Observable Azacyclobutenone Ylides with Antiaromatic Character from 2-Diazoacetyl-azaaromatics

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Abstract: Azacyclobutenone ylides **2** and **11** were generated in solution by laser flash photolysis of 2-diazoacetylpyridine (**1**) and 3-diazoacetylpyridazine (**10**), respectively, together with the corresponding ketenes. The ylides were identified by their characteristic IR and UV spectra: **2**, ν (CH$_3$CN) 1725 cm^{-1}, λ_{max} 360 and 550 (br) nm; **11**, ν (CH$_3$CN) 1776 cm^{-1}, λ_{max} 370 and 550 (br) nm. 2-Triisopropylsilyldiazoacetylpyridine **20** upon photolysis at 5 °C in CH$_3$CN forms the ylide **21** as a rather persistent ($T_{1/2}$ 2 h at 25 °C) purple solution, ν (CH$_3$CN) 1718 cm^{-1}, λ_{max} 245, 378 and 546 (br) nm, but no ketene is observed. Quinolyl ylide **14** and pyridyl ylides **17** and **19** with Me and 2-pyridyl substituents, respectively, with characteristic IR and UV spectra were also generated. The ^{1}H NMR spectrum of the pyridyl ring of **21** shows substantial upfield shifts relative to those of **20**. Calculated nucleus-independent chemical shifts (NICS) for **2**, **11**, and **21** are comparable to those for benzocyclobutadiene (**22**) and benzocyclobutenone enolate (**23**), with substantial positive values for the 4-membered rings, while the NICS values for the 6-membered rings are significantly more positive than for benzene or pyridine. Significant bond alternation is also found in the calculated ylide structures, and these results suggest strong antiaromatic character for the 4-membered rings of **2**, **11**, **14**, **17**, **19**, and **21**, and greatly reduced aromatic character for the 6-membered rings.

Photolysis of 2-diazoacetylpyridine **1** in an argon matrix was reported to give the ylide **2**, as identified by the IR and UV spectra, and upon further photolysis in the matrix this rearranged to ketene **3** with IR bands at 2123 and 2132 cm^{-1} for the *E* and *Z* conformations, respectively (eq 1).[1a] Upon warming, **3** formed
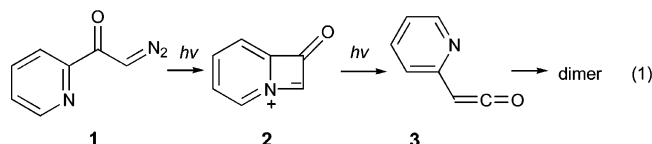

a [4 + 2]-cycloaddition dimer.[1] Flash vacuum thermolysis (FVT) of triazoles **4** (R = Ph, Me, MeO) at 680−750 °C with collection of the pyrolysates at 7 K was suggested to form diazo ketones which then formed the corresponding ketenes **5**, as identified by their ketenyl IR absorptions (eq 2).[1c,d] Heating of **4** (R = 2-pyridyl) in benzylamine gave *N*-benzyl bis(2-pyridyl)acetamide, possibly via ketene **5** (R = 2-pyridyl).[1e,f] However in these studies further examples of ylides analogous to **2** were not observed.[1c,d]

The ylide **2** may be compared to a ketene-derived 5-membered ring zwitterions **6**, with the structures established
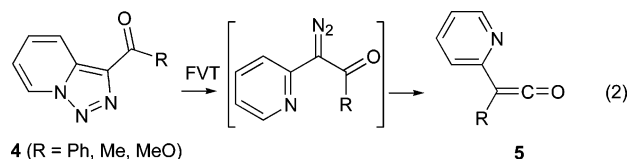
by X-ray.[2a] Open-chain zwitterions **7** and **8** were observed from intermolecular addition of pyridines to ketenes.[2b,c] Computations showed that the 4-membered ring ketene-ylide form of **3** is not an energy minimum.[1a]
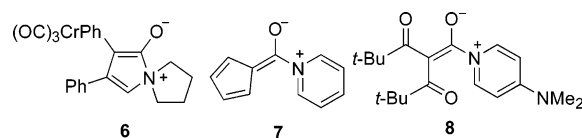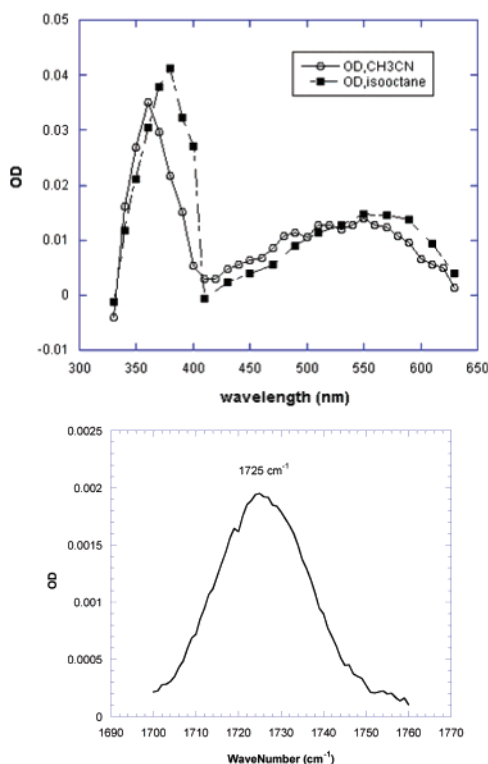

