The Multiplicity of Substituted Acyclic Carbenes and Related Molecules

James F. Harrison,*[1a] Richard C. Liedtke,[1a] and Joel F. Liebman*[1b]

Contribution from the Departments of Chemistry, Michigan State University, East Lansing, Michigan 48824, and the University of Maryland Baltimore County, Catonsville, Maryland 21228. *Received April 20, 1978*

Abstract: On the basis of various first principles calculation (most already in the literature) on substituted acyclic carbenes, nitrenium ions, and silylenes we suggest that the electronegativity of the substituents is an important, perhaps decisive, factor in determining the multiplicity of the ground state in these and the isoelectronic phosphenium ions. In particular as the substituents go from F to Li the ground state goes from singlet to triplet.

Introduction

Carbenes are divalent carbon compounds of considerable chemical consequence and while these reactive intermediates are often invoked in the formulation of reaction mechanisms little is known of their physical properties. A notable exception is the parent carbene, methylene,[2] which for many reasons has emerged as the polyatomic molecule most thoroughly scrutinized by theoretical chemists in the last decade and perhaps since the dawn of quantum mechanics.[3] This activity has resulted in our knowing the geometry and relative energies of the two lowest states of methylene with unprecedented reliability.[4] Unfortunately, the various substituted carbenes have not fared as well. Although there have been many calculations[5] on substituted carbenes, none have approached the reliability of the CH_2 studies. In spite of this we believe that the trends inherent in these calculations are sufficiently reliable as to suggest a simple rationalization for the effect of substituents on the singlet–triplet (S–T) gap. This rationalization in turn permits us to predict the multiplicity of several, as yet unknown, reactive intermediates. Our work builds upon previous theoretical work by Schaefer[5d] and Baird[5f] and introduces a new dimension in the analysis.

Background

Figure 1 displays a schematic representation of the two low-lying states of methylene.[1] The ground state is a bent (132°) triplet with the two unpaired electrons occupying an in-plane (σ) orbital and an orbital (p) perpendicular to the molecular plane. As we open the HCH angle the σ orbital (which is sp^2-"like") loses its s character and evolves into a pure p orbital at 180°. The perpendicular orbital is little affected by the change in angle. The singlet state is more strongly bent with an angle of 103°. Insight into the electronic structure of the singlet is gained by noting that in the linear geometry the singlet is of $^1\Delta_g$ symmetry, which, with real atomic orbitals, requires two equally weighted determinants for its description. As we bend the molecule the component with the electron pair in plane (σ^2) becomes increasingly more important (sp hybridization) until at the equilibrium geometry it is dominant.

As we replace the hydrogens in CH_2 with other atoms (R and R′ in Figure 2) we expect to keep this low-lying pair of states but anticipate a change in the RCR′ angle and the singlet-triplet gap. Our concern is the dependence of this gap on the substituents R and R′.

Electronegative Substituents

Figure 3 summarizes the results of several high-quality ab initio calculations by Schaefer[5d] et al. and displays vividly the effect of substituting various halogens for one or both hydrogens in CH_2. The results of F substitution are most dramatic. One fluorine results in a singlet ground state with a companion triplet approximately 10 kcal/mol higher, while two fluorines increase the gap to approximately 45 kcal/mol. While the results of chlorine substitution are not so dramatic, the resulting pattern is identical. The one calculation available for bromine substitution suggests that CBr_2 will be a singlet in its ground state but will have a low-lying triplet state, perhaps 10 kcal/mol above the singlet.

For what follows it is important to recognize that those calculations which predict absolute energy separations unreliably may very well predict trends reliably. To illustrate this we display in Figure 4 the results of ab initio calculations[6a] which, although not of the same absolute accuracy as Schaefer's,[5d] faithfully track his predicted geometries and, more importantly, the trend upon fluorine substitution. In fact one need only drop the singlets relative to the triplets by approximately 10 kcal/mol to bring the two calculations into good agreement. This 10 kcal[5f] is the differential stabilization of the singlet due to optimized d functions on the carbon. Both sets of calculations suggest that as the electronegativity of the substituent increases the singlet becomes more stable than the triplet. To further probe this correlation we require substituents that are increasingly less electronegative than the halogens and in particular, electropositive relative to carbon. To this end we will consider the effect of Li substitution on the electronic structure of carbenes.

