Carboalkoxymethyl ligands thus represent kinetically viable intermediates in the reductive coupling of two carbonyls. The first CO is secured by reducing FpCO$^+$, for example, to FpCH$_2$OMe (**1**).[21a] The second CO is incorporated as a carboalkoxymethyl ligand either by an alkyl–CO migratory insertion on **1**, followed by protic isomerization of the methoxyacetyl intermediate,[21b] or by the methylidene carbonylation route using **1** reported here.

Acknowledgment. support from the Department of Energy, Office of Basic Energy Service, is gratefully acknowledged.

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(21) (a) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275. (b) Bodnar, T.; Coman, E.; LaCroce, S.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* **1981**, *103*, 2471. (c) Lambert, C.; Cutler, A., manuscript in preparation.

Measurement of the Rotational Barrier of a Tetraalkylhydrazine Radical Cation

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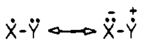
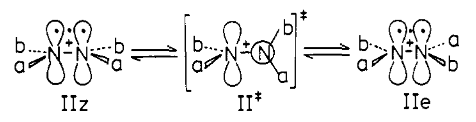
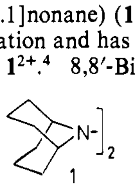
Heteroatom-substituted radicals are resonance stabilized by donation of a lone-pair electron to the radical center, as symbolized in Ia,b. The bonding involved is a three-electron bond in the



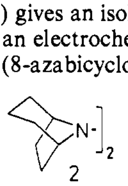
Linnett[1] sense; in MO terms the odd electron is in the antibonding combination of the p orbitals at X and Y, assuming the pure p orbitals are involved. Resonance stabilization should be maximized when the atomic orbital energies of X and Y are the same[2] and when the radical is charged.[3] Hydrazine radical cations should be among the most stable compounds with three-electron π bonds. The strength of the three-electron π bond of hydrazine radical cations is thus of interest in assessing the degree of stabilization of a radical center by a heteroatom. As indicated in IIz $\rightleftarrows$ IIe,



rotation about the three-electron π bond of a hydrazine radical cation leads to a loss of resonance stabilization when the orbital axes are perpendicular (at the transition state for rotation (II‡)). We report here the measurement of the barrier to rotation in a tetraalkylhydrazine radical. It was previously shown that 9,9′-bi(9-azabicyclo[3.3.1]nonane) (**1**) gives an isolable, Bredt's Rule protected radical cation and has an electrochemically reversible second oxidation to $\mathbf{1}^{2+}$.[4] 8,8′-Bi(8-azabicyclo[3.2.1]octane) (**2**)

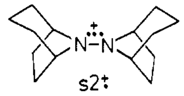


1

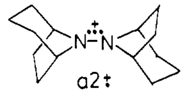


2

has similar kinetic protection and also lower symmetry, so that 180° rotation about the NN bond interconverts syn and anti isomers. The CV curve of **2** shows a single reversible first oxidation wave ($E°_1$ = 0.13 V), but two reversible second oxidation waves ($E°_2{}'$ = 1.02, 1.14 V).[5] The relative sizes of the second-oxidation waves are scan-rate dependent, the 1.02-V wave being small at slow scan rates but growing until it is about as large as the 1.14-V wave at fast scan rates. This behavior suggests that the isomeric radical cations $\mathbf{s2}^{+\cdot}$ and $\mathbf{a2}^{+\cdot}$ oxidize to their respective dications

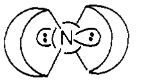


s2$^{+\cdot}$

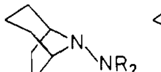


a2$^{+\cdot}$

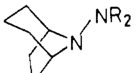
at different potentials and that they interconvert during slow scans. The reason for the nearly equal sizes of the two second oxidation waves at fast scan rates was revealed by low-temperature ^{13}C NMR study of neutral **2**. As does **1**,[4] **2** exists only in the electronically destabilized lone pair, lone pair dihedral angle θ = 180° conformations shown in Newman projection along the NN bond as III, because of the steric demands of the substituents. At each



