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STRUCTURE AND BONDING OF CH_2Li_2 DIMERS

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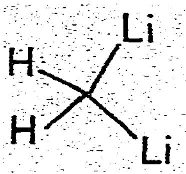
Summary

As models for polymeric dilithiomethane, a number of head-to-tail and head-to-head CH_2Li_2 dimer structures were optimized by means of *ab initio* molecular orbital calculations using the RHF/STO-3G minimal basis method. Split valence basis RHF/4-31G single point calculations indicated VIII, with four lithium atoms bridging two perpendicular CH_2 units, to be the most stable geometry for $(CH_2Li_2)_2$. The dimerization energy at this level of theory, 37 kcal/mole, is already considerable; it should be even larger with higher association. Possible trimer and polymer structures are suggested.

Introduction

When solvent-free methyl lithium is heated to 250°, methane is lost and dilithiomethane remains as a light brown amorphous powder[1]. Although useful synthetically[2,3], polymeric dilithiomethane has not been studied to any significant extent physically[4], and the structure is unknown. Recent *ab initio* molecular orbital calculations on CH_2Li_2 monomer have revealed remarkable features: the *cis*-planar form (I) is found to be only 2-10 kcal/mole less stable than the "tetrahedral" (C_{2v}) geometry (II)[5,6,7]. In contrast to methane, where the planar inversion barrier is inaccessibly high[5], monomeric CH_2Li_2 should undergo rapid stereomutation even at room temperature. To investigate the structure of polymeric dilithiomethane, it



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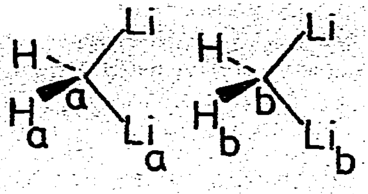

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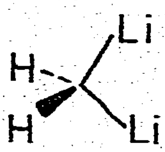

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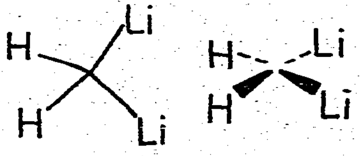


IV

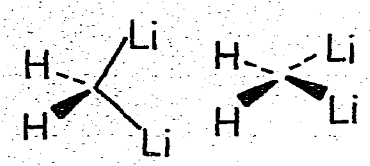
is desirable to have some indication of the structure of small oligomers and the nature and strength of the interaction. Also, the association with neighboring molecules may favor either the planar or the tetrahedral arrangement. In this paper, we present the results of an ab initio molecular orbital study of the structure of the dimer, $(CH_2Li_2)_2$, as a first step in answering these questions.

Computational Methods

All calculations were carried out using the Gaussian 70 series of programs[8a]. The minimal basis RHF/STO-3G method[9] was employed for full geometry optimization; single point calculations were then made at these geometries using the extended-basis RHF/4-31G method (5-21G for lithium)[10]. An SCF damping routine was used to achieve convergence in many cases[8b]. No allowance was made for electron correlation.

Dimer Structures

Two types of dimer structures were considered. In the first, designated "head-to-tail", the lithium atoms of one molecule interact with the hydrogens of the other. We have considered four such structures (III-VI), each with $\underline{C}_{2v}$ symmetry. III has tetrahedral arrangements at both carbons, IV has planar arrangements, and V and VI are mixed planar-tetrahedral



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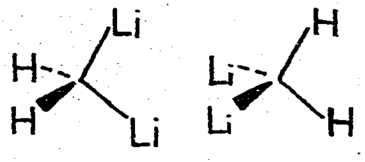

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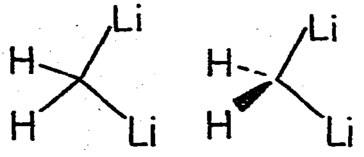

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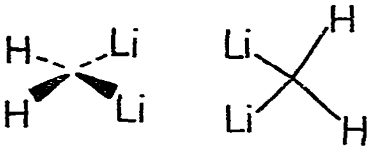
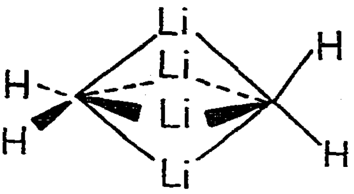


