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 $\mathbf{2}^{+}\mathbf{PF_6}^{-}$; 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

Eugene P. Janulis, Jr., and Anthony J, Arduengo, III*

The Roger Adams Laboratory, Department of Chemistry
University of Illinois, Urbana, Illinois 61801

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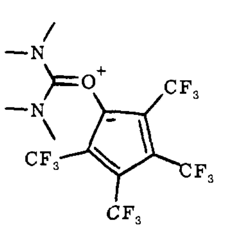
We report the first structure determination of a stable carbonyl ylide, **1**.[1] Since the mid-sixties there has been much interest in the chemistry and structure of carbonyl ylides.[2] While much chemistry has been uncovered, the isolation of a stable carbonyl ylide has not been possible until recently.[1] 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.



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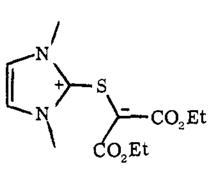

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The absence of stable "push–pull" carbonyl ylides has been bothersome from a theoretical point of view. The stabilizing influence of the electron-donating and -releasing groups on thione ylides is believed to act in concert with a sulfur conjugative 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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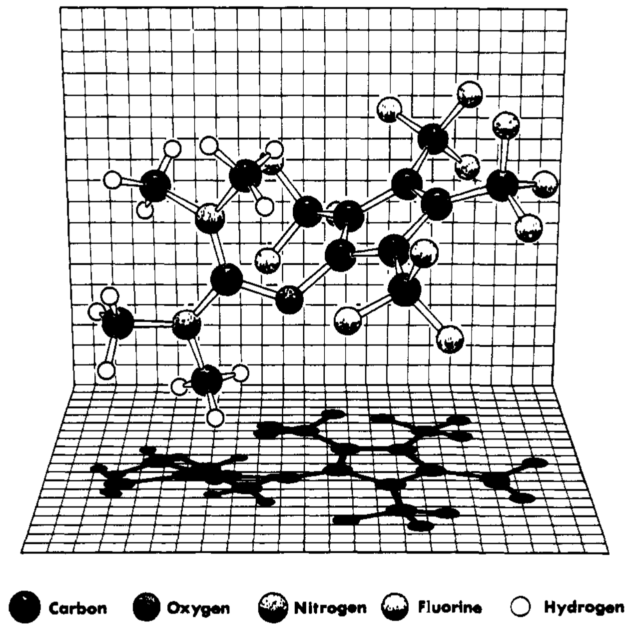

Figure 1. Perspective drawing[7] of the carbonyl ylide **1**.

crystallographic analysis.[6] Figure 1 illustrates the solid-state structure observed for this carbonyl ylide, As would be expected the central COC angle of 121.1 (5)° is close to a trigonal angle of 120° and much larger than the central CSC angle (104°) in thione ylide **2**.

The two carbon–oxygen bonds are quite different in length with a distance of 134.8 (8) pm at the onium terminus and 142.2 (7) pm at the ylide terminus, These distances suggest a partial C–O π bond between the carbonium center and oxygen while the oxygen cyclopentadienylide bond appears to be a single σ bond. This differs from the thione ylide **2** in which both C–S bonds were the same length (intermediate between a CS double and single bond[4a]), This model for bonding in the carbonyl ylide is also supported by the orientation of the two termini as depicted in Figure 2,

The excised ylidic system from **1** is presented in Figure 2 as a view along the bisector of the COC angle with the ylide terminus to the right. The ylide terminus is inclined to the central COC plane with an angle of 55,4° while the urea plane is twisted only 25.4°. The termini are twisted in a conrotated fashion to adopt a sterically least hindered orientation. This orientation is noticeably closer to a planar geometry than the related thione ylide, **2**. Along with the short onium terminus-oxygen bond this geometry suggests a greater participation of an oxygen vs. sulfur lone pair in stabilizing the carbonium center. The stabilization of the anionic center seems to be handled completely within the cyclopentadienyl system.

It is instructive to compare the structure observed for **1** with that calculated by Houk, Griffin, and co-workers for some models of the "push–pull" carbonyl ylides.[3a] For the highly perturbed ylides bearing two amino and two cyano substituents a nonplanar structure in which the ylide terminus is twisted by 90° is preferred. The calculated COC angle is 117° and the C–O bonds are very similar to those observed for **1**. Overall there is good agreement of the calculated structure with that observed for **1**.