III



2E



2A

bicyclic ring, the NR$_2$ substituent can be equatorial (**2E**) or axial (**2A**) to the piperidine fragment, so neutral **2** exists in three conformations of different energy, **2EE**; **2EA**/**2AE**; and **2AA**. Both NN rotation and N inversion are frozen out on the NMR timescale at low temperature, and all three conformations are present at equilibrium. Integration of the ^{13}C NMR at −75 °C was consistent with **2EE** being stabler, **2EA**/**2AE** being 0.2$_4$ kcal/mol higher in free energy, and **2AA** being an additional 0.2$_4$ kcal/mol higher in energy. Because electron removal from both **2EE** and **2AA** without NN rotation gives $\mathbf{a2}^{+\cdot}$ and from **2EA**/**2AE** gives $\mathbf{s2}^{+\cdot}$, the NMR work predicts a ratio of 0.86 for $\mathbf{s2}^{+\cdot}/\mathbf{a2}^{+\cdot}$ at the fast scan-rate limit (assuming no solvent effect on the equilibrium and that $\Delta S°$ = 0), in excellent agreement with the experimental observation of about equal sizes for the 1.02 and 1.14 V second-oxidation waves.

The difference in $E°_2{}'$, corresponding to oxidation of the isomers of $\mathbf{2}^{+\cdot}$ to those of $\mathbf{2}^{2+}$, is 0.12 V, corresponding to a 2.8-kcal/mol difference in ease of second-electron removal. A large $\Delta E°_2{}'$ is crucial for analysis of the isomeric mixture. We would not have predicted a large difference. We would have expected an energy difference for either $\mathbf{2}^{+\cdot}$ or $\mathbf{2}^{2+}$ similar to that for the corresponding hydrocarbons, *syn*- and *anti*-bi(bicyclo[3.2.1]oct-8-ylidine), for which Allinger's MM2 program[6] predicts only a 0.1-kcal/mol difference, with the syn form being the least stable.

Oxidation of **2** with NOPF$_6$ gives $\mathbf{2}^+$PF$_6^-$ as a yellow solid, which was crystallized from acetone to analytical purity. Solutions of this solid in acetonitrile gave a UV spectrum having λ_m 334 nm (ϵ 2100), and ESR parameters of g = 2.0033 and a(2N) = 13.7 G and complex proton splitting patterns with a major line separation of about 4 G. When the solid is dissolved at −30 °C,

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(1) Linnett, J. W. "The Electronic Structure of Molecules" Meuthuen: London, 1964.

(2) Baird, N. C. *J. Chem. Educ.* **1977**, *54*, 291.

(3) Clark, T. *J. Comput. Chem.* **1981**, *2*, 261; *Ibid.*, in press.

(4) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1977**, *99*, 2392. (b) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *Ibid.* **1978**, *100*, 7876.

(5) (a) All CV data are reported for 1–2 mM solutions in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, with a planar gold working electrode and a saturated calomel reference electrode. (b) The first oxidation wave resolves into two observed waves at low temperature. The $\mathbf{2},\mathbf{2}^+$ wave is complicated by the fact that *syn*- and *anti*-$\mathbf{2}^+$ can interconvert without undergoing rotation about the three-electron π bond by the following electron transfer:

$$(\text{syn})^0 + (\text{anti})^+ \rightleftarrows (\text{syn})^+ + (\text{anti})^0$$

This electron transfer is remarkably slow, and will be discussed, along with the scan rate and temperature dependence of the $\mathbf{2},\mathbf{2}^+$ oxidation wave, in a later publication.

(6) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127; Program No. 395, QCPE, Indiana University, Bloomington, IN.

