

## Proposal for the Mechanism of Inversion of Alkyl-lithiums

By TIMOTHY CLARK and PAUL V. R. SCHLEYER\*

(Institut für Organische Chemie der Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany)

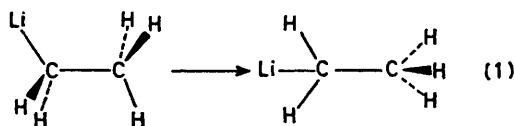
and JOHN A. POPLE

(Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213)

**Summary** The experimentally observed inversion at the  $\text{RCH}_2\text{Li}$  carbon within alkyl-lithium aggregates is indicated by *ab initio* molecular orbital calculations on model compounds to involve novel  $\text{RCH}_2\text{Li}_2$  fragments in which two lithium atoms stabilize a planar  $\text{RCH}_2$  group.

THE inversion barriers in primary alkyl-lithiums,  $\text{RCH}_2\text{Li}$ , are known experimentally to be unusually low (ca.  $63 \text{ kJ mol}^{-1}$ ,  $15 \text{ kcal mol}^{-1}$ ), and appear to be independent of solvent.<sup>1,2</sup> A dissociation-recombination mechanism ( $\text{S}_{\text{E}}1$ ) via carbanions has been considered as a possibility,<sup>1</sup> but can be ruled out on energetic<sup>3</sup> and experimental grounds.<sup>2</sup> Although lithium substitution has been shown by *ab initio* molecular orbital theory to be remarkably effective in reducing the tetrahedral-planar energy difference in tetraco-ordinate carbon compounds,<sup>4</sup> planar methyl-lithium monomer ( $C_{2v}$ ) is calculated to be  $147.9 \text{ kJ mol}^{-1}$  ( $35.3 \text{ kcal mol}^{-1}$ ) less stable than the normal form ( $C_{3v}$ ),<sup>5</sup> a value too high to be consistent with the experimentally observed result. Fraenkel's n.m.r. line-shape analysis<sup>2</sup> indicates that inversion occurs within the strongly associated alkyl lithium aggregates,<sup>6</sup> which are found both in solution<sup>7</sup> and in the gas phase.<sup>3b</sup> We therefore have used *ab initio* molecular orbital theory<sup>8</sup> to investigate the effects of aggregation on alkyl-lithium inversion barriers.

Although the magnitude of alkyl-lithium aggregation energies<sup>6</sup> precludes a mechanism whereby inversion occurs in the monomers, we first considered the effect of alkyl substitution on the inversion of the carbon bonded to lithium in such species. As the planar-tetrahedral energy difference for ethyl-lithium (equation 1) ( $200.1$  and  $163.1 \text{ kJ mol}^{-1}$  at the minimal STO-3G<sup>9</sup> and split valence 4-31G<sup>10</sup> basis set levels on STO-3G geometries, respectively) is

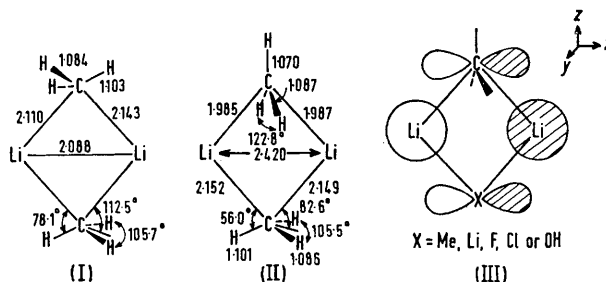


calculated to be  $15$ – $19 \text{ kJ mol}^{-1}$  less than that for MeLi ( $219.3$  and  $177.7 \text{ kJ mol}^{-1}$ ; Table), we believe that methyl can

safely be used to model the behaviour of the primary alkyl groups which have been used in the experimental studies.<sup>1,2</sup>

