

## Structure of Solvent-Free, Monomeric CH<sub>3</sub>Li and CH<sub>3</sub>Na

Douglas B. Grotjahn,<sup>\*,†</sup> T. C. Pesch,<sup>‡</sup> J. Xin,<sup>‡</sup> and L. M. Ziurys<sup>\*,‡</sup>

Department of Chemistry  
San Diego State University, 5500 Campanile Drive  
San Diego, California 92182-1030

Department of Chemistry and Biochemistry  
Box 871604, Arizona State University  
Tempe, Arizona 85287-1604

Departments of Chemistry and Astronomy  
and Steward Observatory, University of Arizona  
Tucson, Arizona 85721

Received July 31, 1997

Organoalkali derivatives are among the strongest bases known, and are widely used to make other bases by deprotonation or to introduce organic groups into organic and organometallic compounds by substitution or addition reactions.<sup>1</sup> The reactivity of organoalkalis depends on their structure, which is dominated by the tendency toward aggregation. The degree of aggregation in solution as well as in the solid phase depends critically on the organic residue, the solvent(s), and coligands present during the synthesis or crystallization.<sup>2</sup> However, with few exceptions,<sup>3c,e</sup> theoretical treatments of organoalkalis have focused on monomeric, solvent-free species,<sup>3</sup> particularly the simplest compounds CH<sub>3</sub>M. Monomeric but solvated aryllithiums have been generated with use of sterically demanding aryl groups,<sup>4a</sup> and monomeric, unsolvated LiCH(SiMe<sub>3</sub>)<sub>2</sub>, featuring sterically and electronically non-innocent substituents, was studied by gas-phase electron diffraction.<sup>4b</sup> Thus, detailed comparison of the theoretical structure of archetypal organoalkalis CH<sub>3</sub>M with experimental data has been impossible because the solvent-free monomers have been characterized only by IR spectroscopy at low temperatures in a matrix,<sup>5,6</sup> and because vaporization of the CH<sub>3</sub>Li tetramer does not seem to lead to the monomer.<sup>7</sup> Here we report the first unambiguous structural characterization of monomeric CH<sub>3</sub>Li and CH<sub>3</sub>Na in

the absence of other ligands, using millimeter/submillimeter spectroscopy. These results should serve as a benchmark by which further calculations can be refined.

Measurements of CH<sub>3</sub>Li and CH<sub>3</sub>Na and isotopomers were taken with a direct absorption spectrometer in the continuous-wave mode.<sup>8</sup> Phase-locked Gunn oscillators with frequencies in the range 65–140 GHz were used as the radiation source. Schottky-barrier diode multipliers were used to double, triple, or quadruple the frequency to obtain an overall frequency range of 65–560 GHz. The reaction chamber was a double-pass cell 0.5 or 0.7 m in length. In the cell either (CH<sub>3</sub>)<sub>4</sub>Sn or (CH<sub>3</sub>)<sub>2</sub>Hg (~5 mTorr) was reacted with Li or Na vapor (≤1 mTorr) to produce CH<sub>3</sub>Li or CH<sub>3</sub>Na.<sup>9</sup> Argon (~10–20 mTorr) was used as a carrier gas for the metal. (CD<sub>3</sub>)<sub>2</sub>Hg and Li enriched in <sup>6</sup>Li were used to make isotopomers. To carry out a frequency measurement, scans 5 MHz in width were made, both in decreasing and in increasing frequency, and one or two pairs of such scans were then averaged.<sup>10</sup> Line widths varied from 200 to 900 kHz in the frequency range 91–510 GHz, primarily because of modulation broadening, and typically 20–40 data points were taken over an absorption line. Gaussian functions were used to fit the data. Experimental accuracy of frequencies is estimated to be ±50–100 kHz.