Lithium-Substituted Methylenes

First, some expectations are given. The electrons in LiCH may be distributed with two in both the carbon and lithium 1s orbital, two in each σ bond and two, shown in Figure 5 as occupying carbon p_π orbitals, not necessary for the bonding of the ligands to carbon. If we recognize the electronegativity difference between Li and C, the ionic structure becomes reasonable. To the extent that this ionic structure contributes significantly to the character of the lowest triplet state the two Π states shown in Figure 5 should be low lying.

When we substitute both hydrogens in CH_2 with lithium a similar scenario obtains. On the left (Figure 5) we have the covalent structure, on the right, the ionic counterpart. Exciting from an occupied σ_u or σ_g orbital into one of the occupied π_u orbitals will result in a $\Pi_g(3)$ or $\Pi_u(3)$ state; similarly, exciting from one of the occupied π_u orbitals into a vacant σ_u or σ_g orbital (the Li 2s bonding and antibonding molecular orbitals) will result in $\Pi_u(1)$ and $\Pi_g(1)$ states.

Figure 6 shows the results of standard restricted open shell SCF calculations on the low-lying triplet states of LiCH. The carbon basis set is the standard Huzinaga[6b] 9s, 5p contracted to (6111/41); the hydrogen 4s and lithium 8s are also Huzinaga's contracted to (31) and (611), respectively. The lithium p orbital is the four-component expansion of Williams[7] et al.

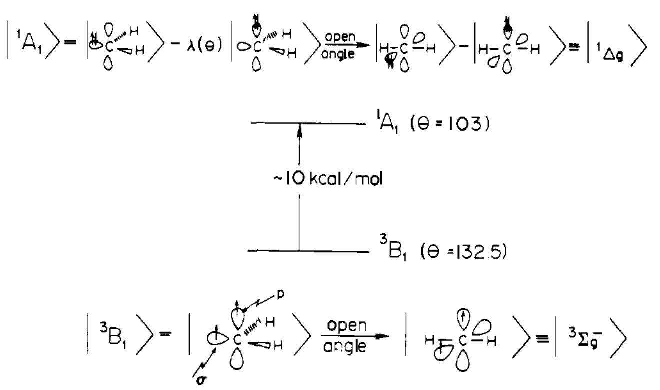


Figure 1. Low-lying states of methylene.

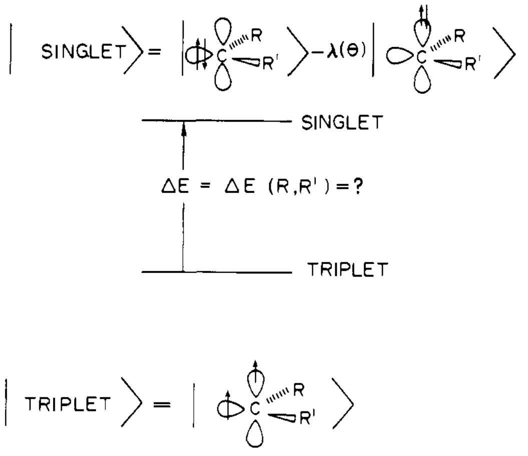


Figure 2. Low-lying states of acyclic carbenes.

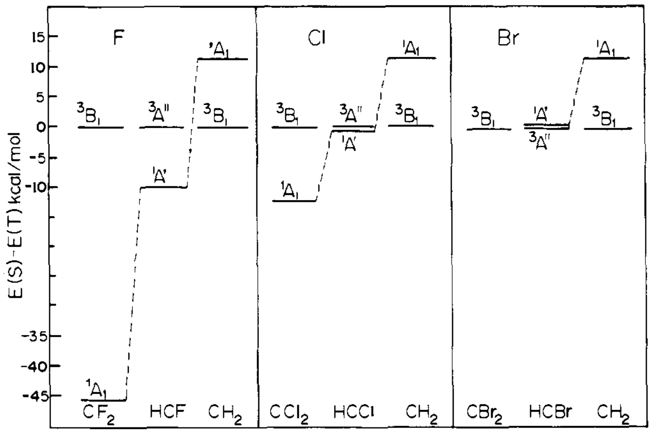


Figure 3. Approximate singlet-triplet separation in halogenated carbenes. Data from ref 4a.

