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ON THE COMPUTATIONAL REALIZATION OF PLANAR TETRACOORDINATE CARBON

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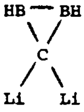
Abstract: 3,3-dilithio-1,2-diboracyclopropane (1), 1,1-dilithiocyclopropane (2), and 3,3-dilithiocyclopropene (3), three compounds indicated by earlier ab initio molecular orbital calculations to prefer planar geometries, have been re-examined at higher levels of theory, including effects of polarization functions and correlation energy.

For 1 and 2 the planar-tetrahedral energy difference previously reported is increased or remains the same on going to higher levels of theory. The contribution of lithium pi-acceptance to this reversal of the usual stability order is discussed. The stability of 2 to decomposition and isomerization to known compounds is considered.

Planar 3 is found to have no barrier to decomposition to cyclopropenylidene and dilithium, and so does not constitute a candidate for planar tetracoordinate carbon.

Introduction:

In spite of several proposed and/or attempted syntheses of compounds containing planar tetracoordinate carbon[1] and the evident fascination of the concept[1,2], there would seem to be only one experimental observation of such a compound[3], although there is strong evidence for the occurrence of low-energy rotational transition states of this geometry[4]. There have, however, been several computational realizations[5-9]. Minimal basis set ab initio molecular orbital calculations predict lithium substituents and/or small ring systems to be particularly effective in stabilizing planar tetracoordinate carbon[5-7]. Thus 1 - 4 were predicted by Pople, Schleyer and co-workers[5,6] to prefer planar to tetrahedral geometries, and this was attributed in part to



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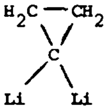

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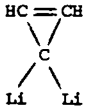

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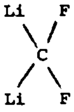

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the potential pi-acceptor ability of the lithium atom. It has been realized for some time, however, that minimal basis sets exaggerate the importance of lithium p-orbitals[10], and hence of lithium pi-acceptor ability. For this reason we have reinvestigated 1 - 4 at higher levels of theory. The results on dilithiodifluoromethane 4 have been reported elsewhere[11], and in this paper we report the results of our calculations on 1 - 3.

Computational Method:

Standard ab initio molecular orbital calculations were carried out using the GAUSSIAN 76[12], GAUSSIAN 82[13], and GAMESS[14] packages on the University of Manchester Regional Computer Centre CDC7600, University of Sussex VAX, and University of London Computer Centre CRAY-1S computers respectively. We have used the STO-3G minimal[15], 4-31G split-valence[16], and 6-31G*(5d) split-valence plus polarization[17] basis sets. Geometries were optimized by analytic evaluation of gradients of the energy[13,14] and the resulting stationary points were characterized by evaluation of harmonic vibrational frequencies[14]: if all the harmonic frequencies are real, the point is a local minimum (and not just a minimum within any imposed symmetry constraints), and if just one is imaginary the point is a saddle point (transition state). The effects of correlation energy were estimated by second-order Moller-Plesset perturbation theory (MP2)[18].

Results and Discussion:

3,3-dilithio-1,2-diboracyclopropane (1) and 1,1-dilithiocyclopropane (2).

The STO-3G and 4-31G optimum geometrical parameters of the planar and tetrahedral structures of 1 and 2 constrained to C_{2v} symmetry are given in Table 1. In an effort to assess the effects of further improvements of the basis set and correlation energy, we have carried out 6-31G*(5d)//4-31G[19] and MP2/4-31G//4-31G single point calculations. The energies[20] and energy differences obtained at the various levels of theory are given in Table 2.

Table 1. Optimum geometrical parameters of C_{2v} tetrahedral and planar geometries of 1 and 2. Bond lengths in Ångstroms, bond angles in degrees.