CH<sub>3</sub>M has a C<sub>3v</sub> symmetry axis, making it a symmetric top molecule with a <sup>1</sup>A ground electronic state when M is an alkali metal. Hence, its rotational quantum number is *J* and the quantized projection of rotational angular momentum along the symmetry axis results in a *K*-ladder structure (*J* ≥ *K*) for each transition. Since the Li and Na compounds are closed shell species, no fine or magnetic hyperfine structure was present. Nuclear quadrupole interactions involving <sup>6</sup>Li, <sup>7</sup>Li, or <sup>23</sup>Na were not seen, but the *J* = 1 ← 0 transitions where this is most likely to be resolved were below the frequency range of the spectrometer. The resulting molecular constants are shown in Table 1 and were derived with use of a <sup>1</sup>A Hamiltonian. Also listed in Table 1 are the number of transitions per isotopomer and the *J* and *K* ranges. The rotational constant *B*<sub>v</sub> (= *B*<sub>0</sub>), the first order centrifugal distortion constants *D*<sub>*JK*</sub> and *D*<sub>*J*</sub>, and second order distortion parameters *H*<sub>*KJ*</sub> and *H*<sub>*JK*</sub> were needed to fit the data within experimental uncertainty,<sup>11</sup> but only *B*<sub>0</sub> was needed to determine the moment of inertia *I*<sub>0</sub> and hence the structure. The structure of CH<sub>3</sub>M (Scheme 1) was considered to be a function of three variables, bond lengths *r*<sub>CM</sub> and *r*<sub>CH</sub> and the H–C–H angle (*θ*).<sup>12</sup>

The pivotal role of CH<sub>3</sub>Li in theoretical treatments of organolithium compounds led us to synthesize the three isotopomers <sup>12</sup>C<sup>1</sup>H<sub>3</sub><sup>7</sup>Li, <sup>12</sup>C<sup>2</sup>H<sub>3</sub><sup>7</sup>Li, and <sup>12</sup>C<sup>1</sup>H<sub>3</sub><sup>6</sup>Li, so as to indepen-

<sup>†</sup> San Diego State University (current address) and Arizona State University. E-mail: grotjahn@chemistry.sdsu.edu.

<sup>‡</sup> University of Arizona.

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(9) Schlenk, W.; Holz, J. *Ber.* **1917**, *50*, 262–274. CH<sub>3</sub>Li was made without using a discharge, whereas CH<sub>3</sub>Na required application of a dc discharge with a current of 30 mA at 300 V. Other precursors have been explored: CH<sub>3</sub>Na can be made from Na and CH<sub>4</sub> with a discharge, and very recent results show that CH<sub>3</sub>Li can be made from Li and CH<sub>3</sub>I without a discharge.

(10) Transition frequencies and an example of a spectral scan appear in the Supporting Information.

(11) The rotational constant *A*<sub>v</sub> and centrifugal distortion parameters *D*<sub>*K*</sub> and *H*<sub>*K*</sub> could not be determined because only transitions involving Δ*K* = 0 were measured. The errors quoted in Table 1 are 3σ and are based only on the statistics of the analysis. Residuals *ν*<sub>obs</sub> – *ν*<sub>calc</sub> using the five parameters were typically less than 70 kHz.<sup>10</sup>

(12) Some workers report the H–C–H angle *θ*, others the H–C–M angle. If the latter quantity is defined as α, one can calculate *θ* using the expression cos *θ* = 1 – [<sup>3</sup>/<sub>2</sub> sin<sup>2</sup> α].

**Table 1.** Molecular Constants for CH<sub>3</sub>Li and CH<sub>3</sub>Na Isotopomers ( $\tilde{X}^1A_1; v = 0$ )<sup>a</sup>