All contractions are as recommended by Dunning.[8] While the lowest triplet is the expected linear $^3\Sigma^-$ state, the two other triplets, anticipated in Figure 5, and shown in Figure 6, are very low lying relative to the lowest excited triplet in CH_2 (which is approximately 200 kcal/mol above the ground triplet).[9]

The six valence electrons in $^3\Sigma^-$ LiCH occupy orbitals whose density contours are shown in Figure 7. Note the well-defined C-H bond, the extremely ionic C-Li bond, and the highly localized π orbital. We conclude from these results and the results of a population analysis that LiCH is a very ionic molecule.

To estimate the singlet-triplet gap we constructed the singlet state wave function from the triplet state molecular orbitals.

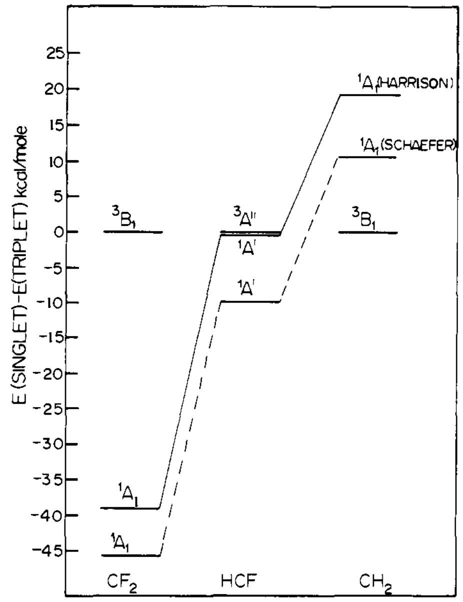


Figure 4. Approximate singlet-triplet separation in fluorinated carbenes.

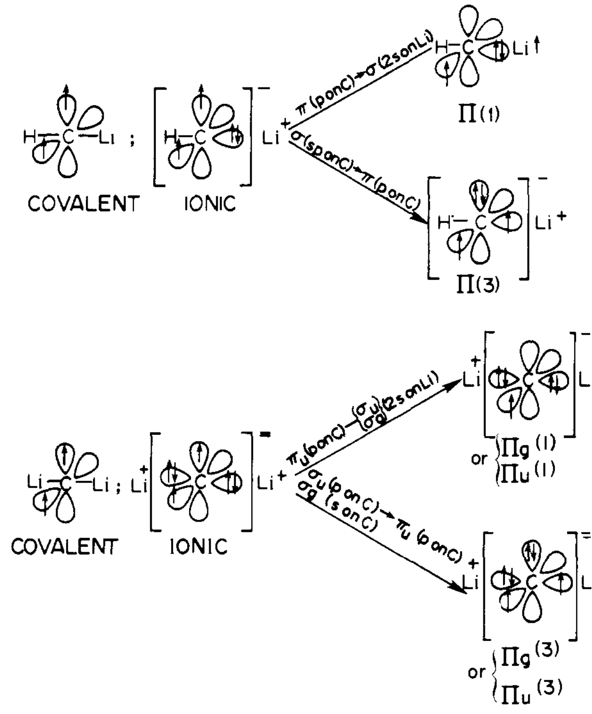
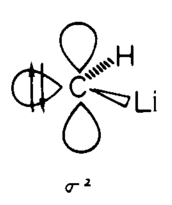
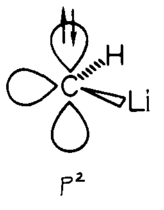


Figure 5. Expectations for lithium-substituted carbenes. The ground-state triplet configurations are given on the left while possible excited-state orbital occupations are given on the right. Although the "unpaired electrons" are indicated as both having spin "up", they could be coupled either singlet or triplet.

We considered both the σ^2 and p^2 configurations and for each





one constructed all double excitations. These were ordered on the basis of a two-by-two CI with the reference configurations.

