Journal of Organometallic Chemistry, 116 (1976) 251—256

AB INITIO CALCULATIONS ON VARIOUS FORMS OF CH_2Li_2

EDVIN WISLØFF NILSSEN * and ANNE SKANCKE
Department of Mathematical Sciences, University of Tromsø, 9000 Tromsø (Norway)
(Received March 5th, 1976)

Summary

Ab initio molecular orbital calculations have been carried out on tetrahedral and three different planar forms of CH_2Li_2. In terms of the energy differences between tetrahedral and planar forms, all the planar CH_2Li_2 forms are stabilized relative to those of unsubstituted tetravalent hydrocarbon compounds. An analysis has been made of the various factors contributing to this stabilization.

Introduction

The energy difference between tetrahedral and planar conformations of the methane molecule has been computed by several methods, giving energy differences of 5.5 to 10.8 eV [1—3] depending on the methods of calculations. Obviously, for existence, any planar derivative of methane must be stabilized in some way. Hoffmann [4] has suggested several possible ways of stabilizing a planar geometry.

Hoffmann's analysis begins with a consideration of the molecular orbitals for the planar structure of methane. Two electrons are engaged in normal sp^2 type hybrids at the carbon and form normal σ bonds with two hydrogens. The two other hydrogens are weakly engaged in three-center two electron bonds and the remaining two electrons on the carbon atom are placed in a pure $2p$ orbital perpendicular to the molecular plane. Resonance makes all C—H bonds equivalent.

Hoffmann suggests two ways to stabilize such a system: (1) substitution by electron-withdrawing groups; (2) participation of two $2p$ electrons in a $(4n + 2)\pi$ system. The latter was examined in a recent paper by Schoeller [5], and indeed, a substantial amount of stabilization has been obtained in spiro systems such as the ethylenebenzenium and acetylenebenzenium cations. In the MINDO/2 * approximation, planar forms are about 20 kcal mol^{-1} more stable than the tetrahedral forms.

---

* Modified Intermediate Neglect of Differential Overlap. (This method has been worked out by M. Dewar.)

We now describe an investigation of a different type of stabilization. It was thought that in addition to participation in a π system, the two carbon p electrons might also go to vacant p orbitals of a suitable acceptor.

A lithium molecule contains the following favourable features for this purpose: (a) the two electrons on the Li—Li σ bond may be donated to the vacant orbital in the HCH plane; (b) vacant p orbitals may accept the carbon p electrons; (c) little steric effect is expected because of the small size of lithium. The idea of a planar conformation of CH_2Li_2 has been introduced by Schleyer [6], but to our knowledge no complete study of the various conformers of this species has been published. We therefore made an investigation of this, looking explicitly at the electron transfer in each case. In particular, we were seeking possible stable conformers.

Method of calculation

This work is an ab initio all electron calculation. We have used the MOLECULE programme, kindly put at our disposal by Jan Alml0f [7]. The computation was carried through using a (7,3) gaussian type basis contracted to a double ζ set. For the carbon atom orbital exponents and contraction coefficients were taken from the work by Roos and Siegbahn [8]. Values for p orbitals on the Li atom were not found in the literature, and since these orbitals are essential in the present work, an optimization of Li—H was carried out. The results were in agreement with those obtained by extrapolation of the corresponding values for the elements B—Ne [8]. The resulting orbital exponents and contraction coefficients are given in Table 1. For hydrogen, a 4s contracted to double ζ basis set was used, the numerical values were taken from the work by Huzinaga [9]. All values were multiplied by a scaling factor of 1.25.

Four different models were considered in this calculation, see Fig. 1. In the following discussion the four forms are named A, B, C, and D, the symbols referring to Fig. 1. All forms have been geometry optimized; the resulting parameters are given in Table 2. A Mulliken type population analysis has been carried out for all four forms.

