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Photoselection of Carbene Stereoisomers with Surprisingly Different Electronic Spectra: 3-Furylchlorocarbene

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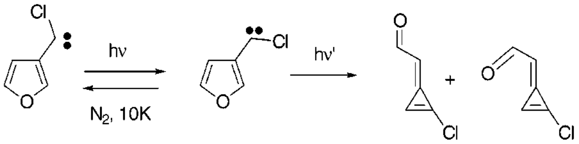
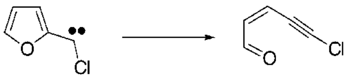
ABSTRACT

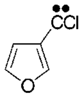


Syn and anti conformational isomers of 3-furylchlorocarbene were characterized in low-temperature matrixes by IR, UV/vis, chemical trapping, and calculational modeling. Displaying significantly different electronic spectra, the two isomeric carbenes could be photochemically interconverted. At shorter wavelengths, the carbene rearranges to a conjugated methylenecyclopropene.

Although phenylchlorocarbene has been characterized in depth,[1] there is little information available on singlet carbenes appended to heteroaromatics. In such systems, there is the possibility of significant perturbation of the carbene electronics,[2] while at the same time new avenues may open for rearrangement.[3,4] Moreover, the influence of the heteroring has the potential for revealing geometric-isomer dependencies on reactions. In this vein, we earlier reported characterization of 2-furylchlorocarbene (**1**), where we uncovered a stereoelectronic effect in one geometric isomer that selectively accelerated ring fragmentation.[3] We now describe significantly different behavior in the 3-furyl system **2**, where two conformations exhibit surprisingly distinct UV/vis spectra, permitting wavelength-controllable photoselection.



1



2

Diazirine **3** was synthesized from the corresponding amidinium hydrochloride[5] through standard Graham conditions.[6] The UV spectrum of **3**, matrix isolated in N_2 (1:800) at 10 K,[7] showed maxima at 394, 373, and 355 nm which were blue-shifted somewhat from those of the 2-isomer.[3] Irradiation at 366 nm caused rapid disappearance (30 m) of the IR and UV/vis bands of **3**. New spectra appeared that could be attributed to 3-furylchlorocarbene (**2**), based on in

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[1] See, for example: (a) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517. (b) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W. *Tetrahedron*, **1985**, *41*, 1587. (c) Wierlacher, S.; Sander, W.; Liu, M. T. H. *J. Org. Chem.* **1992**, *57*, 1051. (d) Trindle, C.; Datta, S. N.; Mallik, B. *J. Am. Chem. Soc.* **1997**, *119*, 12947. (e) Sander, W. *Spectrochim. Acta, Part A* **1987**, *43A*, 637.

[2] Pyridylchlorocarbenes: (a) Baird, M. S.; Bruce, I. *J. Chem. Res., Synop.* **1989**, 374. (b) Moss, R. A.; Jang, E. G.; Kim, H.; Ho, G.; Baird, M. S. *Tetrahedron Lett.* **1992**, *33*, 1427.

[3] Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233.

[4] For solution generation of 3-furylcarbene, see: Hoffman, R. V.; Opphanides, G. G.; Schechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927.

[5] Decroix, B.; Pastour, P. *J. Chem. Res., Synop.* **1978**, *4*, 132.

[6] Graham, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

[7] For a description of the matrix isolation instrumentation and experimental techniques, see: (a) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. (b) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

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situ trapping and calculational modeling. The IR spectrum of this initial photoproduct showed major bands at 1504, 1487, and 1156 cm^{-1} (Figure 1).[8] The UV/vis spectrum exhibited absorptions at λ_{max} 345 (vs) and 575 (w, broad) nm, the latter lending a blue tinge to the matrix (Figure 2). The same spectral features were produced on irradiation of **3** in an N_2 matrix containing 2% HCl. Warming the matrix to 35 K caused the disappearance of the UV/vis spectrum of carbene **2**, together with conversion of the IR bands of **2** into those of trapped product **4** (Scheme 1).