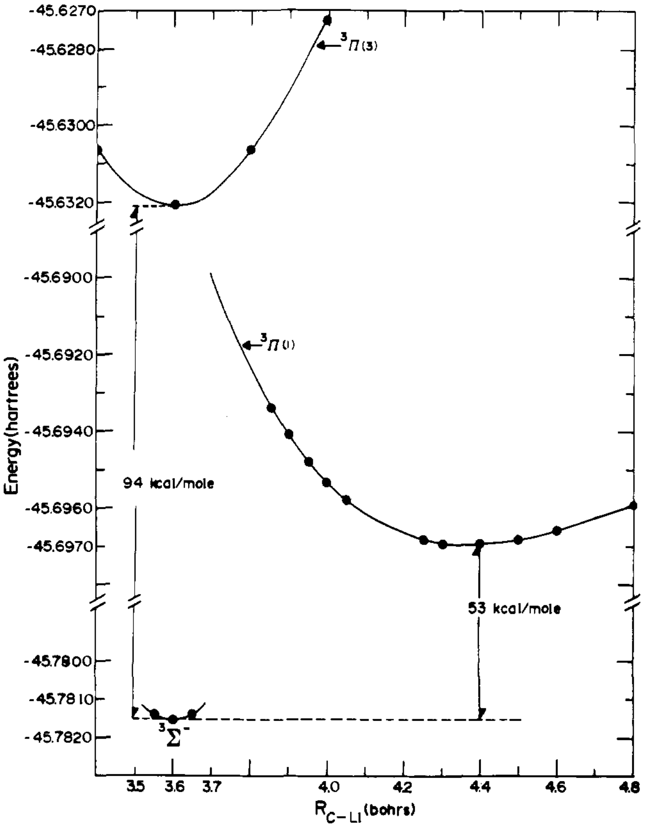


Figure 6. Restricted open shell SCF results for three low-lying triplets of linear LiCH as a function of Li-C bond length.

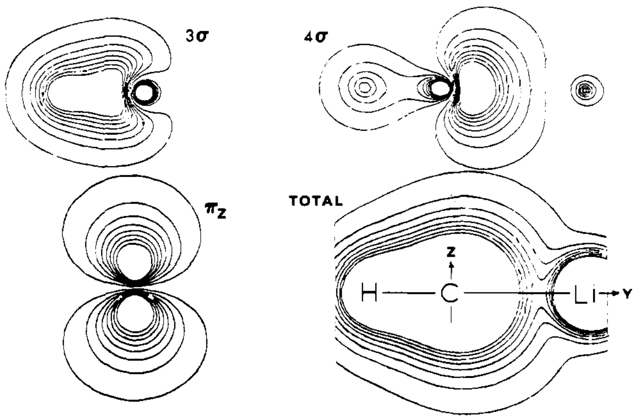
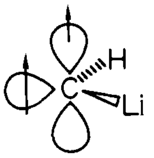


Figure 7. Electron density contours of valence orbitals in LiCH.

All singles and those doubles which contributed more than 10^{-5} hartree were included in the subsequent CI. The two inner-shell molecular orbitals were always doubly occupied. The CI function for the triplet was constructed in the same way from the reference configuration.



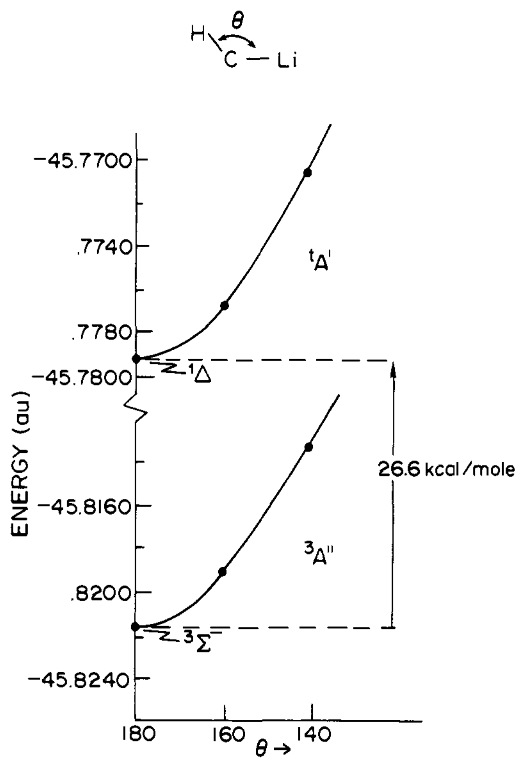


Figure 8. Configuration interaction predictions for the lowest singlet and triplet states of LiCH as a function of angle.