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a CV curve showing only the 1.14-V oxidation peak is obtained, showing that the solid consists of the isomer that is harder to oxidize to the dication. After equilibration at room temperature, a solution of the solid shows a small $E^\circ{}_2' = 1.02$ V wave in its CV curve, and simulation of the curve shows that the concentration ratio of the $E^\circ{}_2' = 1.02$ V to the 1.14-V isomer is $0.07_5 \pm 0.01_5$, corresponding to ΔG° (22 °C) = 1.5 ± 0.1 kcal/mol, showing that the stabler isomer of $\mathbf{2}^{+\cdot}$ (by 1.5 kcal/mol = 0.065 V) is the less stable dication (by about 1.2 kcal/mol = 0.055 V). It seems clear that different interactions must somehow be involved in the radical cations and dications, to make the stabler radical cation isomer be the less stable dication isomer. The dications ought to be olefin-like in geometry, but their C—N= and N=N bond lengths will doubtless be significantly shorter than those of the corresponding olefins. We expect that $\mathbf{s2}^{2+}$ would be the less stable dication, because steric interactions between the $(CH_2)_3$ bridge methylenes and the bridgehead hydrogens would be worse in the syn than anti isomer. Hydrazine radical cations are known to bend easily at nitrogen,[7] which we suggest might allow $\mathbf{s2}^{+\cdot}$ to stabilize itself more than $\mathbf{a2}^{+}$. Firm assignment of the stabler isomer of $\mathbf{2}^{+\cdot}$ must await obtaining an X-ray crystallographic structure of $\mathbf{2^+PF_6^-}$; we have not yet succeeded in growing an X-ray quality crystal.

Photolysis of $\mathbf{2}^{+\cdot}$ solutions enriches the amount of the $E^\circ{}_2' =$ 1.02 V isomer. This is expected because the 334-nm absorption band is assigned as the $\pi^* \leftarrow \pi$ absorption. The excited state will have one bonding and two antibonding π electrons, should show a strong electronic preference for perpendicular p orbitals at nitrogen, and should demote to an equal mixture of $\mathbf{s2}^{+\cdot}$ and $\mathbf{a2}^{+\cdot}$, by analogy with olefin behavior.[8] Although extended photolysis destroys $\mathbf{2}^{+\cdot}$, irradiating a 2×10^{-3} M CV solution of $\mathbf{2}^{+\cdot}$ in a CV cell thermostated at 6 ± 0.3 °C for 90 s with a 275-W Sylvania sunlamp, caused conversion from the equilibrium 0.06:1 concentration ratio of the $E^\circ{}_2' = 1.02$ to 1.14 V isomers to a 1.31:1 ratio without a detectable decrease in oxidation current. Return to the equilibrium mixture was followed by measurement of the isomer ratio as a function of time using CV. The barriers obtained are $\Delta G^\ddagger$ (6 °C) = 23.3 kcal/mol (stabler → less stable isomer) and 21.8 kcal/mol (less stable → stabler isomer). These barriers agree reasonably with ab initio calculations of the rotational barrier for the parent $(H_2NNH_2)^{+\cdot}$: 28.6 kcal/mol (3-21 G calculation), 28.8 (6-31 G*), and 30.2 (MP2 (6-31 G*)).[9] We believe that the tetraalkyl substitution of $\mathbf{2}^{+\cdot}$ will stabilize the transition state, in which charge is predicted to be localized on one nitrogen, relative to the ground state.

The $(R_2NNR_2)^{+\cdot}$ three-electron π bond is observed to be substantially stronger than the $(R_3NNR_3)^{+\cdot}$ three-electron σ bond, for which a bond strength of 14.5 kcal/mol was estimated from solution lifetime measurements,[10] which is consistent with vapor phase $D(NH^+)$ values.[11] We believe our work is the first experimental measurement of the barrier to rotation about a three-electron π bond that is not conjugated. The closest analogy in the literature is the estimation of the NN three-electron π-bond rotational barrier in diphenylpicryl hydrazyl to lie in the range 9.3–12.0 kcal/mol,[12] because it is fast on the NMR time scale and slow on the ESR time scale.[13]

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(7) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131.

(8) Saltiel, V.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1.

(9) The GAUSSIAN76 series of programs was employed: Birkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D., Program No. 368, QCPE, Indiana University, Bloomington, IN.

(10) Nelsen, S. F.; Alder, R. W.; Sessions, R. B.; Asmus, K.-D.; Hiller, K.-D.; Göbl, M. *J. Am. Chem. Soc.* **1980**, *102*, 1429.

(11) Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heilbronner, E.; Kovac, B.; Huper, H.; Taagepera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137.

(12) Biehl, R.; Mobius, K.; O'Connor, S. E.; Walter, R. I.; Zimmerman, H. *J. Phys. Chem.* **1979**, *83*, 3449.

