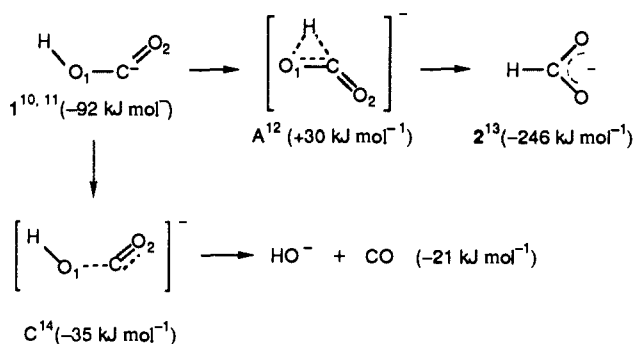Figure 1. Potential surface map for the system H^-/CO_2 (RMP2-FC/6-311++G**//RHF/6-31+G*). **1** ≡ HOCO⁻; **2** ≡ HCO_2^-; A is the saddlepoint for the reaction HOCO⁻ → HCO_2^-; B is the saddlepoint for the reaction HOCO⁻ → H⁻ + CO_2; C and D are saddlepoints for the reaction HOCO⁻ → HO⁻ + CO.
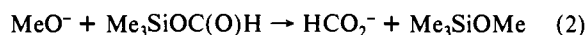
Scheme Iᵃ

ᵃ All energies relative to H⁻ + CO_2 (0 kJ mol⁻¹).

respect to reactants H⁻ and CO_2) and geometries were computed for points on a rectangular 5 × 10 Å grid: at 1-Å intervals in flat potential regions and 0.125-Å intervals in regions where the energy varied in a complex manner.

The map shows that HOCO⁻ (**1**) will not form directly from H⁻ and CO_2 in a thermal ion molecule reaction, since the saddlepoint (B) for this reaction is endothermic by some 65 kJ mol⁻¹. In contrast, there is no barrier to the formation of HCO_2^- (**2**) directly from H⁻ and CO_2. In principle, **1** is convertible **2** over saddlepoint A, but this barrier is endothermic by 122 kJ mol⁻¹ even though the reaction is exothermic by 154 kJ mol⁻¹ (see Figure 1 and Scheme I). In addition, there are two channels (through saddlepoints C and D) whereby HOCO⁻ may decompose to HO⁻ and CO. This reaction is endothermic (Scheme I), but since the barrier to C is only 57 kJ mol⁻¹, it follows that HOCO⁻ should dissociate to HO⁻ and CO rather than transform to the stable formate anion.[15]

$$HO_2CCO_2^- \xrightarrow{\text{CID}} HOCO^- + CO_2 \qquad (1)$$

$$MeO^- + Me_3SiOC(O)H \rightarrow HCO_2^- + Me_3SiOMe \qquad (2)$$

(13) C_{2v} (singlet state): CH (1.1172 Å), CO (1.2346 Å), HCO (114.750°). Energy, –188.800 91 au.

(14) Saddlepoint C: O_1C (1.45 Å), CO_2 (1.20 Å), O_1H (0.96 Å), HO_1C (135°), O_2CO_1 (115°).

(15) A reviewer has asked that we compare our ab initio energies with experimentally determined standard enthalpies of formation. In order to do that, we must convert those experimental energies to be directly comparable to our standard system (i.e., H⁻ plus CO_2, 0 kJ mol⁻¹, see Figure 1 and Scheme I). $\Delta H°_f$ for H⁻, HO⁻, and HCO_2^- are 145, –137.4, and –464 ± 13 kJ mol⁻¹, respectively (Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*(Suppl. 1)); for CO and CO_2, –110.5 and –393.5 kJ mol⁻¹, respectively (Benson, S. W. *Thermochemical Kinetics*; John Wiley and Sons, Inc.: New York, London, Sydney, 1968). From these values we obtain the following formation energies of products from the reactants H⁻ and CO_2 (taken as 0 kJ mol⁻¹): (a) HO⁻ + CO; 0 kJ mol⁻¹ (cf. –21 kJ mol⁻¹, Scheme I); and (b) HCO_2^-; –216 kJ mol⁻¹ (cf. –246 kJ mol⁻¹, Scheme I).

The hydroxycarbonyl and formate anions were synthesised in the mass spectrometer as shown in eqs 1 and 2. The hydroxycarbonyl ion was formed by collision-induced dissociation of carbon dioxide from deprotonated oxalic acid,[16] the formate ion by an S_N2 (Si) displacement.[17] The collisional activation mass spectra[18] of the two ions are as follows [*m/z* (loss) relative abundance]: –HOCO⁻, 17 (CO) 100; HCO_2, 44 (H•) 100[19], 16 (HCO•) 1. Thus HOCO⁻ specifically decomposes to HO⁻, and since the spectra contain no common fragmentation, this indicates that conversion of HOCO⁻ to HCO_2^- does not occur under the experimental conditions used in these experiments. Thus theory and experiment are in accord.