VIII

species. In the second dimer type the four lithium atoms are adjacent. For these "head-to-head" species we first considered the $\underline{D}_{2d}$ structures VII (two tetrahedral molecules) and VIII (two planar molecules). It should be noted that VII and VIII are interconvertible by moving the pairs of lithium atoms past each other. IX, in which all four lithium atoms lie in a single plane, is an intermediate structure in such a conversion. Structures X and XI can be obtained from IX first by bringing the CH_2 groups into one plane (X, $\underline{D}_{2h}$) and then by rotating the Li_4 ring by 45^{o} (XI, $\underline{D}_{2h}$). X and XI correspond to an ethylene, the CH_2 groups of which are separated by rings of four lithium atoms.



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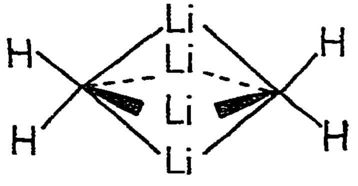

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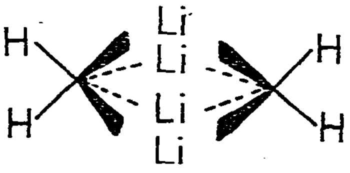

XI

The dimer structures III- XI were completely optimized within the imposed symmetry constraints at the RHF/STO-3G level. The resulting geometries are summarized in Table 1. The total and relative energies (optimized RHF/STO-3G and single-point RHF/4-31G values) are listed in Table 2. The last two columns give the dimerization energies relative to two monomers in the most stable (tetrahedral) conformation (II). Geometry optimization

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Table 1

RHF/STO-3G Optimized Structures of CH_2Li_2 Dimers[a,b]

Molecule	Point group	Parameter	Distance	Parameter	Angle
III	C_{2v}	C_aLi_a	1.950	$<Li_aC_aLi_a$	80.9
		C_aH_a	1.088	$<H_aC_aH_a$	104.0
		C_bLi_b	1.963	$<Li_bC_bLi_b$	106.5
		C_bH_b	1.102	$<H_bC_bH_b$	112.4
		C_aC_b	3.474		
IV	C_{2v}	C_aLi_a	1.798	$<Li_aC_aLi_a$	79.1
		C_aH_a	1.104	$<H_aC_aH_a$	100.2
		C_bLi_b	1.799	$<Li_bC_bLi_b$	100.1
		C_bH_b	1.104	$<H_bC_bH_b$	107.5
		C_aC_b	3.453		
V	C_{2v}	C_aLi_a	1.969	$<Li_aC_aLi_a$	84.4
		C_aH_a	1.088	$<H_aC_aH_a$	104.0
		C_bLi_b	1.817	$<H_bC_bLi_b$	97.7
		C_bH_b	1.105	$<H_bC_bH_b$	105.6
		C_aC_v	3.347		
VI	C_{2v}	C_aLi_a	1.787	$<Li_aC_aLi_a$	77.3
		C_aH_a	1.103	$<H_aC_aH_a$	100.4
		C_bLi_b	1.944	$<Li_bC_bLi_b$	108.7
		C_bH_b	1.094	$<H_bC_bH_b$	114.2
		C_aC_b	3.604		
VIII	D_{2d}	C_aLi_a	2.041	$<Li_aC_aLi_a$	93.3
		C_aH_a	1.104	$<H_aC_aH_a$	97.3
		C_aC_b	2.978		
IX	D_{2d}	C_aLi_a	2.117	$<Li_aC_aLi_a$	89.8
		C_aH_a	1.101	$<H_aC_aH_a$	97.8
		C_aC_b	3.001		
X	D_{2h}	C_aLi_a	2.103	$<Li_aC_aLi_a$	88.9
		C_aH_a	1.101	$<H_aC_aH_a$	97.1
		C_aC_b	3.002		
XI	D_{2h}	C_aLi_a	2.106	$<Li_aC_aLi_a$	88.9
		C_aH_a	1.100	$<H_aC_aH_a$	97.7
		C_aC_b	3.006		

[a] Distances in Ångströms and angles in degrees. [b] In the structures III-IX the atoms belonging to the CH_2Li_2 unit shown at the left are labelled *a* and those to right *b*.