Finally, we have been able to synthesize other carbonyl ylides through the use of DTTC as a carbene precursor, The chemistry and solution structure of these ylides is currently under study and will be reported in future articles,

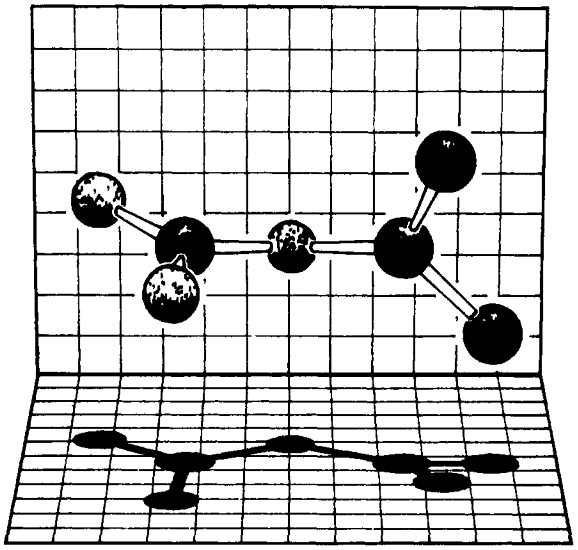

Figure 2, Perspective drawing of the central COC system in **1**.

Acknowledgment is made to the National Science Foundation (NSF CHE 81-04980) for its support of this work. We also thank Dr, Scott R. Wilson for his work on the X-ray structure of **1** and Dr, Egbert Keller, Kristallographisches Institut der Universität Freiburg, for providing a copy of the SCHAKAL molecular graphics program from which KANVAS was written.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determination of **1** and tables of positional and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(6) The crystal data were as follows: $C_{14}H_{12}N_2OF_{12}$, monoclinic, space group $P2_1/c$, $a = 995.1$ (2) pm, $b = 1320.0$ (3) pm, $c = 1399.3$ (3) pm, $\beta = 104.78°$, $Z = 4$, $D_c = 1.690$ g/cm^{-3}, crystal size $0.10 \times 0.15 \times 0.18$ mm. With 965 reflections of intensity greater than 3 σ, the structure was solved by direct methods (MULTAN 80) and standard difference Fourier techniques. The final R factors were $R = 0.0405$ and $R_w = 0.0409$.

(7) The perspective drawings were made with the E. *K*eller–A. J. *A*rduengo *N*eodimensional *V*iews of *A*toms with *S*hadows (KANVAS) program. The back and shadowed planes are at right angles and bear a 50-pm grid. The lighting source is at infinity so that the shadow size is meaningful.

CLi_5, CLi_6, and the Related Effectively Hypervalent First-Row Molecules, $CLi_{5-n}H_n$ and $CLi_{6-n}H_n$[1]

Paul von Ragué Schleyer,* Ernst-Ulrich Würthwein,
Elmar Kaufmann, and Timothy Clark

Institut für Organische Chemie
der Friedrich-Alexander-Universität Erlangen-Nürnberg
D-8520 Erlangen, Federal Republic of Germany

John A. Pople

Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15235

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The octet rule predicts the stoichiometries of first-row hydrides remarkably well. Thus, "CH_5" and "CH_6" are only likely to exist as weak complexes between methane and a hydrogen atom or a hydrogen molecule. Surprisingly, when lithium is involved instead of hydrogen, the situation is completely different. Both trigonal-bipyramidal CLi_5 (**1**, D_{3h}) and octahedral CLi_6 (**2**, O_h) are indicated by ab initio calculations using the 3-21G basis set and full geometry optimization[2] to be highly stable toward all possible

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(1) Part 2 of a series on effectively hypervalent molecules. (a) Part 1: Schleyer, P. v. R.; Würthwein, E.-U.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5839. (b) Schleyer, P. v. R., plenary lecture presented at the Fourth International Congress of Quantum Chemistry, Uppsala, Sweden, June, 1982. Löwdin, P.-O.; Pullman, A., Eds., "New Horizons of Quantum Chemistry"; Reidel: Dordrecht, 1983; pp 95–105.

(2) The GAUSSIAN80 series of programs and the standard basis sets and MP2 routines were used (Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406).