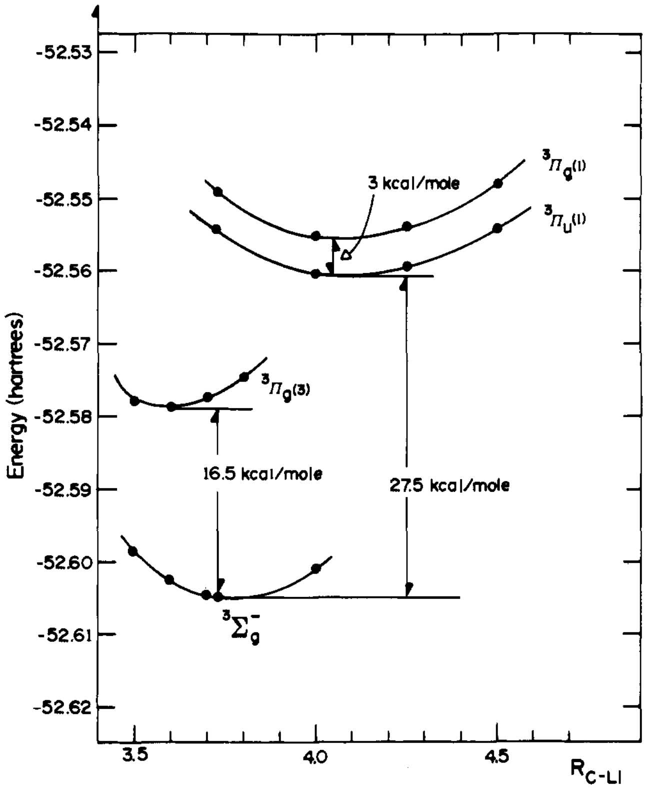


Figure 9. Restricted open shell SCF results for the low-lying triplets of linear Li_2C as a function of Li-C bond length.

The resulting CI energies (at the triplet SCF bond lengths) are given as a function of angle in Figure 8, from which we see that the singlet-triplet separation is estimated as 27 kcal/mol. The primary deficiency in this calculation is that cautioned against earlier, i.e., lack of polarization functions on the carbon. It is important to note that correcting this deficiency will result in a smaller singlet-triplet gap but by no means will it reverse the order of the states. In fact the polarization function should be less significant for linear LiCH than bent CH_2.

In Figure 9 we display the results of standard restricted open-shell SCF calculations on the low-lying triplet states of

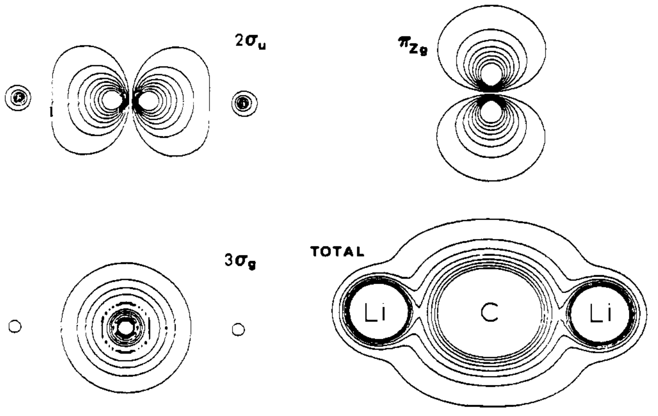


Figure 10. Electron density contours of valence orbitals in Li_2C.

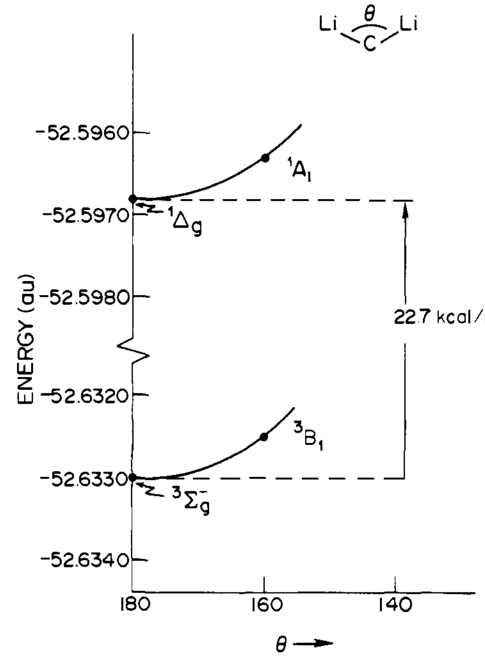


Figure 11. Configuration interaction predictions for the lowest singlet and triplet states of Li_2C as a function of angle.

