more "allenic" geometry. For example, as shown in Scheme 4, **5** is predicted to have a C=C=C angle of 133° compared to 118° for **1**. Moreover, in **5** the S, Cl, H, and aryl-C ligands

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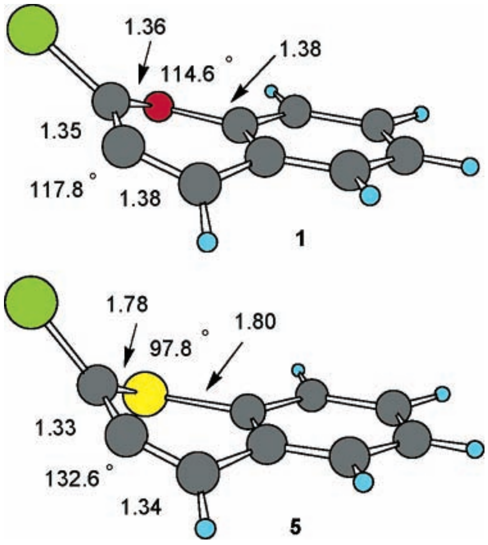
(12) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Freeman, P. K. *J. Org. Chem.* **2005**, *70*, 1998 and references therein.

Scheme 4. DFT Geometries[a]



[a] Bond lengths are reported in angstroms.

attached to the allene termini are deformed 22, 34, 24, and 16° from the plane defined by the three allenic carbons. The oxoallene **1** is closer to planarity, with analogous dihedral angles of 18, 20, 19, and 11°, respectively. Differences in the spectra of **5** and **1** reflect these geometric distinctions. Hence, the asymmetric C═C═C stretch in **5** appears at 1686 cm^{-1} (calcd 1748 cm^{-1} by B3LYP, scaled by 0.97) compared to 1600 cm^{-1} for **1** (calcd 1642 cm^{-1}), consistent with somewhat greater double bond character in the thioallene. Both **1** and **5** exhibit moderate intensity absorptions in the visible, arising from electron promotion from the approximately in-plane HOMO, significantly localized on the central allenic carbon, to a more delocalized π* LUMO. The greater allenic character in **5** leads to a widening of the HOMO−LUMO gap, with a concomitant blue-shift in this transition, with λmax 425 nm (421 nm by TD-B3LYP), compared to 545 nm (calcd 499 nm) in **1**.

In summary, we have investigated the allenic-didehydrothiopyran **5** by IR and UV/Vis spectroscopy, chemical trapping, and theory. The experimental spectra and calculations indicate that **5** is more allenic in character than the oxygen analogue **1**, with greater deviation from planarity. Although these deformations apparently lead to less aromatic character in **5**, simple isodesmic calculations suggest nevertheless that the sulfur allene is more stable compared to its hydrogenated analogues than is **1**. It is interesting to note that McKee, Shevlin, and Zottola[13] have reported indirect chemical and theoretical evidence for the parent thiacyclohexa-2,3,5-triene as an intermediate in reactions of atomic carbon with thiophene. Pathways similar to **4**−**5**−**7**, interrelating the twisted allene with thienylcarbene and the corresponding ring-opened isomer, were suggested.[14−17]

Acknowledgment. We thank the National Science Foundation (CHE-0072894 and CHE-0456280) and the donors of the American Chemical Society Petroleum Research Fund for support. We also thank Prof. Ben King and Dr. Pawel Rempala for calculational assistance.

Supporting Information Available: Synthetic, spectroscopic, and calculational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) McKee, M. L.; Shevlin, P. B.; Zottola, M. *J. Am. Chem. Soc*. **2001**, *123*, 9418.

(14) All structures were fully optimized by analytical gradient methods using Gaussian 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998, or Gaussian 03, Revision B.02, Gaussian, Inc., Pittsburgh, PA, 2003. See the Supporting Information for the full references. Energies were corrected for zero-point energy differences (ZPVE) (unscaled), and Stability calculations indicated that all intermediates had wave functions that were stable toward unrestricted character. Vibrational analyses established the nature of all stationary points as either energy minima (no imaginary frequencies) or first-order saddle points (one imaginary frequency).

(15) Trace photolabile bands at ca. 2045 cm^{-1} were also observed on irradiations of diazirine **3**, which we attribute to the corresponding diazo isomer.[16]

(16) Josefredo, P. R., Jr.; De Almeida, W. B.; Celebi, S.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 7481.

(17) As is usual for chlorocarbenes,[2,10,11,16] the singlet states of carbenes **4a** and **4b** are calculated at the DFT level to be 5.4 and 8.1 kcal/mol more stable than the respective triplet states. The triplet state of allene **5** is predicted to lie 17 kcal/mol higher in energy than the singlet.