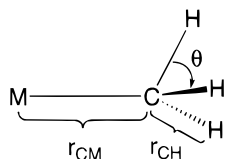
| parameter                                  | <sup>12</sup> C <sup>1</sup> H <sub>3</sub> <sup>7</sup> Li <sup>b</sup> | <sup>12</sup> C <sup>1</sup> H <sub>3</sub> <sup>6</sup> Li <sup>c</sup> | <sup>12</sup> C <sup>2</sup> H <sub>3</sub> <sup>7</sup> Li <sup>d</sup> | <sup>12</sup> C <sup>1</sup> H <sub>3</sub> <sup>23</sup> Na <sup>e</sup> | <sup>12</sup> C <sup>2</sup> H <sub>3</sub> <sup>23</sup> Na <sup>f</sup> |
|--|--|--|--|---|---|
| <i>B<sub>v</sub></i>                       | 22945.7401(22)   | 25283.349(11)  | 19272.84(27)   | 9485.05828(59)  | 7963.3412(34)   |
| <i>D<sub>J</sub></i>                       | 0.124548(12)   | 0.148732(62)   | 0.0763(20)   | 0.0236518(13)   | 0.0153931(33)   |
| <i>D<sub>JK</sub></i>                      | 3.06741(12)  | 3.64753(38)  | 1.690(13)  | 0.565704(61)  | 0.337048(46)  |
| <i>H<sub>JK</sub></i> (× 10 <sup>5</sup> ) | 18.804(60)   | 24.47(14)  | 4.1(8.5)   | 0.9615(27)  | 0.5435(52)  |
| <i>H<sub>KJ</sub></i> (× 10 <sup>4</sup> ) | 6.587(12)  | 8.115(68)  | 1.89(90)   | 0.8537(33)  | 0.2949(71)  |

<sup>a</sup> In MHz; errors quoted are 3σ in units of the last quoted decimal places. <sup>b</sup> 65 transitions observed; *J* = 1–11, *K* = 0–10. <sup>c</sup> 34 transitions observed; *J* = 6–9, *K* = 0–8. <sup>d</sup> 24 transitions observed; *J* = 6–9, *K* = 0–8. <sup>e</sup> 81 transitions observed; *J* = 15–27, *K* = 0–10. <sup>f</sup> 34 transitions observed; *J* = 20–24, *K* = 0–9.

**Table 2.** Comparison of Experimental and Calculated Metrical Parameters for CH<sub>3</sub>Li and CH<sub>3</sub>Na

| molecule                          | source               | basis set   | Li–C (Å)      | C–H (Å)            | H–C–H angle (deg)           | ref       |
|-----------------------------------|----------------------|-------------|---------------|--------------------|-----------------------------|-----------|
| CH <sub>3</sub> Li                | mm wave <sup>a</sup> |             | 1.959         | 1.111              | 106.2                       | this work |
|                                   | IR in matrix         |             | ca. 2.10      | ca. 1.12           | 107.3 or 109.5 <sup>b</sup> | 5a        |
|                                   | <i>ab initio</i>     | STO-4G      | 1.969         | 1.122              | 104.2                       | 3a        |
|                                   |                      | SS          | 2.032         | 1.092              | 107.1                       |           |
|                                   |                      | SS+d        | 2.021         | 1.089              | 105.8                       |           |
|                                   |                      | various     | 2.000 ± 0.004 | 1.096 ± 0.003      | 106.8 ± 0.7                 | 3c        |
|                                   | <i>ab initio</i>     | MP2/6-311G* | 1.983         | 1.098              | 106.2                       |           |
|                                   |                      | 6-31G*      | 2.0013        | 1.0934             | 106.2                       | 3d        |
| 6-31+G*                           |                      | 2.005       | 1.099         | 107.3              | 3e                          |           |
| (CH <sub>3</sub> Li) <sub>4</sub> | X-ray                |             | 2.31(5)       | 0.96(5)            | 111(8)                      | 6a        |
| CH <sub>3</sub> Na                | mm wave <sup>a</sup> |             | 2.299         | 1.091 <sup>c</sup> | 107.3                       | this work |
|                                   | <i>ab initio</i>     | 6-31G*      | 2.3236        | 1.0910             | 107.2                       | 3d        |

<sup>a</sup> *r*<sub>0</sub> structure. <sup>b</sup> Assumed values. <sup>c</sup> Assumed value (from ref 3d).