Recent investigations in our laboratory have examined the generation and direct observation of 2-pyridylketene (**3**) generated in solution by laser flash photolysis (LFP) of **1**,[3a−c] with confirmation of the structure by the observation of the characteristic ketenyl absorption in solution at 2127 cm^{-1}.[1a] The

[†] University of Toronto.
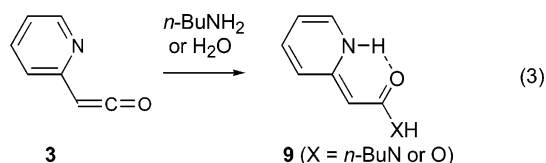[‡] Institute for Materials Chemistry and Engineering.
(1) (a) Kuhn, A.; Plüg, C.; Wentrup, C. *J. Am. Chem. Soc.* **2000**, *122*, 1945−1948. (b) Plüg, C.; Kuhn, A.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1366−1368. (c) Anderson, H. G.; Bednarek, P.; Wentrup, C. *J. Phys. Org. Chem.* **2003**, 519−524.

(2) (a) Chelain, E.; Goumont, R.; Hamon, L.; Parlier, A.; Rudler, M.; Rudler, H.; Daran, J.; Daran, J. C.; Vaissermann, J. *J. Am. Chem. Soc.* **1992**, *114*, 8088−8998. (b) Qiao, G. G.; Andraos, J.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 5634−5638. (c) Kollenz, G.; Holzer, S.; Kappe, C. O.; Dalvi, T. S.; Fabian, W. M.; Sterk, H.; Wong, M. W.; Wentrup, C. *Eur. J. Org. Chem.* **2001**, 1315−1322.

Figure 1. UV spectrum and IR band of ylide **2** in solution.

Figure 2. UV absorption of ylide **11** from laser flash photolysis of 3-diazoacetylpyridazine (**10**) in CH$_3$CN (lower trace) and isooctane (upper trace).
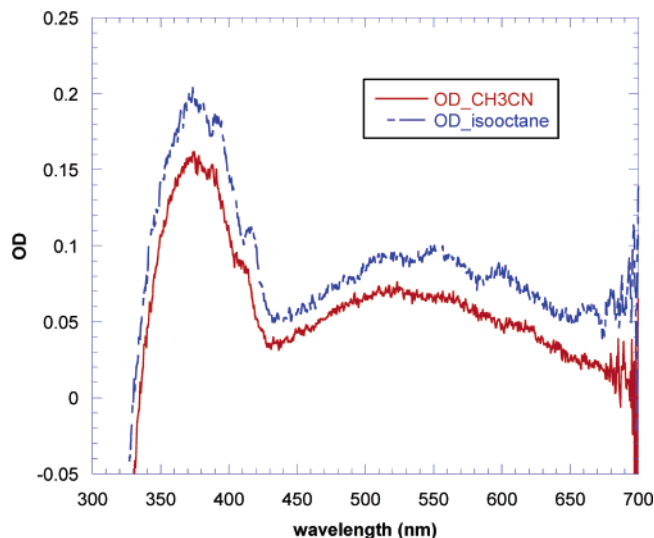
reactions of **3** with *n*-butylamine and with water were found to proceed with formation of intramolecularly H-bonded dihydropyridine transients **9** (eq 3), which in slower processes were converted to the observable amide and acid, respectively.[3a,b]

During these investigations it was observed that in addition to UV absorptions attributed to 2-pyridylketene (**3**) and the intermediates **9**, another absorption at longer wavelength was also detected in solution. Further studies of the photolysis of **1** and other 2-diazoacetyl azaaromatics in solution have now been carried out. Ylides such as **2** have not previously been detected in solution, and we now report experimental observations of this and related ylides in solution at room temperature, and find that these are surprisingly long-lived despite their thermodynamic instability.

Results and Discussion

Upon LFP with 308 nm excitation of **1** in isooctane at 22 °C a transient absorption is observed with maxima at 380 and 570 nm (Figure 1). A similar absorption is observed by LFP in CH$_3$-CN. These closely resemble that reported by Wentrup et al.,[1a] during matrix photolysis of **1**, and are also assigned as due to **2**. With LFP in CH$_3$CN at 25 °C, IR detection revealed a band at 1725 cm^{-1} (Figure 1), similar to the keto absorption for **2** noted by Wentrup, et al.[1a] of 1759 cm^{-1} in an Ar matrix at 10 K. The shifts to shorter wavelength in the more polar CH$_3$CN

in the UV spectrum and to lesser wave number in the IR are also observed in some other ylides (vide infra), as tabulated in Table S-5, Supporting Information.