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(18) (a) The spectrum of HOCO⁻ was determined by a CA MS/MS/MS experiment measured with an MS 50 TA instrument; experimental details have been described previously (Burinsky, D. J.; Cooks, R. G.; Chess, E. K.; Gross, M. L. *Anal. Chem.* **1982**, *54*, 295. Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243). (b) The spectrum of HCO_2^- was measured under CA MS/MS conditions by using a VG ZAB 2HF instrument; for experimental details, see: Stringer, M. B.; Bowie, J. H.; Holmes, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3888.

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Some Observations Concerning the Structure of Dilithiomethane

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As small-volume cationic charge centers and as a source of unoccupied valence orbitals, the early main group metals have a well-documented but remarkable organometallic chemistry. Unusual structural configurations are observed for organolithium,[1] -beryllium, and -aluminum compounds including semibridging σ–π coordination in organometallic acetylenes such as $(C_6H_5)_2$-AlC≡CC$_6H_5$,[2] π back-donation which leads to planar three coordinate metal atom configurations as in $[BeN(CH_3)_2]_3$,[3] alkyl C–H coordination as in $LiB[CH_3]_4$[4] or $[LiC_6H_{11}]_2$,[5] and frontier
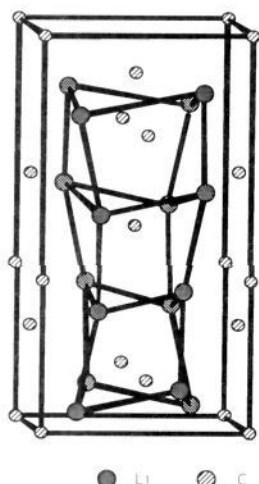
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Table I. Atomic Coordinates for Deuterated Dilithiomethane (5 K)

atom	x	y	z	U (isotropic) $\times 10$
C(1)	0.0	0.25	0.4267 (8)	0.00 (3)
D(1)	−0.034 (3)	0.323 (2)	0.336 (1)	10.6 (9)
D(2)	−0.019 (6)	0.044 (2)	0.406 (1)	6.1 (6)
Li(1)	0.189 (2)	0.461 (3)	0.028 (1)	0.00 (7)

Figure 1. Lithium and carbon atom positions for CD_2Li_2 within the tetragonal unit cell.

orbital directed coordination away from charge potential energy minima in π carbanions.[6] The lithium (or beryllium or aluminum) atom in all cases finds the best available source of electrons in the vicinity and makes use of them to resolve orbital electron deficiency[7] and minimize the cationic Coulombic charge potential.

Dilithiation of a common carbon atom can be expected to further amplify these singular properties and, as pointed out early by Schleyer and Pople,[8] who noted the stability of the cis-planar
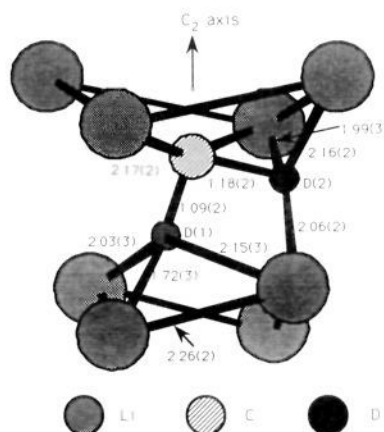

Figure 2. CD_2 coordination in CD_2Li_2.

form of monomeric dilithiomethane, can also lead to novel electronic and structural configurations. As a consequence, theoretical modeling of monomeric and dimeric Li_2CH_2 molecules has been the subject of considerable interest.[9] We present here the results of recent structural studies of Li_2CD_2 as obtained from neutron and X-ray scattering experiments[10] (Table I). The nontrivial synthesis of a *pure* phase of Li_2CD_2 used in this study was carried out by the Kawa–Lagow[11] modified Ziegler[12] technique.

The structure is a very distorted version of the antifluorite structure of Li_2O[13] and Be_2C[14] in which one of the cubic cell edges is doubled (Figure 1). To a first approximation, the carbon atoms are located at the face-centered sites of the parent cubic antifluorite cell and the lithium atoms are near the (0.25,0.25,0.25) body diagonal positions. The shortest lithium–lithium atom distance in the refined tetragonal structure is 2.26 (2) Å, which can be compared with the Li–Li distance of 2.314 (1) Å in Li_2O, 2.383 (6) Å in $[LiC_6H_{11}]_2$,[5] and 2.56 (1) Å in $(CH_3Li)_4(tmeda)_2$.[15] Both the lithium and carbon atoms were found to be in ordered sites.