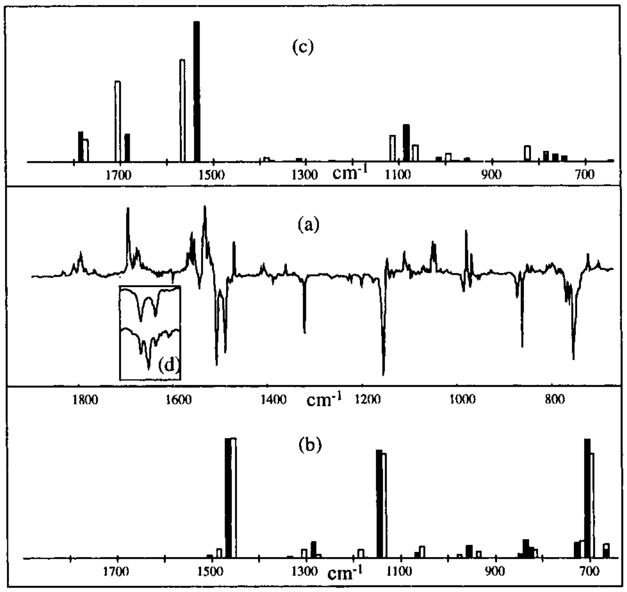


Figure 1. (a) Difference IR spectrum of N_2 matrix isolated carbene **2a** ("down bands") before and after 313 nm conversion to methylenecyclopropene **5** ("up bands"). (b) B3LYP/6-31G** calculated IR spectra for anti-**2a** (solid) and syn-**2b** (open). (c) B3LYP/6-31G** calculated IR spectra for s-cis (solid) and s-trans (open) **5**. (d) Inset: IR spectra of 1535−1470 cm^{-1} region of carbene spectrum before (upper, **2a**) and after (lower, **2b**) irradiation at 578 nm. Frequencies of calculated spectra are scaled by 0.96.

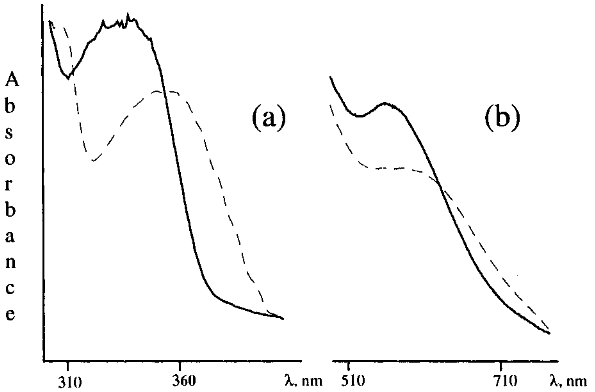
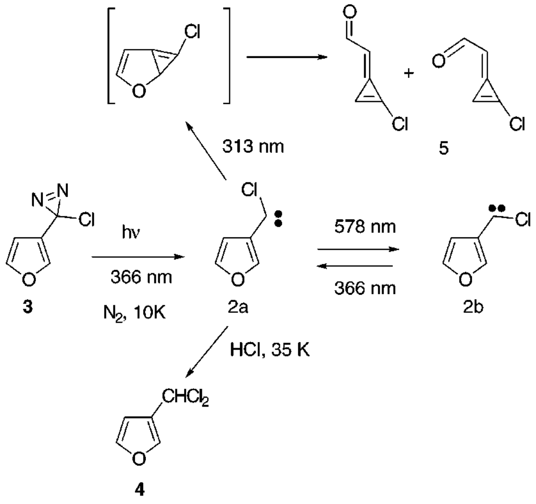


Figure 2. (a) UV spectra of matrix isolated 3-furylchlorocarbene before (solid, **2a**) and after (dotted, **2b**) irradiation at 578 nm. (b) Visible spectra (note scale change) of more concentrated matrix before (solid, **2a**) and after (dotted, **2b**) irradiation at 578 nm.

Scheme 1



Interestingly, irradiation of matrixes containing **2** at the center of the long-wavelength absorption (578 nm, 22 h) caused substantial shifts in the UV/vis spectra of the carbene. Yet, at the same time, only subtle changes in the IR spectra were discerned. The strong UV absorption of **2** moved to 360 nm, while the long-wavelength maximum shifted to 645 nm (Figure 2). However, the only prominent change in the IR spectrum was the merging of the 1504−1487 cm^{-1} absorption into a band centered at 1498 cm^{-1} (Figure 1). These transformations were reversible; irradiation of the matrix again at 366 nm (2 h) returned the original IR and UV/vis spectra, and this process could be cycled multiple times. Trapping experiments and DFT calculations confirmed that the new species was assignable to another geometric isomer of carbene **2**. Specifically, warming an HCl-containing N_2 matrix of this "photoproduct" of **2** again cleanly produced **4** in the IR spectrum.

B3LYP/6-31G** calculations[9] match the experimental IR spectra closely (Figure 1) and predict that the vibrational spectra of anti **2a** and syn **2b** isomers of the carbene should be very similar. Irradiation of matrixes containing either isomer of **2** at 313 nm rapidly produced a new species in the IR with strongest bands at 1691, 1558, and 1529 cm^{-1} (Figure 1).[8] Albers and Sander[10] observed similar photo-

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[8] Experimental and calculated IR spectra for **2** and **5** are tabulated in the Supporting Information.

[9] Gaussian 94, Revision D.4. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995. For calculated geometric parameters and vibrational spectra, see the Supporting Information. Molecular orbital surfaces were calculated with PC Spartan 1.3, Wavefunction, Inc.

products in unsuccessful attempts to characterize the parent 3-furylcarbene and attributed them to aldehyde derivatives of methylenecyclopropene. We found that DFT calculations[9] of the vibrational spectra of methylenecyclopropene **5**, as a mixture of s-cis and s-trans isomers, likewise fit the IR of the photoproduct of **2** (Figure 1). These results are summarized in Scheme 1. Analogous to speculation by others,[10] we believe that formation of **5** might logically arise from internal cyclization, followed by rearrangement as shown. No intermediates were observed in this photoprocess, however.