In H$_2$O LFP of **1** with 308 nm excitation also gives rise to transient absorption at 520 nm assigned to **2**, and this decays with first-order kinetics, with a rate constant of $(3.22 \pm 0.13) \times 10^5$ s^{-1} at room temperature. Rate constants in H$_2$O/CH$_3$CN mixtures reported in Table S-1 (Supporting Information) give an empirical correlation of (log k) with the molar [H$_2$O], as has been previously demonstrated for ketenes.[3c]

Observation of ylide **2** may seem improbable, as this was calculated[1a] to be less stable than the ketene **3** by 43.4 kcal/mol. However, as shown in Figure S-2 (Supporting Information) there is a direct route for forming **2** upon photolysis of **1**, and the conversion of **2** to **3** through a carbene-like transition state is calculated to be 47.6 kcal/mol above **2** in energy. Experimentally the formation of **2** and the photochemical conversion to **3** was observed to occur upon photolysis in a matrix.[1a] The half-life of **2** formed by photolysis of **1** in CH$_3$CN was between $300-500 \times 10^{-6}$ s at 22 °C when followed by IR and UV, respectively. In H$_2$O the rate of disappearance of **2** (Table S-1) was 140−230 times greater than in CH$_3$CN, but as no products from these reactions could be identified after removal of the solvent, the nature of the decay of **2** is not known.

3-Diazoacetyl pyridazine (**10**) was prepared from the known acid,[4a] and LFP in CH$_3$CN using 266 nm light resulted in immediate disappearance of the infrared absorption of the diazo ketone at 2112 cm^{-1} and formation of a new band at 1776 cm^{-1},

(3) (a) Acton, A. W.; Allen, A. D.; Antunes, L. M.; Fedorov, A. V.; Najafian, K.; Tidwell, T. T.; Wagner, B. D. *J. Am. Chem. Soc.* **2002**, *124*, 13790−13794. (b) Allen, A. D.; Fedorov, A. V.; Tidwell, T. T.; Vukovic, S. *J. Am. Chem. Soc.* **2004**, *126*, 15777−15783. (c) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1987**, *109*, 2774−2780.

(4) (a) Karapanayiotis, T.; Dimopoulos-Italiano, G.; Bowen, R. D.; Terlouw, J. K. *Int. J. Mass. Spectrom.* **2004**, *236*, 1−9. (b) Murti, K.; Bhandari, K.; Ram, S.; Prabhakar, Y. S.; Saxena, A. K.; Jain, P. C.; Gulati, A. K.; Srimal, R. C.; Dhawan, B. N.; Nityanand, S.; Anand, N. *Indian J. Chem.* **1989**, *28B*, 934−942. (c) Eistert, B.; Schade, W. *Chem. Ber.* **1958**, *91*, 1411−1415. (d) Boyer, J. H.; Goebel, N. *J. Org. Chem.* **1960**, *25*, 304−305. (e) Maas, G.; Brückmann, R. *J. Org. Chem.* **1985**, *50*, 2801−2802. (f) Brückmann, R.; Schneider, K.; Maas, G. *Tetrahedron* **1989**, *45*, 5517−5530.
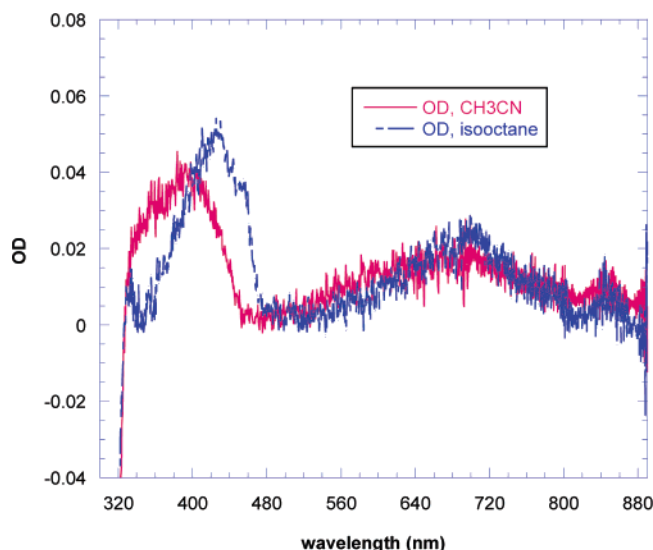
Figure 3. UV spectrum of quinolyl substituted ylide **14** in CH₃CN (lower) and in isooctane (upper).

attributed to the azacyclobutenone ylide **11**, and at 2132 cm⁻¹, attributed to the ketene **12** (eq 4). The ylide absorption decayed
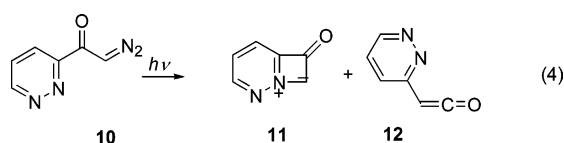
with a half-life of approximately 5×10^{-4} s. The UV absorption of ylide **11** was observed in both CH₃CN and isooctane (Figure 2). Details of the lifetime measurements for **2**, **11**, and other ylides (vide infra) in CH₃CN are given in Table S-4, Supporting Information.