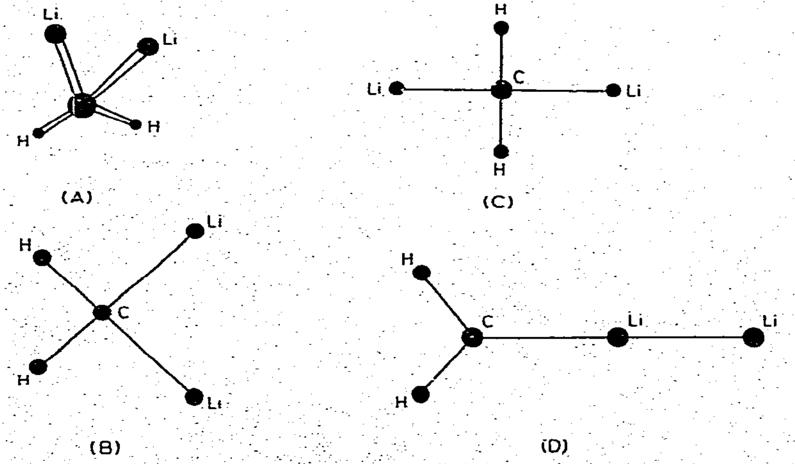

Fig. 1. Spatial arrangements of the various forms A, B, C, and D.

TABLE 1

p TYPE ORBITAL EXPONENTS AND CONTRACTION COEFFICIENTS FOR THE Li ATOM

Orbital exponent	Contraction coefficient
1.15	0.0832
0.15	0.433
0.04	1.0

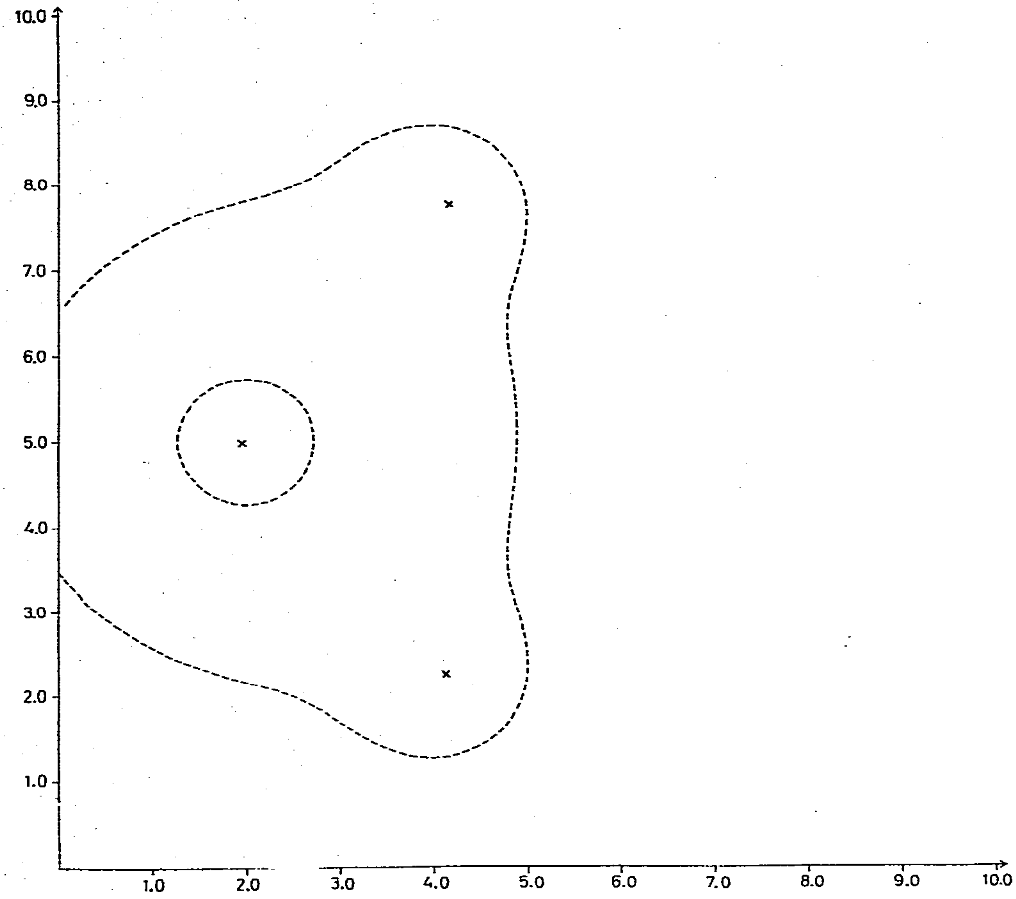

Fig. 2. Plot of the $1b_2$ orbital for form B.