Table 2

Total And Relative Energies of CH_2Li_2 Monomers and Dimers and Dimerization Energies Using STO-3G Optimized Geometries

Molecule	Total energy (a.u.)		Relative energy (kcal/mole)		Dimerization energy[a] (kcal/mole)	
	STO-3G	4-31G/5-21G	STO-3G	4-31G/5-21G	STO-3G	4-31G/5-21G
I[b]	-53.10751	-53.75805	16.7	10.4		
II[b]	-53.13407	-53.77454	0.0	0.0		
III	-106.30574	-107.57730	0.0	19.3	23.6	17.7
IV	-106.25721	-107.55187	30.5	35.3	-6.9	1.8
V	-106.28181	-107.56196	15.0	28.9	8.6	8.1
VI	-106.27826	-107.56291	17.2	28.3	6.4	8.7
VIII	-106.30526	-107.60807	0.3	0.0	23.3	37.0
IX	-106.30412	-107.60500	1.0	1.9	22.6	35.1
X	-106.28935	-107.59479	10.3	8.3	13.3	28.7
XI	-106.29177	-107.59476	8.8	8.4	14.8	28.7

[a] Relative to the energy of two tetrahedral monomers (II). [b] Reference 5

of VII leads directly to the other $\underline{D}_{2d}$ structure (VIII).

At both levels of theory, the most stable head-to-tail dimer is III, corresponding to the interaction of two tetrahedral molecules. The strength of this interaction (17.7 kcal/mole with the 4-31G basis) is due partly to dipole-dipole forces and partly to direct bonding between Li_a---H_b and Li_a---C_b. The direct bonding is indicated by the total Mulliken overlap populations of 0.05 for Li_a---H_b and 0.08 for Li_a---C_b (using the STO-3G basis). One significant structural feature is the closing of the Li_a-C_a-Li_a angle from 119.8° in the tetrahedral monomer II to 80.9° in the dimer III. This presumably increases the direct bonding to H_b and C_b.

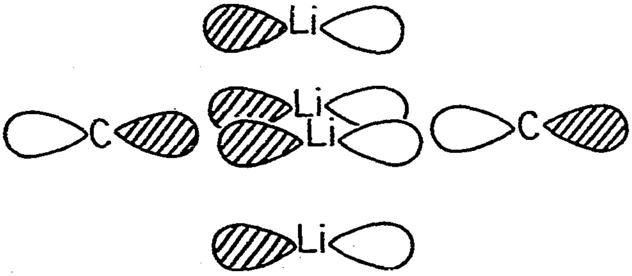
The head-to-head dimers have CLi_2 groups facing eath other. Of the structures studied, VIII is the most stable. At the higher level of theory (RHF/4-31G), the dimerization energy is 37.0 kcal/mole (19.3 kcal/mole more than for the best head-to-tail structure). This result strongly suggests that VIII represents the lowest energy structure for $(CH_2Li_2)_2$, but it must be emphasized that all possible geometrical arrangements were not considered.

The geometrical parameters for VIII are significant. The Li_a-C_a-Li_a and H_a-C_a-H_a angles are only 93.3° and 97.3°, respectively; thus, the dimer structure resembles closely the interaction of two planar monomers with square-planar geometries. As noted previously, if two tetrahedral monomers approach head-to-head to give a $\underline{D}_{2d}$ structure VII, no minimum is found and the energy continues downward as the lithium pairs pass each other (structure IX), a minimum finally being reached at VIII. In fact, the four lithium atoms in VIII are only slightly removed from planarity. Structure IX, which is not a local minimum, is only 1.9 kcal/mole above VIII (RHF/4-31G). Thus, even though the optimized structure VIII can be considered to be a head-to-head dimer of planar monomers, the distinction between "planar" and "tetrahedral" nearly vanishes; the carbon nuclei are 2.041Å from the "near" and 2.166Å from the "far" lithium atoms. From a conventional viewpoint, VIII has a remarkable structure indeed! The CH_2 groups comprise a perpendicular ethylene, but one whose components have been separated by a girdle of four bridging lithiums to the point where the direct interaction between carbons has essentially vanished. Rotation of one of the CH_2 groups in IX leads to X which is only 6.4 kcal/mole (4-31G/5-21G level) higher in energy than IX. Rotation of the girdle of lithiums in X by 45° leads to XI with relatively little change in energy; the lithium ring rotation is essentially free. We have not checked if X and XI represent local minima on the potential energy surface.