Similarly LFP of 2-diazoacetylquinoline (**13**)[4b] in CH₃CN with 266 nm light gave immediate disappearance of the diazo ketone infrared absorption at 2107 cm⁻¹ and formation of a new absorption at 1725 cm⁻¹, attributed to the azacyclobutenone ylide **14**, and at 2124 cm⁻¹, due to the ketene **15** (eq 5). The ylide absorption at 1725 cm⁻¹ decayed with a half-life of approximately 5×10^{-6} s (IR) or 3×10^{-5} s (UV). The UV absorption of ylide **14** was also observed in both CH₃CN and in isooctane (Figure 3).
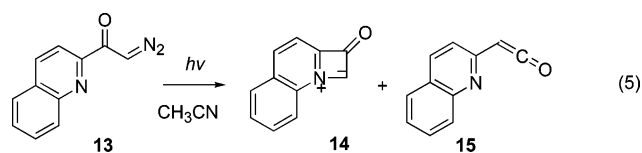


Upon LFP 2-pyridyl 1-diazoethyl ketone (**16**) gave the ylide **17** (eq 6), identified by the characteristic UV spectrum in CH₃-CN and in isooctane (Figure S-16, Supporting Information) and the IR absorption at 1722 cm⁻¹.
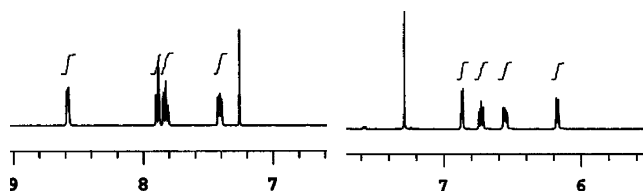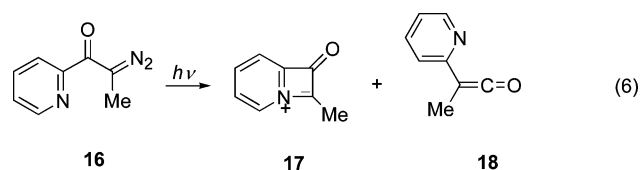
Figure 4. ¹H NMR of pyridyl H of diazo ketone **20** (left) and ylide **21** (right). The signal at δ 7.3 ppm is due to CHCl₃.

In CH₃CN the ketene **18** was also observed and identified by the IR absorption at 2112 cm⁻¹. Photolysis of the triazole **4** (R = 2-pyridyl)[4c,d] in CH₃CN led to the ylide **19** (eq 7), identified by the characteristic UV absorption with λ_{max} 385 and 470 (br) nm, and IR absorption at 1730 cm⁻¹ (Figure S-13). However, the corresponding ketene was not observed.
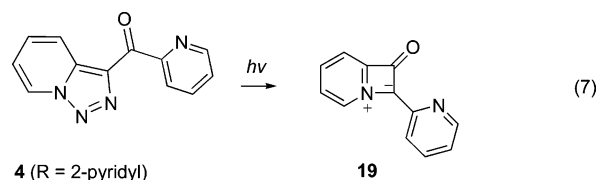
Reaction of diazo ketone **1**[1,3c,d] with triisopropylsilyl triflate following a reported general procedure[4e,f] gave the diazo ketone **20** (eq 8). Continuous photolysis of **20** with 300 nm light in CH₃CN or pentane resulted in formation of ylide **21** identified by the carbonyl absorption at 1718 cm⁻¹ or 1746 cm⁻¹, respectively (eq 8) (Figures S-8 and S-9, respectively). No ketene IR absorption was detected.
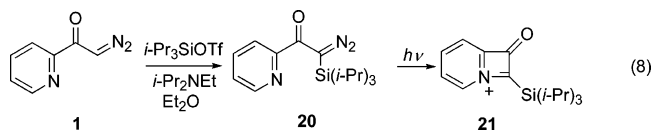
The ylide was further characterized by the UV spectrum, with a strong absorption at 378 nm and broad absorption at 546 nm in CH₃CN (Figure S-10). In pentane UV absorption was observed at 397 nm and at 582 (br) nm with fine structure (Figure S-11).

Ylide **21** is remarkably long lived in solution and decayed with a half-life of 2 h at 25 °C after generation in CH₃CN as monitored by UV spectroscopy. The decay gave approximately first-order kinetics, but upon removal of the solvent at room temperature no recognizable products could be identified. Photolysis of **20** in pentane and cooling to −78 °C led to precipitation of a solid, and removal of the solvent at −78 °C gave **21** as a dark-purple solid, but efforts to obtain an X-ray structure were unsuccessful. Analysis by UV and IR of solutions obtained by photolysis indicated approximately 85% conversion of **20** to **21**, while dissolution of the solid in CDCl₃ and ¹H NMR analysis at −30 °C showed 70% conversion.

