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Author

Laidig, William D.

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William D. Laidig and Henry F. Schaefer III

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Structures and Energetics of Planar and Tetrahedral Dilithiomethane:

A Near Degeneracy of Singlet and Triplet Electronic States

William D. Laidig and Henry F. Schaefer III

**Department of Chemistry and Lawrence Berkeley Laboratory
University of California,
Berkeley, California 94720**

In a very important recent paper,¹ Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger, and Pople (CDJASSP) have shed new light on the stabilization of planar tetracoordinate carbon. Pople and Schleyer predict¹ that because of their π acceptor and σ donor character, electropositive substituents, especially lithium, are particularly effective in stabilizing the planar arrangements selectively. Perhaps the simplest viable candidate for planar carbon is CH_2Li_2 , dilithiomethane, for which the predictions of Pople and Schleyer are summarized in Table I. Although not particularly emphasized by CDJASSP, we were particularly struck by their prediction that both planar and tetrahedral CH_2Li_2 have triplet electronic ground states. CDJASSP explicitly note that the triplet states are artificially favored in their work, since the single determinant Hartree-Fock approximation does not treat singlet and triplet states of this type on an equal footing.² They conclude that "it is difficult to assign the ground state configuration of CH_2Li_2 but the two states should be close in energy." The purpose of the present research is to provide state-of-the-art theoretical predictions, including the effects of electron correlation,^{2,3} of the relative energies of planar and tetrahedral CH_2Li_2 in its lowest singlet and triplet electronic states.

The basis set used in the present research was of double zeta plus polarization (DZ+P) quality⁴ and may be precisely designated C(9s 5p 1d/4s 2p 1d), Li(9s 4p/4s 2p), H(4s 1p/2s 1p). Experience with systems such as methylene⁵ suggest that in conjunction with large scale configuration interaction (CI) techniques⁶ and many body theory corrections⁷ for unlinked clusters, predictions of singlet-triplet separations reliable to within 3 kcal may be achieved. With the above specified basis set, self-consistent-field (SCF)

theory was used to predict the equilibrium geometrical structures, shown in the Figure, of the four species in question. Our structures are in qualitative agreement with the minimum basis predictions of CDJASSP, although a few quantitative differences may be cited. The present C-Li distances are all longer, by from 0.058 Å to 0.100 Å, and the LiCLi bond angles are from 0.2° to 4.7° (planar triplet) longer than those of CDJASSP. However, the most important conclusion of CDJASSP, that the singlet LiCLi bond angles are much greater than the comparable triplet angles, is given strong support here.

At the predicted SCF equilibrium geometries, CI wave functions including all single and double excitations were determined variationally using the BERKELEY system⁸ of minicomputer-based programs. The numbers of space- and spin-adapted configurations actually included were 7075, 9241, 6724, and 8814. The original Davidson correction⁷ was also applied to these results, which are summarized in Table II. Before going on to the energetic results, we note the remarkable dipole moment predictions also seen in the Table. The planar and tetrahedral singlets have very large dipole moments, with polarity C^-Li^+ , while the triplet μ values are much smaller, and, quite surprisingly, of C^+Li^- polarity.

As suggested by Pople and Schleyer,¹ electron correlation preferentially lowers the singlet states, and in a dramatic fashion. From lying 16.5 kcal above the tetrahedral triplet at the SCF level of theory, the cluster corrected CI eliminates this gap and actually predicts the tetrahedral singlet to lie 2.1 kcal lower. However, the planar triplet lies only 1.8 kcal above the tetrahedral triplet. The near degeneracy of these four electronic moieties is to our knowledge without precedent and suggests an

urgent need for experimental studies of this simple molecule.

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Figure Caption

Predicted geometries of planar (upper) and tetrahedral (lower) CH_2Li_2 in its lowest singlet and triplet electronic states. Bond distances are in Å.

Table I. Summary of the self-consistent-field predictions of Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger, and Pople (CDJASSP)¹ concerning the relative energies of CH₂Li₂.

Species	Minimum Basis	Double Zeta Basis
Tetrahedral Singlet	0	0
Tetrahedral Triplet	-12	-16
Planar <u>cis</u> Singlet	17	10
Planar <u>cis</u> Triplet	- 2	-13
Planar <u>trans</u> Singlet	54	48

Table II. Relative energy predictions for dilithiomethane. The absolute energies of the tetrahedral singlet are -53.8362 hartrees (SCF) and -54.0216 hartrees (CI).

	E (SCF) kcal	μ (SCF) debye	E (CI) kcal	E (CI corrected for unlinked clusters) kcal
Planar Singlet	3.2	4.85	7.4	8.3
Planar Triplet	-15.8	-1.22	+0.9	3.9
Tetrahedral Singlet	0.0	5.42	0.0	0.0
Tetrahedral Triplet	-16.6	-0.76	-0.8	+2.1

3B_1

1A_1

3B_2

1A_1

Fig. 1

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