We next examined the methyl-lithium dimer, optimizing five geometries at the RHF/STO-3G level. The  $C_{2h}$  structure (I) is the most stable conformation of  $(\text{MeLi})_2$ .<sup>11</sup> To investigate a structure close to a possible inversion transition state, we chose the  $C_s$  structure (II) in which one methyl group is constrained to lie in a plane bisecting the Li-C-Li angle. Single point RHF/4-31G calculations were performed on these geometries. The results show that (II) is only  $60.5$  and  $97.3 \text{ kJ mol}^{-1}$  ( $14.5$  and  $23.3 \text{ kcal mol}^{-1}$ ) at STO-3G and 4-31G, respectively, less stable than the  $C_{2h}$  structure (I). Thus, even this degree of association is sufficient to lower the tetrahedral-planar energy difference of a Me group to a value compatible with the experimental results.

Stabilization of planar methyl groups in structures of type (III) appears to be a general phenomenon. The carbon  $p_x$  orbital of the planar methyl group interacts with an antisymmetric combination of lithium  $s$ -orbitals as in (III). The resulting molecular orbital is favoured by a planar methyl group, as the overlap of the carbon  $p_x$



orbital is more effective than that of a  $\pi \text{ CH}_3$  orbital of a pyramidal methyl group. The weak Li-Li bond found in (I) (Li-Li overlap population =  $+0.221$ ) is destroyed by the increase in Li  $2s$  coefficients for the antisymmetric combination (III), and the two lithiums in (II) become antibonding (overlap population =  $-0.501$ ). Ultimately this type of bonding results in the stable  $D_{3h}$   $\text{MeLi}_2^+$  ion.<sup>12</sup>

TABLE. Total energies and reaction enthalpies at the RHF/STO-3G optimized geometries for alkyl-lithium species.

Formula	Symmetry, Structure	Total energy/a.u. <sup>a</sup>		Relative energy/(kJ mol <sup>-1</sup> )	
		RHF/STO-3G	RHF/4-31G	RHF/STO-3G	RHF/4-31G
MeLi	$C_{3v}$	-46.42159 <sup>4</sup>	-46.95962 <sup>4</sup>	0.0	0.0
	$C_{2v}$ , planar	-46.33805 <sup>4</sup>	-46.89192 <sup>4</sup>	219.3	177.7
EtLi	$C_s$ , staggered <sup>b</sup>	-84.99605	-85.92765	0.0	0.0
	$C_s$ , C planar <sup>b</sup>	-84.91983	-85.86552	200.1	163.1
$(\text{MeLi})_2$	$D_{2d}$ (I)	-92.90686	-93.98554	0.0	0.0
	$C_s$ (II)	-92.88380	-93.94847	60.5	97.32
$(\text{MeLi})_4$	$T_d$ , eclipsed	-185.88464	—	0.0	—
	$T_d$ , staggered	-185.85778	—	70.5	—

<sup>a</sup> A.u. =  $2625.4 \text{ kJ mol}^{-1}$ . <sup>b</sup> See equation (1).

The most important consequence for alkyl-lithium inversion, however, is that the planar methyl group should be preferentially stabilized by association with a Li-Li edge, rather than a Li<sub>3</sub> triangular face.

Alkyl-lithium tetramers and hexamers consist of triangular Li<sub>3</sub> faces with attached pyramidal alkyl groups.<sup>7</sup> Alkyl-lithium hexamers have eight such Li<sub>3</sub> faces associated with the roughly octahedral arrangement of the six lithium atoms, but these are occupied by only six alkyl groups.<sup>13</sup> Inversion might take place during migration of one of these alkyl groups *via* an Li-Li edge to a vacant Li<sub>3</sub> face. This process would appear to be less favourable in tetramers (tetrahedral or approximately so) which have no vacant

faces, although concerted centre-to-edge movement of three of the four methyls (*via* a C<sub>3v</sub> transition state) is possible. The proposed inversion mechanism should be specific to methyl and primary alkyl-lithiums since at least two hydrogens are required on the α-carbon. Thus, because of steric problems secondary and tertiary alkyl-lithiums should have higher barriers to inversion by this mechanism.<sup>14,15</sup>

We thank the S.R.C./N.A.T.O. for a Postdoctoral Fellowship (to T.C.) and the N.S.F. (at Carnegie-Mellon) and the Fonds der Chemischen Industrie (at Erlangen) for support.