The arrangement of the lithium atoms about the carbon atom is shown in Figure 2. A crystallographic C_2 axis passes through C(1) in the vertical direction of the figure, and only one of the two disorder orientations for the deuterium atoms is shown.[16] The closest carbon–lithium atom approach (2.17 (2) Å) is comparable to that in cyclohexyllithium[4] (2.172 (5) Å) or ethyllithium[17] (2.19 (1) Å). The shortest Li–D distances (1.72 (3)–2.17 (2) Å)[18] are

(4) LiB[CH$_3$]$_4$ is an important example of a methyl-bridged electron-deficient compound which has both a linear Li–CH$_3$–B bridge and a semi-bridging CH$_3$ group. Rhine, W.; Groves, D.; Stucky, G. D. *J. Am. Chem. Soc.* **1971**, *93*, 1553. Rhine, W.; Peterson, S. W.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 6401.

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(6) Stucky, G. D. *Adv. Chem. Ser.* **1974**, *No. 130*, 56–112 and included references. In response to a reviewer's comments, we would point out that the author concluded in the Summary (p 108) of this paper that "the position of the lithium atom in N-chelated organolithium compounds, (TMEDLi)$_2$R cannot be predicted from electrostatic considerations *alone* but...is consonant with *some* directed covalent bonding involving the HOMO of the carbanion" (see ref 7) and not "Stucky has argued that electrostatic factors are unimportant" (Bushby, R. J.; Tytko, M. P. *J. Organomet. Chem.* **1984**, *270*, 266 (in reference to the same paper)). Unlike the 100% electrostatic calculations of Bushby and Tytko, the model proposed in this reference is consistent with properties such as the absolute minimum which experimentally defines the lithium atom position in fluorenyllithium L$_2$, the orientation of the N–Li–N fragment with respect to the π carbanion, and variations in N–Li distances as a function of aromatic pK_a. See, also: Sygula, A.; Lipkowitz, K.; Rabideau, P. W. *J. Am. Chem. Soc.* **1987**, *109*(22), 6602.

(7) The early main group metals (e.g., Li, Be, Al) make use of their vacant s/p orbitals to a varying degree. In the case of methyllithium, the degree of ionicity has been suggested to range from 100% (Streitwieser, A. J.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. Collins, J. B.; Streitwieser, A., Jr. *J. Comp. Chem.* **1980**, *1*(1), 81) to 60% (Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 4572). The most recent theoretical work supports the point of view that while the lithium–carbon bond is predominantly ionic, a significant amount of covalent or *directed* polarization bonding is present in organolithium chemistry (Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*(2), 735. Schiffer, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1986**, *124*(2), 172). Messmer, R. P.; Tatar, R. C. *Gov. Rep. Announce. Index (U.S.)* **1987**, *87*(24), Abstr. 1987, No. 756,470. Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*(20), 5909. Organolithium compounds are therefore electron deficient both in the sense of having more available orbitals than electrons and as sources of strong Lewis acid sites with high polarizabilities and charge/volume ratios.

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(10) Neutron diffraction data were measured at 5, 101, and 293 K on the H4 satellite beam line at Brookhaven National Laboratory. All lines were indexed in the tetragonal system with lattice constants at the above temperatures of a = 5.622 (1), 5.631 (1), and 5.833 (1) Å and c = 10.865 (2), 10.901 (1), and 10.938 (1) Å, respectively. The structure was solved by a combination of (1) using Patterson techniques and estimated peak intensities, (2) packing models based on the relative intensities of the Bragg reflections, and (3) comparisons with known binary structures of the form AB$_2$. The fact that the c unit cell axis is approximately 2a and the above considerations led to the refined structure (5 K) shown in Figure 1 in the space group $I4_1/a$ with wR_p = 0.098, R_p = 0.077, χ^2 = 1.70.

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comparable, but shorter than Li–H distances previously observed for organolithium compounds (e.g., 1.96 (1) Å for the shortest α-carbon hydrogen atom in cyclohexyllithium[5,19]), The puckering of the four-atom lithium rings shown in Figure 2 optimizes the close approach of C(1)–Li(1) (2.17 (2) Å) and Li(1)–D(1) (1.72 (2) Å). The observed D(1)–C(1)–D(2) angle is 100 (1)° with C–D distances of 1.09 (1) Å (C(1)–D(1)) and 1.18 (2) Å (C-(1)–D(2)).