We[11] and others[12] have reported evidence previously for detection of multiple conformations in a variety of carbenes. What is striking in the case of the 3-furyl system **2** is the significantly different UV and visible absorptions for the two isomers. Although inaccurate in absolute wavelengths, CIS/6-31G** calculations[9] also predict sizable differences in long-wavelength transitions for anti (**2a** 464 nm) and syn (**2b** 507 nm) 3-furylchlorocarbene. We attribute the blue-shifted absorptions (λ_{max} 575 and 345 nm) to anti-**2a** and the lower-energy absorptions (λ_{max} 645 and 360 nm) to syn-**2b** on this basis. Hence, irradiation at either 366 or 730 nm selectively drives the conformational mix toward the shorter-wavelength-absorbing isomer **2a**. Irradiations at 578 nm have the converse effect.

B3LYP results[9] suggest that overall geometries for **2a** and **2b** differ little, particularly at the carbene carbon, and thus this is not the origin of the excited state differences. At the 6-31G** level, the anti conformer **2a** is predicted to be marginally lower in energy than **2b** (2.6 kcal/mol, vibrationally corrected). The CIS calculations indicate that the excited-state configurational mix for both isomers is dominated by electron promotion into the LUMO, as would be expected. This π-MO (Figure 3) is predicted (albeit in the ground state) to have a large coefficient at the 2-carbon and much smaller contribution at the 4-carbon of the furan ring. Moreover, there is a significant participation of the Cl π lone pair, producing an orbital reminiscent of the LUMO in 1,3-butadiene.[13] It is thus tempting to speculate that transitions populating this orbital are preferentially stabilized in the syn isomer, resulting in lower-energy transitions in **2b**, although confirmation must await higher-level calculations.[14]

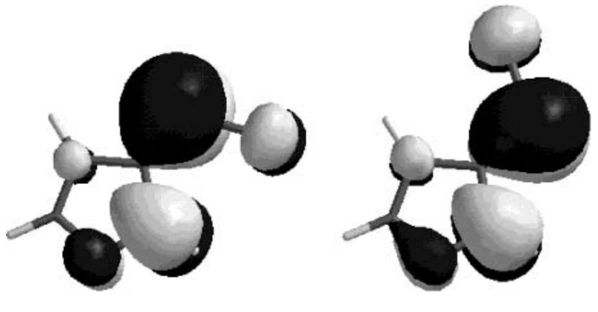

Figure 3. LUMOs for **2b** and **2a** calculated at the HF/6-31G* level.

Despite significant differences in the electronic spectra of the two conformational isomers **2a** and **2b**, their IR spectra differ only slightly. The major feature distinguishing the two isomers is the sizable splitting in the 1500 cm^{-1} band in the anti isomer **2a** (Figure 1). The DFT calculations indicate that this normal mode has significant C(2)−C(3) stretching character in both isomers. Moreover, at approximately one-half this frequency is a predominantly C−Cl stretch at 750 cm^{-1}. Examination of the normal modes associated with these absorptions suggests that the two vibrations are better aligned for coupling in the anti isomer **2a** than in syn-**2b**. We thus speculate that Fermi splitting[15] with the overtone of the 750 cm^{-1} vibration in the anti isomer is more effective.

Finally, we note the interesting contrast between the 2-isomer **1** and the 3-isomer **2** of the chlorocarbenes. The IR spectra of syn and anti isomers in **1** were quite distinct, and the isomers showed significant differential photoreactivity, but the UV/vis spectra were not measurably different.[3] The 2-isomer **1** readily underwent photofragmentation at long wavelengths, preferentially from the syn isomer. Here, however, the photoconversion of **2** to **5** is only observed on excitation to higher levels (presumably $\pi\pi^*$). We are continuing to explore the chemistry of these and related heterocyclic singlet carbenes.

Acknowledgment. We thank the National Science Foundation for generous support of this work.

Supporting Information Available: Experimental procedures for the synthesis of diazirine **3**, geometries, and tabulated experimental/calculated IR spectra for **2a**,**b** and **5** (s-cis and s-trans). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Albers, R.; Sander, W. *Ann.* **1997**, 897.

[11] (a) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 436. (b) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 844. (c) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563. (d) Du, X.-M.; Fan, H.; Goodman, J. L.; Kesselmayer, M. A.; Krogh-Jespersen, K.; LaVilla, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 1920.

[12] For leading references, see: (a) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583. (b) Roth, H. D.; Platz, M. S. *J. Phys. Org. Chem.* **1996**, *9*, 252. (c) Zhu, Z.; Bally, T.; Stracener, L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 2863.

[13] Cave, R. J.; Davidson, E. R. *J. Phys. Chem.* **1987**, *91*, 4481.

[14] A referee has asked wherther polarity differences in the two isomers might influence the electronic spectra. However, we find the calculated dipole moments in **2a** and **2b** to be quite similar (B3LYP and CIS/6-31G**): **2a** ground state 3.26 D, first excited singlet 1.54 D; **2b** ground state 3.78 D, first excited singlet 1.49 D.

[15] Herzberg, G. *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Norstrand, Inc.: New York, 1945.