(Received, 10th October 1977; Com. 1053.)

<sup>1</sup> M. Witkowski and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 737.

<sup>2</sup> G. Fraenkel, W. E. Beckenbaugh, and P. P. Yang, *J. Amer. Chem. Soc.*, 1976, **98**, 6878.

<sup>3</sup> (a) The RHF/STO-3G energy for (MeLi)<sub>4</sub> → Me<sub>3</sub>Li<sub>4</sub><sup>+</sup> + Me<sup>-</sup> is 603 kJ mol<sup>-1</sup>; W. McLean, L. G. Pedersen, and R. C. Jarnagin, *J. Chem. Phys.*, 1976, **65**, 2491; see also A. Streitwieser, Jr., J. E. Williams, Jr., S. Alexandratos, and J. M. McKelvey, *J. Amer. Chem. Soc.*, 1976, **98**, 4778; (b) The appearance potential of the Et<sub>3</sub>Li<sub>4</sub><sup>+</sup> ion in the mass spectrum of (EtLi)<sub>4</sub> is 772 kJ mol<sup>-1</sup>; J. Berkowitz, D. A. Bafus, and T. L. Brown, *J. Phys. Chem.*, 1961, **65**, 1380.

<sup>4</sup> J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Amer. Chem. Soc.*, 1976, **98**, 5419.

<sup>5</sup> 6-31G\* calculations on 4-31G optimized geometries; M. B. Krogh-Jespersen, unpublished results.

<sup>6</sup> The calculated dimerization energies for methyl-lithium are -167 and -174 kJ mol<sup>-1</sup> at STO-3G and 4-31G, respectively. The STO-3G tetramerization energy is -521 kJ mol<sup>-1</sup>. (Energies are per dimer or tetramer). The clear preference of the tetramer for the eclipsed conformation also has been noted by McLean *et al.* (ref. 3a), and is in direct contrast to the X-ray results, which show a staggered conformation; E. Weiss and G. Hencken, *J. Organometallic Chem.*, 1970, **21**, 265).

<sup>7</sup> T. L. Brown, *Adv. Organometallic Chem.*, 1965, **3**, 365; *Pure Appl. Chem.*, 1970, **23**, 447; B. J. Wakefield, 'The Chemistry of Organolithium Compounds,' Pergamon Press, Oxford, 1974.

<sup>8</sup> All calculations were performed using the Gaussian 70 series of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople. Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

<sup>9</sup> W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657; the optimized geometries of MeLi, EtLi, (MeLi)<sub>2</sub>, and (MeLi)<sub>4</sub> (Table) will be made available upon request.

<sup>10</sup> R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 4064; the 5-21G basis set is used for lithium; J. D. Dill and J. A. Pople, *J. Chem. Phys.*, 1975, **62**, 2921.

<sup>11</sup> For an earlier calculation on (MeLi)<sub>2</sub> see: N. C. Baird, R. F. Barr, and R. K. Datta, *J. Organometallic Chem.*, 1973, **59**, 65.

<sup>12</sup> E. D. Jemmis, P. v. R. Schleyer, and J. A. Pople, manuscript in preparation.

<sup>13</sup> For X-ray structures of organolithium hexamers see, R. Zerber, W. Rhine, and G. Stucky, *J. Amer. Chem. Soc.*, 1974, **96**, 6048; T. F. Schaaf, W. Butler, M. D. Glick, and J. P. Oliver, *J. Amer. Chem. Soc.*, 1976, **96**, 7593.

<sup>14</sup> See, *e.g.* H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, 1964, **86**, 3283; M. P. Periasomy and H. M. Walborsky, *ibid.*, 1977, **99**, 2631.

<sup>15</sup> G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron Suppl.*, 1966, **7**, 189; R. L. Letsinger, *J. Amer. Chem. Soc.*, 1950, **72**, 4842; D. Y. Curtin and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, 1962, **84**, 1967.