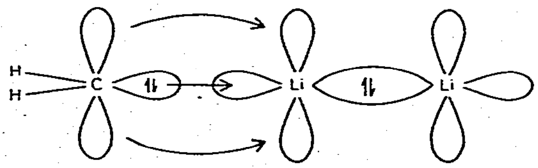

Fig. 3. Possible electron transfer in form D.

Results and discussion

As is seen in Table 1, the tetrahedral conformer A has the lowest energy, but an appreciable stabilization of planar forms B, C and D is observed; the energy difference between A and B being only 8.7 kcal mol^{-1}. Forms C and D are of about equal energy and some 43 kcal mol^{-1} less stable than A.

The optimized geometry of A shows a normal tetrahedral structure. The C—Li distance of 1.98 Å is 0.04 Å shorter than the optimized value for the $LiCH_3$ molecule in a minimum basis ab initio calculation by Fitzpatrick [10]. This may be taken as an indication of a greater ionic character of the C—Li bond in A, further confirmation of this is seen in Table 4 which gives the electronic charges. The increased positive charge on Li in our calculation compared to $LiCH_3$ [10] (0.365 and 0.143) clearly demonstrates ionic character, as does the very strongly negatively charged carbon. Furthermore, the calculated dipole moment of 2.23 D for this form also clearly shows ionic character.

Form B is seen to have geometric parameters rather different from A (Table 2). The C—Li bond of 1.83 Å is drastically shortened, while the ionic character, as judged from electronic charges, seems comparable. An explanation of the short C—Li bond distance and the high stability of this species is found by examining the orbital energies, which are given in Table 3. It is seen that the highest occupied orbital is of π type; that means that two electrons on the carbon atom are in a *p* orbital perpendicular to the HCH plane, and are able to form a three-centre two electron bond with the vacant lone pair orbitals on the Li atoms. A plot of this orbital is shown in Fig. 2. A ring current is seen to be generated over the CLiLi framework, the existence of which much be responsible for the favourable energy of this species and for the exceptionally short C—Li bond. In comparing orbital energies between A and B there is a tendency for lower orbital energies for B with respect to both inner shells and valence electrons. Neverthe-

TABLE 2

MOLECULAR PROPERTIES OF CH_2Li_2 CONFORMERS

Bond distances in Å units, dipole moments (μ) in D units and energies in atomic units

	Form			
	A	B	C	D *
C—Li	1.98	1.83	1.90	2.22
C—H	1.08	1.09	1.09 [a]	1.08 [a]
Li···Li	3.31	2.96	3.80	2.91
∠Li—C—Li	113°	108°	180° [a]	180° [a]
∠H—C—H	109°	85.9°	180° [a]	109°
Total energies	—53.7851	—53.7711	—53.7165	—53.7179
Nuclear repulsion energies	19.7409	20.8784	20.2471	15.5678
Dipole moments	2.23	1.44	0	2.63

* Note added in proof: Preliminary unrestricted Hartree—Fock calculations on this form assuming a triplet configuration $\cdots(6a,\,^{1}(1b_2)^1$ give a total energy of —53.7714 a.u. Further calculations on this point will be carried out within the framework of the restricted Hartree—Fock framework.

[a] Assumed values.

TABLE 3

ORBITAL ENERGIES FOR VARIOUS FORMS OF CH_2Li_2 (in a.u.)

A		B		C		D	
$1a_1$	−11.0874	$1a_1$	−11.1186	$1a_{1g}$	−11.1132	$1a_1$	−11.3618
$2a_1$	−2.3818	$2a_1$	−2.4057	$2a_{1g}$	−2.3938	$2a_1$	−2.4148
$1b_1$	−2.3817	$1b_1$	−2.4053	$1b_{3u}$	−2.3938	$3a_1$	−2.4137
$3a_1$	−0.7495	$3a_1$	−0.8006	$3a_{1g}$	−0.7697	$4a_1$	−0.9720
$1b_2$	−0.4247	$2b_1$	−0.4455	$1b_{2u}$	−0.5305	$1b_1$	−0.6503
$4a_1$	−0.2701	$4a_1$	−0.3375	$2b_{3u}$	−0.2424	$5a_1$	−0.4788
$2b_1$	−0.1867	$1b_2$	−0.1804	$1b_{1u}$	−0.1690	$6a_1$	−0.1505
				$4a_{1g}$	+0.0193	$1b_2$	−0.1495