The ¹H NMR spectrum of **21** (Figure 4 and Supporting Information) has the signals for the pyridyl ring at δ (CDCl₃) 6.18, 6.56, 6.73, and 6.87, which show substantial upfield shifts compared to those of the precursor diazo ketone **20**, δ (CDCl₃) 7.42, 7.83, 7.89, and 8.59, for an average upfield shift for **21** of 1.35 ppm (17%).

The ¹³C NMR shifts for the pyridyl ring for **21** are at 109.7, 125.6, 125.7, 131.8, and 163.1, while those of the diazo ketone **20** are 122.2, 126.4, 137.2, 147.8, and 155.3 (Table 1). Thus, the ring carbons in **21** are upfield in four cases and downfield

Table 1. NMR Chemical Shift Assignments for **20** and **21**

	20 δ ¹H[st]	21 δ ¹H	δ 20 − 21[a]		20 δ ¹³C	21 δ ¹³C	δ 20 − 21[a]
H(21)	8.59	6.87	1.72	C(2)	147.8	125.6	22.2
H(22)	7.42	6.56	0.86	C(3)	126.4	125.7	0.7
H(23)	7.83	6.73	1.10	C(4)	137.2	131.8	5.4
H(24)	7.89	6.18	1.71	C(5)	122.2	109.7	12.5
				C(6)	155.3	163.1	−7.8
				C(7)	189.8	173.8	16.0
				C(8)	52.3	127.9	−75.6

[a] Difference in chemical shifts of **20** and **21**.

in one by an average of 6.6 ppm (4.8%), in contrast to the average 17% for the ¹H shifts. The greater upfield effects on the ¹H shifts are consistent with these being due to aromaticity/antiaromaticity effects, which are not expected to have a significant effect on the ¹³C shifts. The ¹H and ¹³C chemical shifts (Table 1) were assigned using gCOSY45, ROESY, HSQC, and HMBC techniques. The carbonyl carbon (C7) showed an upfield shift of 16.0 ppm, while the ylide carbon (C8) was downfield by 75.6 ppm, consistent with ylide character for this carbon. Calculated GIAO chemical shifts (Supporting Information, Table S3) were consistently further upfield from the experimental values by $\delta\ 0.76 \pm 0.04$ ppm for ¹H and 8.1 ± 1.1 ppm for ¹³C and showed a similar pattern to the measured shifts.


20   **21**
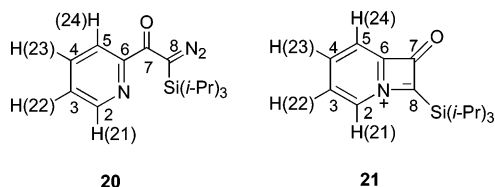
The remarkable upfield ¹H NMR shifts in **21** suggest a loss of aromaticity and to elucidate this phenomenon nucleus-independent chemical shifts (NICS)[5,6] were calculated for ylides **2**, **11**, and **21** and for the model compounds benzene, pyridine, non-planar cyclooctatetraene, benzocyclobutadiene (**22**) and for benzocyclobutenone enolate **23**. The results are given in Table 2, where NICS(0) is the calculated value at the ring center, and NICS(1) is the calculated value 1 Å above the ring center. Aromatic rings are characterized by negative NICS values, whereas positive values are characteristic of antiaromatic rings.[5] The NICS(1) values avoid effects due to σ electrons and are preferred for the analysis of aromaticity, although for the substrates considered here the trends are similar. The ylides **2**, **11**, and **21** have NICS(1) values of −1.21 to 0.48 for their 6-membered rings, indicating much weaker aromatic character than that found for pyridine. The NICS(1) values of 10.07 to 10.27 for their 4-membered rings are indicative of substantial antiaromatic character in these rings. By comparison benzo-cyclobutadiene (**22**), with NICS(1) values of −3.52 for the 6-membered ring and 13.92 for the 4-membered ring, is indicated to have modestly more aromatic character for the 6-membered ring and less for the 4-membered ring. Benzo-cyclobutenone enolate, **23**, with NICS(1) values of −1.87 to

(5) (a) Allen, A. D.; Tidwell, T. T. *Chem. Rev.* **2001**, *101*, 1333−1348. (b) Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317−1331.
(6) (a) Schleyer, P. v. R.; Maerker, C.; Dransfield, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, 3842−3882. (c) Oddershede, J.; Larsen, S. *J. Phys. Chem. A* **2004**, *108*, 1057−1063.

Table 2. GIAO-B3LYP/6-31G(d)//B3LYP/6-31G(d) Calculated NICS Values and Δ_R Values (Å)

	NICS(0) 6-ring	NICS(0) 4-ring	NICS(1) 6-ring	NICS(1) 4-ring	Δ_R 6 ring	Δ_R 4 ring
benzene	−9.64		−11.21		0.000	
pyridine	−7.97		−10.99		0.057	
benzocyclo-butadiene (**22**)	−1.81	23.54	−3.52	13.92	0.076	0.172
benzocyclo-butenone enolate (**23**)	−0.05	14.71	−1.87	8.62	0.082	0.155
2	1.44	14.80	−0.78	10.27	0.109	0.205
11	4.53	15.85	0.48	10.08	0.141	0.214
21	1.07	16.80	−1.21	10.07	0.104	0.196
cyclobutenone enolate (**26**)		13.58		8.59		
cyclobutadiene[a]		21.5		13.3		
cyclooctatetraene[b]	5.74		2.30		0.128[11]	

[a] Reference 6b. [b] 8-membered ring, nonplanar.