(13) We thank the National Science Foundation for support of this work under Grants CHE80-2611 (SFN) and CHE81-11421 (DHE) and NATO for a travel grant (104.80) to SFN which resulted in discussions with TC and the calculations quoted.

Structure of an Electronically Stabilized Carbonyl Ylide

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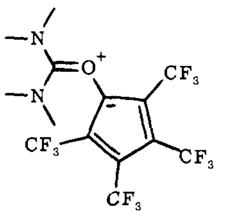
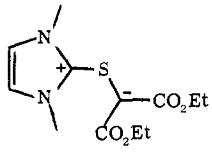
Received May 31, 1983

We report the first structure determination of a stable carbonyl ylide, **1**.[1] Since the mid-sixties there has been much interest in the chemistry and structure of carbonyl ylides.[2] While much chemistry has been uncovered, the isolation of a stable carbonyl ylide has not been possible until recently.[1] There have been numerous theoretical investigations of the carbonyl ylide functionality and these have been in good agreement with the chemistry observed for this function.[3] The lack of stable carbonyl ylides has prevented the confirmation of the theoretically expected structures.

A variety of analogous thione ylides have been synthesized, and many of these ylides are stable and isolable.[4] The most stable of these thione ylides are stabilized by a "push–pull" electronic substitution pattern, and complete structural studies are available on these systems (e.g., **2**[4a]). Early attempts to use the same stratagem to stabilize carbonyl ylides were unsuccessful.



1



2

The absence of stable "push–pull" carbonyl ylides has been bothersome from a theoretical point of view. The stabilizing influence of the electron-donating and -releasing groups on thione ylides is believed to act in concert with a sulfur conjugative link between the termini.[4a] The diminished ability of oxygen to function as a conjugative link demands that the substituent groups perform a cappella in stabilizing the carbonyl ylide. Thus, if stable carbonyl ylides are possible, exceedingly effective electron-releasing and -donating groups will be required. We chose to attempt the synthesis of a carbonyl ylide by the reaction of an electron-deficient carbene with a carbonyl compound.[5]

Diazotetrakis(trifluoromethyl)cyclopentadiene[1] (DTTC) is photolyzed in the presence of tetramethylurea to give tetramethyluronium tetrakis(trifluoromethyl)cyclopentadienylide (**1**) as a stable crystalline solid. The chemical and thermal stability of **1** (mp 200–202 °C) makes it a suitable choice for X-ray

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(1) (a) Janulis, E. P., Jr.; Arduengo III, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 3563. (b) Hamaguchi, M.; Ibuta, T. *Tetrahedron Lett.* **1974**, 4475. Have reported the isolation of an oxazole for which a carbonyl ylide-like resonance structure can be written.

(2) (a) Ullman, E. F.; Milkes, J. E. *J. Am. Chem. Soc.* **1962**, *84*, 315; **1964**, *86*, 3814. (b) Linn, W. J.; Benson, R. E. *Ibid*, **1965**, *85*, 3657. (c) Petrellis, P. C.; Dietrich, H.; Meyer, E.; Griffin, G. W. *Ibid*, **1967**, *89*, 1967. (d) Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *Ibid*, **1970**, *92*, 1402. (e) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537. (f) Husigen, R. *Ibid*, **1977**, *16*, 572.

(3) (a) Houk, K. N.; Rondan, N. G.; Santiago, C., Gallo, C. J., Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504. (b) Bigot, B.; Sevin, A.; Devaquet, A. *Ibid*, **1979**, *101*, 1095; **1974**, *101*, 1101.

(4) (a) Arduengo, A. J.; Burgess, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 5021. (b) Gronski, P.; Hurtke, K. *Tetrahedron Lett.* **1976**, 4139. (c) Nakasuki, K.; Hishion, D.; Murata, I.; Ogoshi, H.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.*, **1977**, *16*, 866.

(5) Our earier report[1] of carbonyl ylides generated by this route is the only example of this type of reaction in which stable ylides are formed. However, there are two reports of free carbene reactions that have been shown to yield transient carbonyl ylide species: Tomika, H.; Miwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 753. Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6631.

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