		STO-3G		4-31G	
		Planar	Tetrahedral	Planar	Tetrahedral
1	r(B-C)	1.489	1.510	1.507	1.518
	r(C-Li)	1.807	1.831	1.886	1.911
	r(B-H)	1.164	1.152	1.198	1.189
	θ(BCB)	61.46	61.15	62.64	63.26
	θ(LiCLi)	132.52	123.49	129.18	110.91
	θ(HBC)	144.29	140.67	139.20	140.07
2	$r(C_1-C_2)$	1.552	1.546	1.540	1.552
	$r(C_1-Li)$	1.728	1.944	1.807	1.965
	$r(C_2-H)$	1.082	1.081	1.079	1.080
	$\theta(C_2C_1C_3)$	58.01	58.99	58.57	57.94
	$\theta(LiC_1Li)$	103.69	107.79	107.68	111.75
	$\theta(HC_2C_1)$	120.26	120.24	120.89	121.02
	$\theta(HC_2H)$	112.93	111.56	112.70	110.70

Table 2. Energies (in Hartrees) of the C_{2v} planar and tetrahedral geometries and the planar-tetrahedral energy differences (kJ per mol) of 1 and 2.

	1			2		
	Planar	Tetrahedral	ΔE	Planar	Tetrahedral	ΔE
STO-3G// STO-3G	-101.91096	-101.89365	45.5	-129.07415	-129.06169	32.7
4-31G// 4-31G	-103.09894	-103.07292	68.3	-130.51126	-130.49976	30.2
6-31G*(5d) //4-31G	-103.23782	-103.20822	77.7	-130.68974	-130.67670	34.2
MP2/4-31G //4-31G	-103.31803	-103.29079	71.5	-130.80809	-130.79655	30.3

For 2 we see that the planar-tetrahedral energy difference is largely independent of the level of theory employed, the planar structure being preferred throughout by about 30 kJ per mol, while for 1 the STO-3G stability order is not merely preserved but the planar structure becomes even more favourable at the higher (more reliable) levels of theory. So, in spite of the well known[10,21] exaggeration of lithium pi-acceptor ability by minimal basis sets, more reliable methods also predict 1 and 2 to prefer planar to tetrahedral geometries. Moreover, computation of harmonic vibrational frequencies shows that planar (but not tetrahedral) geometries for 1 and 2 are local minima.

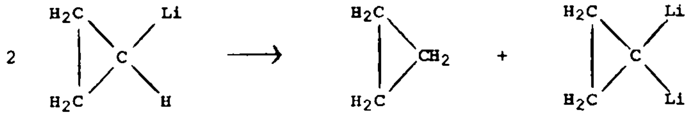
We now consider the role of lithium as a pi-acceptor in stabilizing planar 1 and 2. The usual Mulliken analysis[22] of molecular orbital wave functions of compounds containing lithium can be misleading because lithium 2s and 2p orbitals are very diffuse[21]. The Mulliken values can presumably be taken as upper bounds for the 'real' lithium p-orbital populations. In Table 3

Table 3. Lithium p-pi charges in C_{2v} planar geometries of 1 and 2.

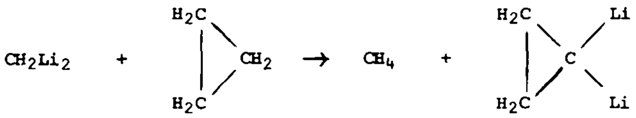
	1	2
STO-3G//STO-3G	0.17	0.47
4-31G//4-31G	0.09	0.30
6-31G*(5d)//4-31G	0.10	0.18

we give lithium pi charges for planar 1 and 2. These results suggest that there is no significant lithium pi-acceptance in 1, which is not unreasonable since boron is a much better pi-acceptor than lithium, and is in accord with the small difference between the Li-C distances in the two geometries (see Table 1). Thus both STO-3G and 4-31G calculations predict a carbon-lithium bond length contraction when 1 becomes planar of less than 0.03Å. Changes of similar magnitude are calculated for PH_3[23], NH_3[24], and CH_4[25], where, of course, no shortening due to pi-bonding may occur. For 2 the position is less clear cut. The degree of lithium pi-acceptance is undoubtedly exaggerated at the STO-3G level (Table 3). Both STO-3G and 4-31G calculations predict an appreciable carbon-lithium bond shortening in the planar form (Table 1). The better basis set predicts a smaller, but still significant lithium pi population, which decreases further on addition of d-functions to the basis set (Table 3). It should be said that the 4-31G basis set is describing lithium much better than carbon[21] (in organolithium compounds carbon is electron-rich and lithium is electron-deficient and the 4-31G basis uses the same number of functions to describe each of the two centres), and in consequence of this there may be a tendency to shorten the bond length. To test this hypothesis we have optimized the C-Li bond length in planar and tetrahedral 2 with the other geometrical parameters fixed at their 4-31G optimum values using the 6-31G basis set augmented with a set of diffuse s and p functions[26] on the carbon atoms. These calculations give carbon-lithium bond lengths of 1.81 and 1.96 Å for planar and tetrahedral 2 respectively and a lithium pi population of 0.19e for planar 2. These results suggest that there is significant lithium pi-acceptance in planar 2, but much less than is predicted by STO-3G and 4-31G calculations.