8.62 for the 6- and 4-membered rings, respectively, is indicated to be a little more aromatic (or less antiaromatic) than the ylides **2**, **11**, and **21**.

22   **23**
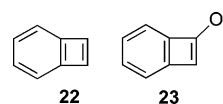
Benzocyclobutenone enolate (**23**), which shares structural and electronic properties with the ylides, is derived from the ketone **24** by proton abstraction (eq 9) and has previously been subject to examination as a possibly antiaromatic species.[7a,b] On the basis of experimental studies of **23** generated in the gas phase combined with *ab initio* calculations it was concluded there was significant double bond character in the C1−C2 bond with electron delocalization to oxygen and into the 6-membered ring, which tended to alleviate antiaromaticity in the 4-membered ring.[7a] Kinetic studies of the enolization of **24** show this is less reactive than 2-indanone (**25**) by a factor of 3.1×10^6, corresponding to an activation energy difference of 8−9 kcal/mol.[7b] Other model ketones were more reactive by factors of 1.6×10^3 to 5.3×10^5.[7b] The large energy difference implied considerable destabilization of **23**, for which ring strain and antiaromaticity were proposed as the cause. Since cyclobutanone has a pK_a similar to that of acetone, it was concluded that antiaromaticity must play a large role in the destabilization of **23**.[7b]

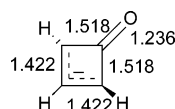**24**   **23**   (9)

25
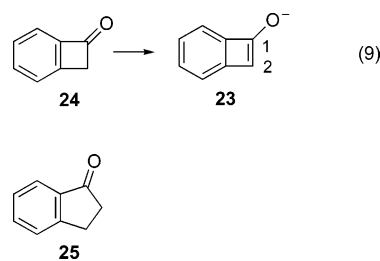
Previously the role of aromaticity/antiaromaticity in **23** had not been analyzed using NICS calculations, and these results found for **23** support the presence of significant antiaromatic effects in this enolate, especially in the 4-membered ring, with weak aromaticity in the 6-membered ring. Similarly, cy-

(7) (a) Broadus, K. M.; Kass, S. R. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2389−2396. (b) Nagorski, R. W.; DeAtley, A. D.; Broadus, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 8428−8429.

Figure 5. MP2/6-31G(d) calculated[7a] bond distances (Å) of cyclobutenone enolate (**26**).

clobutenone enolate (**26**) has been found to be strongly destabilized (as indicated by the energy change in eq 10 calculated at the MP2/6-31G(d) level) and a calculated geometry
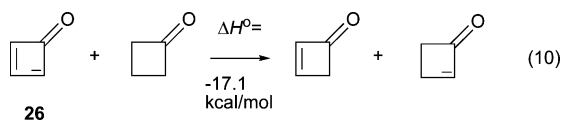
(Figure 5) described as having allylic anion character with the C2 and C4 hydrogens bent out of plane by 43°.[7a] We calculate essentially the same geometry for **26** using DFT methods, and calculate a NICS(1) value of 8.59 (Table 2) indicative of significant antiaromatic character for **26**. This may be compared to the value of 13.3 for cyclobutadiene (Table 2).

Another criterion of antiaromaticity is bond alternation, and the B3LYP calculated geometries of ylides **2**, **11**, and **21** and model compounds are shown in Table S-3 (Supporting Information). Values of the difference Δ_R between the longest and shortest bonds in each ring provide a measure of bond alternation, and as shown in Table 2, these are larger in **2**, **11**, and **21** than in benzocyclobutadiene (**23**)[8] and are also larger than in naphthalene (0.047 Å at 205 K).[6c] Heteroatoms in **2**, **11**, and **21** affect these distances, but the differences are consistent with the other evidence from ^{1}H NMR and NICS calculations. The Δ_R values for enolate **23** are a little greater than for **21** for the 6-ring, and a little less for the 4-ring, but the 6-ring values are significantly larger than that for pyridine. Thus the Δ_R values indicate a significant lack of aromaticity in the 4-membered rings of both the ylides **2**, **11**, and **21**, as well as in benzocyclobutadiene **22** and the enolate **23**, and more aromatic character in the 6-membered rings than in the 4-membered, but less than in benzene or pyridine.