Li_2C using the same lithium and carbon basis as in the LiCH calculation. Once again, the lowest triplet has the expected Σ^- symmetry and there are very low-lying excited triplets. The six valence electrons in $^3\Sigma^-{}_g$ Li_2C occupy orbitals whose density contours are shown in Figure 10. Apparently, Li_2C, like LiCH, is a very ionic molecule.

To estimate the singlet-triplet gap we constructed the singlet and triplet state CI functions from the lowest triplet molecular orbitals using the prescription given for LiCH. The resulting CI energies (at the triplet SCF bond lengths) are given as a function of angle in Figure 11. Note that the triplet is predicted to be the ground state by 23 kcal/mol.

We emphasize that the 27 and 23 kcal/mol estimates for the S-T separation in LiCH and Li_2C are most likely too large. While comparable calculations in CH_2 would result in a S-T gap which is 10 kcal/mol too large, we believe (in view of the linearity of both molecules) that the polarization functions will be less significant than for bent CH_2 and suggest that the resulting decrease in the S-T separation will be less than 10 kcal/mol.

Singlet-Triplet Gap and Electronegativity

Figure 12 traces the evolution of the singlet-triplet gap through a range of substituent electronegativities. Whether the drop in this gap in going from one to two lithiums is real or an artifact of the calculations is not known. It is possible that some of the decrease noted upon double substitution results from the enhanced opportunity for delocalization of the carbon p_π electrons into the lithium p_π orbitals. It is clear, however, that the relative electronegativity of carbon and the attached atoms is a factor, perhaps decisive, in determining the magnitude of the singlet-triplet gap.

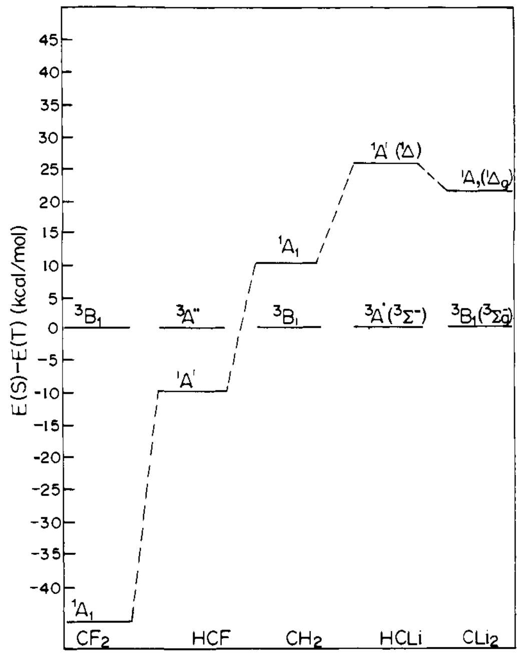


Figure 12. Approximate singlet-triplet separation in several carbenes as a function of substituents.

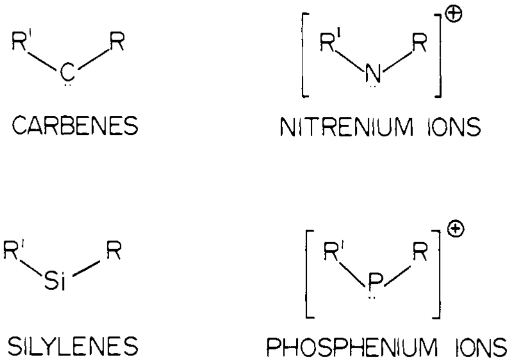


Figure 13. Classes of molecules isoelectronic to the carbenes.

Nitrenium Ions

We may further probe this correlation by varying the electronegativity of the central atom and Figure 13 displays various molecules isoelectronic to RCR′ for which we might expect similar trends. One of these classes, the nitrenium ions, is considered further in Figure 14, where we trace the evolution of the singlet-triplet gap as a function of F and Li substitution on the parent $^+NH_2$.