Only two geminal dilithioalkanes have as yet been prepared, dilithiomethane[27], and, much more recently, 1,1-dilithioethane 5[28]. The method of preparation of 5 is thought[28] to offer a route to the higher 1,1-dilithioalkanes. It is not at present applicable to 1 since the diboracyclopropyl group is not known, although three-membered rings containing two carbon atoms and one boron atom have recently been made[29]. Whether the method of Maercker and co-workers[28] could be used to synthesize 2 we cannot say. We can, however, estimate[30] the thermodynamic stability of 2 to isomerization and decomposition to known compounds. 5 eliminates lithium hydride[28], and this is one possible mode of decomposition of 2. At the 4-31G level 2 is in fact stable relative to 1-lithiocyclopropene 6 and monomeric LiH by 98.7 kJ per mol, but in condensed phases the lithium hydride will be polymeric, and the polymerization energy will be sufficient to render the elimination thermodynamically favourable. Thus we calculate two molecules of 2 to be stable relative to two molecules of 6 and $(LiH)_2$ by only 9.0 kJ per mol (of $(LiH)_2$). Although the organolithium compounds may be solvated or associated, any nett stabilization of the 1,1-dilithioalkanes is presumably less than the polymerization energy of LiH : 5 eliminates LiH[28] but 3-21G calculations[28] predict it to be stable relative to vinyllithium and monomeric LiH by 14.6 kJ per mol. 2 is unstable relative to allene or propyne and dilithium by over 125 kJ per mol, and to isomerization to dilithiated propene[31] by 220 kJ per mol. It is difficult to estimate barrier heights for these processes because molecular orbital wave functions do not usually describe bond breaking correctly, and the location of the transition states of 2 using correlated wave functions is prohibitively expensive. Moreover, the barrier heights for the analogous processes involving hydrocarbons are not a useful guide since the corresponding compounds have very different structural and electronic features to those considered here. Finally, it is of interest to compare the relative thermodynamic stabilities of 2 and 5. The presence of the second lithium atom destabilizes 5 relative to ethyllithium[28], and 2 is likewise destabilized relative to lithiocyclopropane : for the formal disproportionation



we calculate an energy change of 16.2 kJ per mol. The corresponding process for 5 is calculated at a similar level of theory to have an energy change of 25.5 kJ per mol[28]. Again like 5, 2 is destabilized relative to dilithiomethane: we calculate an energy change of 20.0 kJ per mol for the process



Similar calculations[28] predict the corresponding process involving 5 to have an energy change of 51.8 kJ per mol. Unlike 5[28], 2 is calculated to be marginally more stable (4.5 kJ per mol) than its 1,2-isomers. Such an energy difference may, however, easily be reversed at higher levels of theory. The much greater stability of 1,2-dilithioethane arises in part from favourable Li-H interactions[28] not possible in 1,2-dilithiocyclopropane.

3,3-dilithiocyclopropene (3)

The STO-3G calculations of Jemmis, Chandrasekhar, and Schleyer[6] indicate that the planar structure of 3 is preferred to the tetrahedral structure by 58 kJ per mol, and that the planar structure is best considered as a cyclopropenylidene-dilithium complex. Our 4-31G calculations predict the planar structure to have no barrier to loss of dilithium : in Table 4 we give the 4-31G energies obtained by optimizing the geometry of the planar structure (C_{2v} symmetry restriction) at fixed carbon-lithium bond lengths.