**Scheme 1**

dently determine values of *r*<sub>CM</sub>, *r*<sub>CH</sub>, and  $\theta$ .<sup>13</sup> For the Na analog, the isotopomers <sup>12</sup>C<sup>1</sup>H<sub>3</sub>Na and <sup>12</sup>C<sup>2</sup>H<sub>3</sub>Na were made, and a value of *r*<sub>CH</sub> = 1.091 Å from theory<sup>3d</sup> was assumed. The derived geometrical parameters are shown in Table 2 along with previously reported values from *ab initio* calculations. As far as we can tell, the C–Li distance is the shortest one known for an organolithium,<sup>2,14</sup> reflecting the small size of the organic portion: the closest examples are presented by an ether-solvated, hindered monomeric aryllithium [2.017(7) Å]<sup>4a</sup> and unsolvated LiCH(SiMe<sub>3</sub>)<sub>2</sub> [2.03(6) Å].<sup>4b</sup> Similarly, the C–Na distance in CH<sub>3</sub>Na appears to be the shortest reported to date.<sup>2c</sup> The H–C–H angle in CH<sub>3</sub>Li and CH<sub>3</sub>Na is small for CH<sub>3</sub>X compounds,<sup>15</sup> but agrees with results of *ab initio* calculations<sup>3</sup> and qualitative predictions based on distortion of symmetrical sp<sup>3</sup> hybridization by the highly electropositive nature of X = Li or Na.<sup>16</sup> Comparison of our experimental results with those from *ab initio* calculations reveals that the agreement on

(13) (a) The one assumption made is that the C–H and C–D bond lengths are equal. A complete isotopic substitution study on HCN<sup>13b</sup> showed that this assumption altered bond lengths by no more than approximately 0.01 Å. (b) Winnawisser, G.; Maki, A. G.; Johnson, D. R. *J. Mol. Spectrosc.* **1971**, *39*, 149–158. See also: DeLucia, F. C.; Helminger, P. A. *J. Chem. Phys.* **1977**, *67*, 4262–4267.

(14) The trend toward longer metal–carbon bonds on increased oligomerization or solvation is a well-established phenomenon.<sup>2</sup>

(15) (a) Experimental values: Harmony, M. D.; Laurie, V. W.; Kuczowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619–721. (b) Discussion of theory and experiment: Topsom, R. D. *Prog. Phys. Org. Chem.* **1987**, *16*, 85–124.

H–C–H angles and C–H bond length is good, but the experimentally determined C–M bond lengths are somewhat shorter. Because differences in bond lengths in experimental or theoretical *r*<sub>c</sub> and experimental *r*<sub>0</sub> structures such as ours are typically on the order of 0.01 Å or less,<sup>15</sup> precision rivalling or exceeding that from X-ray or neutron diffraction,<sup>15</sup> we ascribe at least some of the difference to the difficulties in calculations involving highly electropositive or electronegative elements.<sup>17</sup>

Finally, from the centrifugal distortion coefficient and the rotational constant we estimated the C–Li stretching frequency to be 670 cm<sup>−1</sup>, in reasonable agreement with the value obtained in matrix isolation studies (530 cm<sup>−1</sup>) considering all the assumptions made.<sup>5a,18</sup>

In summary, we have determined the geometrical parameters of highly reactive CH<sub>3</sub>Li and CH<sub>3</sub>Na for the first time. The extension of these studies to other organoalkalis and low-coordinate organometallics is the subject of ongoing and future work.

**Acknowledgment.** This research was supported by National Science Foundation Grants Nos. CHE 9531244 (to D.B.G. and L.M.Z.) and AST 95-03274, and NASA Grant No. NAGW 2989 (to L.M.Z.).

**Supporting Information Available:** Tables of transition frequencies for the isotopomers presented and a representative K ladder spectrum for <sup>12</sup>C<sup>1</sup>H<sub>3</sub><sup>7</sup>Li (5 pages). See any current masthead page for ordering and Internet access instructions.

JA972613Q

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(18) (a) For Li–H,  $\omega_{Li-H}$  = 1405 cm<sup>−1</sup> and *r*<sub>0</sub> = 1.608 Å,<sup>18b</sup> reflecting the smaller mass and radius of the H atom compared with those of C in LiCH<sub>3</sub>. (b) Plummer, G. M.; Herbst, E.; DeLucia, F. C. *Astrophys. J.* **1984**, *282*, L113–114 and references therein.