The question of aromatic and antiaromatic character in the azacyclobutenone ylides **2**, **11**, **14**, **17**, **19**, and **21** is closely related to similar considerations regarding cyclobutadiene, and the continuing great interest in the latter species has recently been considered in a thoughtful essay.[9] There it is noted "Various criteria have been proposed over time to judge whether a molecule is aromatic or not... and it was generally assumed that several of these criteria have to be met for a molecule to qualify for this distinction." The magnetic criteria, including NICS calculations, indicate antiaromaticity for cyclobutadiene, but energetic considerations are more problematic.[9] For the ylides considered here the criteria used are the measured ^{1}H chemical shifts, and the calculated bond alternations and NICS parameters, and all of these are consistent with significant antiaromatic character. While computations indicate that ylide **2** is strongly destabilized, any relevance of this result to the antiaromatic character of **2** and its derivatives is difficult to quantify and beyond the scope of this investigation.

It may be noted that the calculated geometries of the planar ylides resemble those of polyalkenes. Cyclooctatetraene, which is nonplanar, has δ ^{13}C of 131.5 and δ ^{1}H of 5.69[10] and C−C bond lengths of 1.334 and 1.462 Å, giving Δ_R of 0.128.[11] We have obtained NICS(0) and NICS(1) values for the nonplanar structure as 5.74 and 2.30, respectively, where NICS(0) is taken as the center of the molecule and NICS (1) is 1 Å above this (Table 2). This calculation indicates that nonplanar cyclooctatetraene is nonaromatic, as expected. However, the ylides considered here have the geometric properties of planar nonaromatic nonconjugated polyenes, and this may reasonably be attributed to a significant contribution from antiaromaticity.

In summary, observable azacyclobutenone ylides **2**, **11**, **14**, **17**, **19**, and **21** have been prepared in solution at ambient temperatures and characterized by their distinctive IR and UV spectra. The NMR spectra of the longer-lived triisopropylsilyl-substituted species **21** and calculated NICS values and bond alternations for **2**, **11**, and **21** indicate substantial antiaromatic character for these species. Benzocyclobutenone enolate (**24**) and cyclobutenone enolate (**26**) share some of these properties with the ylides and with benzocyclobutadiene (**23**).

Experimental Section

Diazo ketones **1**[1] and **13**,[4b] and triazole **4** (R = 2-pyridyl),[4c,d] are known compounds prepared by the reported procedures. UV−visible LFP experiments used a Xe-light source (150 W), spectrograph, photomultiplier, and ICCD camera, with 248 nm KrF and 308 nm XeCl excimer lasers, and a 266 and 355 nm Nd:YAG laser. Time-resolved IR experiments were conducted in Japan utilizing a dispersive-type IR spectrometer utilizing 266 nm pulses of a Nd:YAG laser (15 Hz repetition rate, 2 mJ per pulse) as the excitation source. A reservoir of sample solution was continuously circulated between two calcium fluoride plates with 2 mm path length. Computations were carried out using Gaussian 98.[12]

3-Diazoacetylpyridazine (10). To 3-pyridazinylcarboxylic acid[4a] (765 mg, 6.2 mmol) stirred in THF (15 mL) and cooled in an ice bath under argon was added Et_3N (0.945 mL, 6.7 mmol) and isobutyl chloroformate (0.805 mL, 6.2 mmol). The mixture was stirred 1 h with cooling, and then added to a cold ether solution of excess diazomethane, left cold for 1 h, and allowed to warm to room temperature overnight. The ether solution was washed with saturated NaCl solution and dried over anhydrous Na_2SO_4; after evaporation of the solvent, the resulting solid was chromatographed (alumina, CH_2Cl_2/hexanes, 1:1 v/v) to give **10** (435 mg, 48%) as opaque crystals, mp 127−131 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (dd, J = 1.6, 4.9 Hz, 1H), 8.22 (dd, J = 1.6, 8.4 Hz, 1H), 7.67 (dd, J = 4.9, 8.4 Hz, 1H), 6.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 155.2, 153.7, 127.6, 124.3, 55.0. IR ($CHCl_3$) 2112, 1634 cm^{-1}. UV−vis (CH_3CN) λ_{max} (ϵ) 217 nm (9.8 × 10^3), 307 nm (8.1 × 10^3). EI-MS m/z 148 (11, M$^+$), 120 (60, [M − N_2]$^+$), 92 (100), 69 (19), 65 (49). HR-EI-MS m/z calcd for $C_6H_4N_4O$ 148.0385, found 148.0389.

2-Pyridyl 1-Diazoethyl Ketone (16). 2-Pyridylcarboxylic acid (0.2 g, 1.62 mmol) in THF (10 mL) was cooled in an ice bath, Et_3N (0.25 mL, 1.78 mmol) and isobutyl chloroformate (0.21 mL, 1.62 mmol) were added, and the mixture stirred for 1 h. A solution of diazoethane prepared from *N*-nitroso-*N*-ethylurea (1.7 g, 14.5 mmol) was added to the cold solution, which was left standing for 1 h, and then allowed to warm to room temperature overnight. Saturated NaCl solution was added and extracted three times with ether. The combined ether layers

(8) The calculated geometry of **22** at the ab initio MP2 level (ref 6a) gives Δ_R values of 0.146 for the 4-membered ring and 0.065 for the 6-membered ring.

(9) Bally, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 6616−6619.

