Theoret. chim. Acta (Berl.) 13,259—261(1969)

Relationes

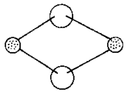
Bonding Properties in Organolithium Aggregates

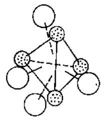
GARY R. PEYTON and WILLIAM H. GLAZE
Department of Chemistry, North Texas State University, Denton, Texas 76203

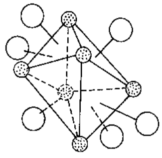
Received January 17, 1969

Results are given of the application of the CNDO/2 method to bonding in alkyllithium aggregates. Calculations relative to monomers and dimers of methyl-, ethyl-, and vinyllithium, plus methyllithium tetramer are described.

Organolithium compounds of the simplest type, *e.g.* methyl- and ethyllithium are known to form aggregates in solution [1] and in the solid [2, 3] and gas phases [4]. X-Ray diffraction data [2, 3] suggest that the tetramer II is a particularly stable structure. Nmr data [1] have also been rationalized in terms of this structure as well as a more reactive unit, the dimer I, which is apparently responsible for various lithium and alkyl group exchange processes. The hexameric structure III has also been postulated to account for six-fold association of ethyl- and *n*-butyllithium in hydrocarbon solution and in the gas phase [4].


I


II


III

Monomeric alkyllithium species have been postulated [5] as reactive intermediates in various chemical processes. Recently, monomers of methyllithium were reportedly produced in a solid argon matrix [6].

The nature of the covalent bonding in simple alkyllithiums has been the subject of three [3, 7, 8] simple treatments. We have extended these calculations by application of the CNDO/2 method [9, 10, 11]. The results of the calculation are shown in the Table. Whereas, the CNDO/2 method is known to give rather inaccurate values of the electronic energy, bond orders and electronic distributions are generally more reliable. We should like to emphasize two points relative to these calculations:

1. In each case, dimer and tetramer formation results in transfer of the excess negative charge from carbon to lithium atoms as reflected by the gross atomic populations. In a sense, the electron-deficient network of the dimer and tetramer may be thought of as an electron sink. The resulting delocalization of charge serves to decrease the polar nature of the carbon-lithium bond, and thereby to decrease the nucleophilicity of the alkyl group in the order; monomer > dimer

Table. *Results of* LCAO-MO-CNDO *calculations of alkyllithium compounds*[a]

Species[b]		MeLi	$(MeLi)_2$	$(MeLi)_4$	EtLi	$(EtLi)_2$	ViLi	$(ViLi)_2^c$	$(ViLi)_2^c$
Total energy, e.v.		−261.2	−539.7	−1113.2	−496.9	−1012.1	−451.3	−918.6	−916.4
	Li	.6322	.8036	.9077	.5881	.7584	.5988	.8394	.8303
Total	α-C	4.4383	4.4190	4.3417	4.3412	4.3095	4.3030	4.2182	4.2462
Atomic	β-C	—	—	—	4.0841	4.1015	4.0857	4.1232	4.1012
Populations	α-H	.9764	.9242	.9206	.9911	.9597	.9954	.9495	.9480
	β-H	—	—	—	1.0000	.9705	1.0086	.9348	.9372
Mulliken	Li–Li	—	.3963	.2282	—	.3777	—	.2829	.3440
Overlap									
Populations	Li–C	.7026	.4057	.2942	.6756	.3895	.6851	.4254	.4135

[a] Basis set included all valence orbitals of carbon and lithium and 1s orbitals of hydrogen; Slater exponents were taken as 1.625, 0.65, and 1.2 for carbon, lithium, and hydrogen respectively. Bond lengths in the monomer from 2.0 to 3.0 Å resulted in only 2% change in total energy and gross atomis populations for methyllithium. Parameters in the Hamiltonian matrix elements were taken from Pople and Segal [10, 11, 12]. Calculations were performed on a CDC 6600 at the University of Texas (Austin) using CNDO/2, QCPE 100.0 obtained from the Quantum Chemistry. Program Exchange, Indiana University.

[b] Me = methyl; Et = ethyl; Vi = vinyl.

[c] The more stable of the two vinyllithium dimers is entirely planar while in the other form the plane of the central C_2Li_2 cluster is normal to that of the organic groups. The C=C length was taken as 1.334 Å.

> tetramer. This result is apparently confirmed by the recent [13] C-nmr data reported by Waack and co-workers [12, 13], who estimated the excess negative charge at the carbon atom in the methyllithium tetramer to be only about 0.1 electron [13].

2. Lithium-lithium bond order (as measured by Mulliken overlap population) is quite substantial in the methyllithium tetramer. Brown [14] has recently suggested that intermetallic bond order may not be large in this system as evidenced by the absence of ^6Li–^7Li coupling in diethyl ether. The present results are consistent with the close Li–Li distance (2.5–2.6 Å) in the solid state [3], and suggest that the structure of the tetramer in donor solvents may be different from that in the solid state. Waack [13] has suggested a cubic structure which seems compatible with all of the data now available.

Note Added in Proof. While the present paper was being refereed, Cowley and White [J. Amer. chem. Soc. **91**, 34 (1969)] reported similar calculations on $LiCH_3$ and $[LiCH_3]_4$. While there are some minor differences, their results generally corroborate those found in this paper. More important, the trends in bonding properties from monomer to oligomer are demonstrated in both sets of calculations.

Acknowledgement. The financial support of the R. A. Welch Foundation and the NTSU Faculty Research Fund are gratefully acknowledged.

References

1. Brown, T. L.: Accts. chem. Res. **1**, 23 (1968).
2. Dietrich, H.: Acta crystallogr. **16**, 681 (1963).
3. Weiss, E., and E. A. C. Lucken: J. organometal. Chem. **2**, 1967 (1964).
4. Berkowitz, J., D. A. Bafus, and T. L. Brown: J. physic. Chem. **65**, 1380 (1961).
5. Waack, R., and P. West: J. organometal. Chem. **5**, 188 (1966).

6. Andrews, J.: J. chem. Physics **47**, 4834 (1968).
7. Brown, T. L.: Advan. organometal. Chem. **3**, 365 (1966).
8. Golovanov, IV., and A. K. Piskunow: Zhur. Struk. Khim. **5**, 933 (1964).
9. Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, S129 (1965).
10. —, and G. A. Segal: J. chem. Physics **43**, S136 (1965).
11. — — J. chem. Physics **44**, 3289 (1966).
12. McKeever, L. D., R. Waack, M. A. Doran, and E. B. Baker: J. Amer. chem. Soc. **90**, 3244 (1968).
13. — — — — Abstracts, 156th National Meeting, American Chemical Society, Atlantic City, New Jersey, September, 1968. We are grateful to Dr. Waack for supplying a preprint of his paper.
14. Brown, T. L., L. M. Seitz, and B. Y. Kimurs: J. Amer. chem. Soc. **90**, 3245 (1968).

Professor William H. Glaze
Department of Chemistry
North Texas State University
Denton, Texas 76203, U.S.A.