Table 4. 4-31G energies (in Hartrees) and relative energies (in kJ per mol) of C_{2v} planar 3,3-dilithiocyclopropene as a function of carbon-lithium bond length (in Ångstroms).

r(C-Li)	Energy	Relative Energy
1.5	-129.19006	251.5
2.0	-129.25588	78.6
2.5	-129.27293	33.9
3.0	-129.27745	22.0
3.5	-129.28147	11.4
4.0	-129.28418	4.3
4.5	-129.28550	0.9
5.0	-129.28583	0.0

At the STO-3G level planar 3 is bound relative to singlet cyclopropenylidene and dilithium by 7.2 kJ per mol[32], and in view of our 4-31G results this is presumably due to basis set superposition error[33]. 3 is therefore not a prospect for the realization of planar tetracoordinate carbon.

We should point out that our 4-31G//STO-3G energy (-129.27237 Hartrees) was obtained by using the STO-3G//STO-3G wave function as the initial guess and that this energy is lower than that obtained by Jemmis et al[6] (-129.19802 Hartrees). Since our STO-3G//STO-3G energies are in agreement, it appears that the 4-31G//STO-3G energy given in reference 6 is that of an excited state of 3 at this geometry.

Conclusions:

We have extended previous work on 1 and 2[5] by providing full geometry optimization at the 4-31G level of the C_{2v} planar and tetrahedral geometries, and in assessing the effects of the addition of polarization functions to the basis set, and of correlation energy on the relative energies of the two geometries. Our more extensive study confirms the predictions of Pople, Schleyer and co-workers[5] that the planar geometry is the more stable for these compounds. Moreover, by computing harmonic vibrational frequencies, we have shown planar, but not tetrahedral, 1 and 2 to be local minima. However, according to our calculations, 2 is thermodynamically unstable to isomerization to dilithiated propene, and to various decompositions. Analysis of the wave functions and C-Li bond lengths indicates there to be negligible Li pi-acceptance in planar 1 and small but significant Li pi-acceptance in planar 2. Finally, we have shown that the STO-3G ground state of planar 3[6] is in fact dissociative, only appearing to be bound relative to cyclopropenylidene and dilithium because of basis set superposition error.

Acknowledgements

We are grateful to a referee for several valuable comments and for bringing to our attention some work of which we were not previously aware:

He informs us that he has carried out further calculations on 1-3 and has come to similar conclusions. In particular, he has found that the energy difference between planar and tetrahedral 2 is essentially independent of the level of theory employed and that 3 is not bound.

Apart from the two compounds we have mentioned, three other geminal dilithioalkanes have been prepared, bis(trimethylsilyl)dilithiomethane and (trimethylsilyl)dilithiomethane [34] and, of particular relevance to the present work, 1,1-dilithio-2,2,3,3-tetramethylcyclopropane (as yet unpublished work by R J Lagow and coworkers).

The referee emphasizes the importance of considering LiH complexes when discussing LiH elimination [35]. Although we have calculated 2 to be stable relative to LiH and 1-lithiocyclopropene, it is quite possible that, like 1,2-dilithioethane [35], it is unstable to the formation of an LiH complex.

He also draws our attention to a theoretical study of LiH and MeLi elimination [36] (which appeared after this paper was submitted). Elimination of MeLi from monomeric propyllithium and of LiH from monomeric ethyllithium are calculated to have activation energies of about 120 kJ per mol, quite close to the experimentally measured activation energy for the elimination of LiH from associated octyllithium.

We thank D B Knowles for help in using the GAMESS program and the SERC for a research studentship to JDW.

Addendum

While this work was being refereed we carried out MP2/6-31G*(5d)//4-31G (frozen core) calculations to examine simultaneously the effects of polarization functions and electron correlation on the energy differences of planar and tetrahedral 1 and 2. For planar and tetrahedral 1 these calculations gave energies of -103.55180 and -103.52066 Hartrees respectively, so favouring the planar geometry by 81.8 kJ per mol. The energies of planar and tetrahedral 2 are -131.11356 and -131.09901 Hartrees respectively, so at this level of theory the planar geometry is preferred by 38.2 kJ per mol.

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32. The STO-3G//STO-3G energies (in Hartrees) of planar 3, cyclopropenylidene, and dilithium are -127.81952 (ref. 6), -113.17804, and -14.63875 respectively. The 4-31G//4-31G energy of cyclopropenylidene is -114.42494 Hartrees.

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