TABLE 4

TOTAL ELECTRONIC POPULATION

	Form			
Atom	A	B	C	D
C	−1.028	−1.013	−1.171	−0.332
H	+0.149	+0.125	+0.280	+0.209
Li(1)	+0.365	+0.382	+0.305	−0.074
Li(2)				−0.01

TABLE 5

TOTAL OVERLAP POPULATION BETWEEN ATOMS

	Form			
Distance	A	B	C	D
Li···Li	−0.9454	+0.1566	−0.2274	+0.8586
C—Li	+0.6455	+0.6073	+0.6147	+0.1570
H—C	+0.6418	+0.5752	+0.6857	+0.6466

TABLE 6

OVERLAP POPULATION OF π ORBITAL

Distance	B $1b_2$	C $1b_{1u}$
Li···Li	0.1335	0.0996
C—Li	0.2426	0.2364

less the total energy of A is lower than B because of a favourable nuclear repulsion term. This term lowers the total energy of A by 1.13 a.u. compared to B. An explanation of the lower core energies may be found in the total populations given in Table 4, indicating higher positive charge on the Li atom in B. A comparison between valence orbitals is rather difficult because of different hybridizations on carbon for A and B. However, one explanation for the lower energies in B may lie in the more favourable electronic distribution due to the three-center bond.

A striking demonstration of the effect of the three-centre bonding is given in Table 5 where the total overlap population is shown. For B, the Li—Li overlap is +0.1566, compared to —0.9454 for A. The main part of the positive overlap in B is contributed by the π system, as shown in Table 6. The unusually high negative Li—Li overlap population in A combined with a Li···Li separation of 3.31 Å indicates substantial van der Waals repulsion. Comparing with the methane molecule, we have stressed the stabilizing effect of the three centre π system. The large negative Li···Li overlap in A may indicate that the tetrahedral structure in A is in fact destabilized by van der Waals repulsion compared to methane.

The planar form C (see Table 2 and Fig. 1) has some features similar to B. Compared to tetrahedral A, the nuclear repulsion term destabilizes C whereas the electronic energy term is more favourable in the planar C form. A three-centre π bond is also found in C, but our computations indicate that this linear three-centre orbital is less effective than the ring system in B. The π systems in B and C are symmetrically separated from other orbitals, meaning that the higher orbital energy of $1b_{1u}$ in C shows a weaker π system for this species.

The D form has a C—Li bond of 2.22 Å, drastically longer than the other forms. The total overlap population of this bond is only 1/4 its value in the other species (Table 5), whereas the Li—Li overlap population is now positive. In fact, this system may be regarded as a CH_2 fragment only weakly interacting with a Li—Li molecule. The total electronic charges differ greatly from those of the other forms. The carbon atom in D is almost neutral, the two inequivalent Li atoms being slightly negatively charged. The nuclear repulsion term is seen to favour D (Table 2) while the total electronic energy is disfavourable. Since the orbital energies are markedly lower in D, this may indicate that the nuclear attraction term is weakened.

Table 3 shows nearly degeneracy between the highest occupied and the lowest virtual orbital which is also bonding. Consequently, our assumption that the singlet state gives the lower energy for the D form, may be invalid.

References

1 R. Hoffmann, J. Amer. Chem. Soc., 92 (1970) 4992.
2 R. Hoffmann, Tetrahedron, 22 (1966) 521,539.
3 J.A. Pople and G.A. Segal, J. Chem. Phys, 44 (1966) 3289.
4 H.J. Monkhorst, Chem. Commun, (1968) 1111.
5 W.W. Schoeller, Chem. Commun., (1974) 872.
6 P.v.R. Schleyer, Communication at the 2. International Symposium of Nonbenzenoid Aromatic Compounds, Lindau, West Germany, 1974.
7 J. Almløf, USIP REPORT 72-09, University of Stockholm, 1972.
8 B. Roos and P. Siegbahn, Theor. Chim. Acta, 17 (1970) 209.
9 S. Huzinaga, J. Chem. Phys., 42 (1965) 1293.
10 N.J. Fitzpatrick, Inorg. Nucl. Chem. Lett., 10 (1974) 263.