The electronic configuration of VIII (D_{2d} symmetry) (valence electrons only) is:

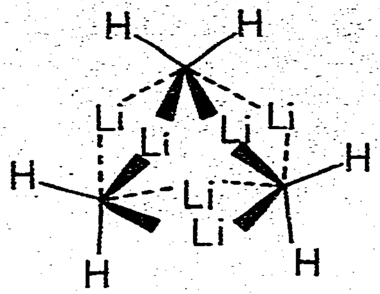
$$(1a_1)^2(1b_2)^2(1e)^4(2a_1)^2(2b_2)^2(2e)^4$$

If the Z-axis is chosen to lie along the line joining the two carbon atoms, the highest occupied molecular orbitals 2e represent "π-bonding" between $2p_x$ and $2p_y$ on carbon and appropriate combinations of lithium orbitals. The lower molecular orbital $1b_2$ would be antibonding if only 2s functions in lithium were included, but it becomes greatly stabilized by participation of lithium $2p_z$ orbitals (Scheme 1). The overlap population between a pair of lithium atoms equidistant from one carbon is antibonding (-0.26 at STO-3G) indicating the absence of a three-center two-electron bond among the CLi_2 groups which characterizes the electronic structure of I [5,6,7]. However, positive overlap population (0.15) is found between lithium atoms not equidistant from one carbon. These changes presumably reflect increased three-center bonding C--Li--C through molecular orbitals such as $1b_2$.

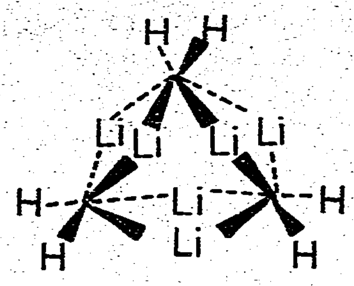


Scheme 1. Representation of the $1b_2$ molecular orbital of VIII.

The theory predicts that stereomutation of the tetrahedral monomer II can occur without activation through dimer formation. This is because structure IX, with all lithium atoms equidistant from both carbons, lies on the path from two monomers to the most stable dimer structure.



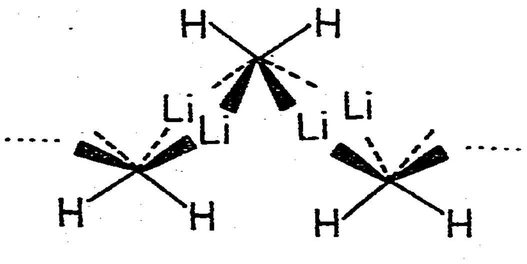
XII $\underline{D}_{3h}$



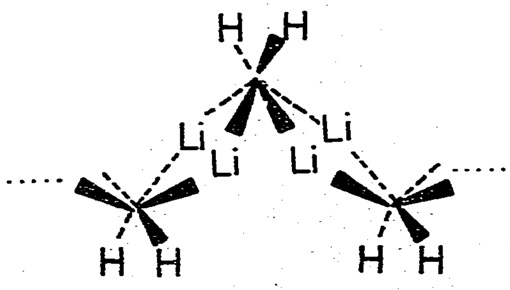
XIII $\underline{D}_{3h}$

Conclusions

The head-to-head structure VIII is indicated by RHF/4-31G molecular orbital calculations to be the most stable arrangement for the CH_2Li_2 dimer. A tendency for lithium to bond to both carbon atoms is the dominant feature in the association[11,12]. On this basis, structures such as XII and XIII are likely candidates for the trimer; similar bridging would be possible in polymeric structures XIV or XV. A number of polylithium compounds with gem-dilithio groupings are known[13]; perhaps these associate by similar head-to-head bonding.



XIV



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Acknowledgment

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