(10) van Eikema Hommes, N. J. R.; Clark, T. *J. Mol. Model.* **2005**, *11*, 175−185.

(11) Schröder, G. *Cyclooctatetraene*; Verlag Chemie: Weinheim, 1965.

(12) Frisch, M. J.; et al. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

were dried over anhydrous CaSO$_4$ and evaporated. The crude product (0.286 g) was recrystallized twice from cold pentane to give **16** as yellow needles (28 mg, 11%), mp 37−38 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.54−8.53 (m, 1H), 7.96−7.94 (m, 1H), 7.86−7.82 (m, 1H), 7.43−7.40 (m, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 185.3, 154.3, 147.8, 137.3, 126.5, 122.4, 62.8, 11.0. IR (CH$_3$CN) 2089, 1630 (sh), 1606 cm^{-1}. EI-MS m/z 161 (5, M$^+$), 133 (70, [M − N$_2$]$^+$), 105 (100, [M − N$_2$ − CO]$^+$), 79 (62). HR-EI-MS m/z calcd for C$_8$H$_7$N$_3$O 161.0589, found 161.0593.

2-(Triisopropylsilyldiazoacetyl)pyridine (20). To a solution of 2-diazoacetylpyridine (**1**, 294 mg, 2 mmol) and *i*-Pr$_2$NEt (348 μL, 2 mmol) in ether (30 mL) was added dropwise at 0 °C under N$_2$ a solution of triisopropylsilyl triflate (538 μL, 2 mmol) in ether (10 mL). A white solid precipitated, leaving a light-yellow solution. The mixture was allowed to warm to room temperature and was stirred overnight. After filtration the solvent was evaporated to afford a yellow oil, which was chromatographed (silica gel, CH$_2$Cl$_2$/hexanes, 2:1 v/v with 1% Et$_3$N) to give **20** as a pale-yellow oil (312 mg, 51%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.59−8.58 (m, 1H), 7.91−7.88 (m, 1H), 7.85−7.81 (m, 1H), 7.43−7.40 (m, 1H), 1.50−1.42 (m, 3H), 1.16 (d, $J = 7.5$ Hz, 18H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 189.8, 155.3, 147.8, 137.2, 126.4, 122.2, 52.3, 18.7, 11.8. IR (CDCl$_3$) 2084, 1602 cm^{-1}. UV−vis (pentane) λ_{max} (ϵ) 225 nm (9.9 × 10^3), 261 nm (5.1 × 10^3), 313 nm (4.6 × 10^3); UV−vis (CH$_3$CN) λ_{max} (ϵ) 226 nm (8.9 × 10^3), 262 nm (5.2 × 10^3), 310 nm (4.7 × 10^3). EI-MS m/z 303 (0.7, M$^+$), 287 (2, [M − CH$_3$]$^+$), 275 (69, [M − N$_2$]$^+$), 260 (50, [M − N$_2$ − CH$_3$]$^+$), 232 (100, [M − N$_2$ − CH(CH$_3$)$_2$]$^+$), 190 (32), 146 (22), 131 (74), 115 (23), 103 (64), 87 (22), 75 (78), 61 (45). HR-EI-MS m/z calcd for C$_{16}$H$_{25}$N$_3$OSi 303.1767, found 303.1763.

Ylide 21. Diazo ketone **20** (23 mg, 0.075 mmol) was dissolved in pentane (50 mL, dried over molecular sieves 4 A), and degassed by argon for 20 min at 5 °C. The solution was irradiated using 300 nm light at 5 °C for 10 min, and the color of the solution changed to deep purple. The solution was cooled with dry ice, and a dark-purple solid precipitated. The pentane solvent was withdrawn carefully with a syringe, and residual pentane was evaporated with a stream of argon, giving the ylide **21** as a dark-purple solid, which was kept with dry ice under argon. ^{1}H NMR (500 MHz, CDCl$_3$, −30 °C) δ 6.87 (d, $J = 4.8$ Hz, 1H), 6.75−6.72 (m, 1H), 6.57−6.54 (m, 1H), 6.18 (d, $J = 6.8$ Hz, 1H), 1.20−1.16 (m, 3H), 1.11 (d, $J = 7.0$ Hz, 18H). ^{13}C NMR (125 MHz, CDCl$_3$, −30 °C) δ 173.8, 163.1, 131.8, 127.9, 125.7, 125.6, 109.7, 18.9, 11.5. IR (CDCl$_3$) 1713 cm^{-1}; IR (CH$_3$CN) 1718 cm^{-1}; IR (pentane) 1746 cm^{-1}. UV−vis (pentane) λ_{max} (ϵ) 249 nm (8.6 × 10^3), 397 nm (4.9 × 10^3), 421 nm (3.6 × 10^3), 582 nm (9.8 × 10^2); UV−vis (CH$_3$CN) λ_{max} (ϵ) 245 nm (7.9 × 10^3), 378 nm (3.6 × 10^3), 546 nm (8.2 × 10^2).

Supporting Information Available: Experimental and computational details, with NMR, UV, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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