The local geometry about the carbon atom (Figure 2) suggests two types of C–D coordination if one considers closest-neighbor interactions. The coordination to D(1) can be viewed as I, while that for D(2) is best represented by the semibridging model II
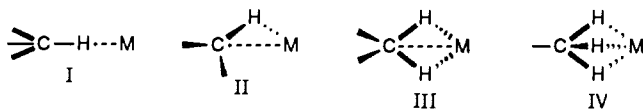
with coordination to the C–D bond (C–Li, 2.17 (2) Å; Li–D, 1.99 (3) Å). This configuration is also found in cyclohexyllithium[5,19] (C–Li, 2.184 (3) Å; Li–H, 2.00 (1) Å). III and IV have been previously described for the CH_3 groups in $LiB[CH_3]_4$[4] (C–Li, 2.207 (9) Å, Li–H, 2.115 (8) Å (III); C–Li, 2.359 (11) Å, Li–H, 2.231 (10) Å (IV)).

In the field of polylithium organic compounds, there have been extraordinary predictions of unusual geometries and, in particular, "hypervalent" polylithium compounds[20,21] which have forecast stabilities of such species as CLi_5,[22] CLi_6, and even CLi_8 neutral species. The environment of the carbon atom in the dilithiomethane structure could easily lead to such fragments, and indeed CLi_3H^+ has been observed by flash vaporization mass spectrometry.[23] Comparisons with previous theoretical models of molecular oligomeric groups made up of Li_2CD_2 units[9] are limited by the difficulty of appropriately including Li–H–C bonding interactions which are primarily responsible for the observed extended structure. The results obtained in this study clearly confirm the importance of metal···H–C bonding in the chemistry and structural properties[4,5,24] of early main group organometallics.

Supplementary Material Available: Structural parameters for CD_2Li_2 including the space group, Rietveld analysis fit of observed diffraction pattern, structural coordinates, and selected bond distances and angles (3 pages). Ordering information is given on any current masthead page.

(18) Another interesting comparison is with BeH_2, which has Be–H distances ranging from 1.38 (2) to 1.44 (2) Å (Smith, G. S.; Johnson, Q. C.; Smith, D. K.; Cox, D. E.; Snyder, R. L.; Zhou, R.-S.; Zalkin, A. Brookhaven National Synchrotron Light Source Annual Report; 1988, p 227.

(19) At 70 °C, cyclohexyllithium eliminates cyclohexene to give LiH. We find that, over a period of a year, dilithiomethane converts extensively to LiH at ambient temperatures. The average α-hydrogen–lithium atom distance in cyclohexyllithium (2.003 (7) Å) is also less than the Li–H distance in lithium hydride (2.043 Å) (Zintl, E.; Harder, A. *Z. Phys. Chem., Abt. B* **1935**, *28*, 478).

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Direct Evidence of the Triplet-State Origin of the Slow Reverse Proton Transfer Reaction of 3-Hydroxyflavone

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For many excited-state intramolecular proton transfer (ESIPT) molecules such as most of the derivatives of salicylic acid,[1-5] both experimental and theoretical results have concluded either the existence of a single minimum potential energy surface or a double minimum potential in which rapid tunneling is responsible for ultrafast proton transfer in the singlet excited state, However, the shape of the ground-state potential energy surface for several ESIPT molecules has raised many controversies. One prominent case is the study of 3-hydroxyflavone (3HF).

The first dynamic study of the ground-state reverse proton transfer of 3HF was reported by Itoh et al. By using transient absorption and two-step laser-induced fluorescence (TSLIF) measurements, they demonstrated that an unexpectedly long-lived ground-state tautomer (~microseconds) is involved in the reverse proton transfer at room temperature.[6,7] Consequently, Aartsma and co-workers reexamined the ground-state reverse proton transfer by means of picosecond time-resolved absorption spectroscopy coupled with a stimulated emission pumping technique.[8] Contradictory to the results of Itoh et al., they put a lower limit of 3 × 10^{10} s^{-1} on the rate of the ground-state reverse proton transfer. Shortly after Aartsma's report, Itoh et al. published detailed transient absorption and TSLIF studies to reconfirm the existence of the long-lived ground-state tautomer.[9,10] However, in the meantime, from the observation of the gain spectrum profile of the amplified spontaneous emission of 3HF, Chou et al. suggested that the energy barrier for the ground-state reverse proton transfer was negligibly small.[11] In addition, Brucker and Kelley, by analysis of the homogeneous bandwidth for matrix-isolated 3HF at 30 K, proposed a lower limit of 60 fs for the ground-state reverse proton transfer reaction.[12]

Most recently we have conducted transient absorption and TSLIF measurements for 3HF in combination with a photo-oxygenation study in order to resolve these controversies.[13-15] Although our kinetic results are qualitatively in agreement with those obtained by Itoh et al., several detailed quantitative analyses discount the assignment of the long-lived species to the ground-state tautomer singlet state. We summarize the key results as follows:

(1) The yield of tautomer emission from the TSLIF measurement (probed at 437 nm) is only ~0.013 of the non-time-resolved tautomer emission at room temperature.

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