We may group the calculations on which this figure is based into three classes. The most reliable is the separation in $^+NH_2$ calculated by Bender[10] et al. using a near-Hartree-Fock level basis set and a single determinant restricted open-shell SCF calculation on the triplet with a double determinant SCF calculation on the singlet. This same technique predicts a singlet-triplet separation of CH_2 of 10.9 kcal/mol, which is within 1-2 kcal/mol of the probable separation.[11] The second class consists of the lithium-substituted molecules and these

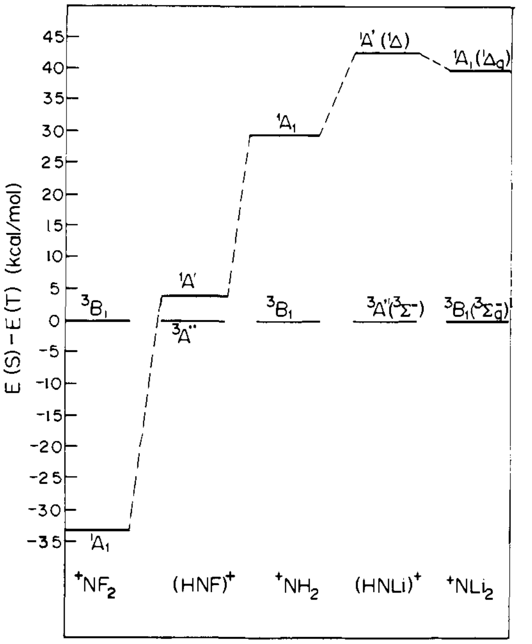


Figure 14. Approximate singlet-triplet separation of several nitrenium ions as a function of substituents.

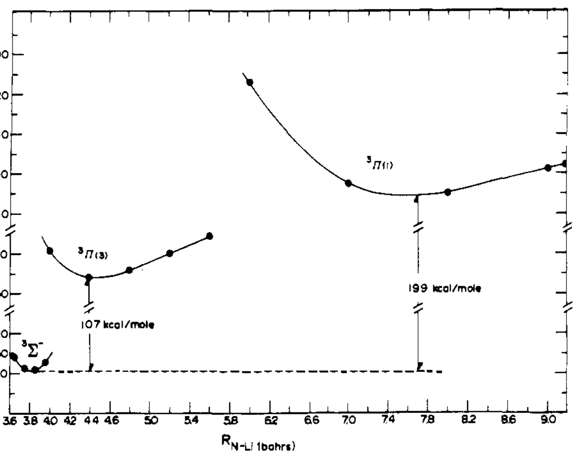


Figure 15. Restricted open shell SCF study of the first two triplets of linear $(LiNH)^+$ as a function of the N-Li bond length.

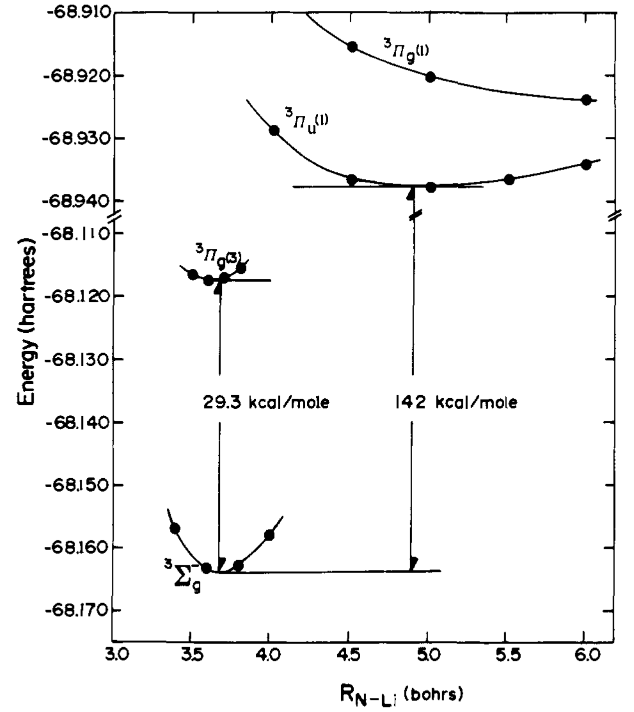


Figure 16. Restricted open shell SCF study of the low-lying triplets of linear Li_2N^+ as a function of the N–Li bond length.

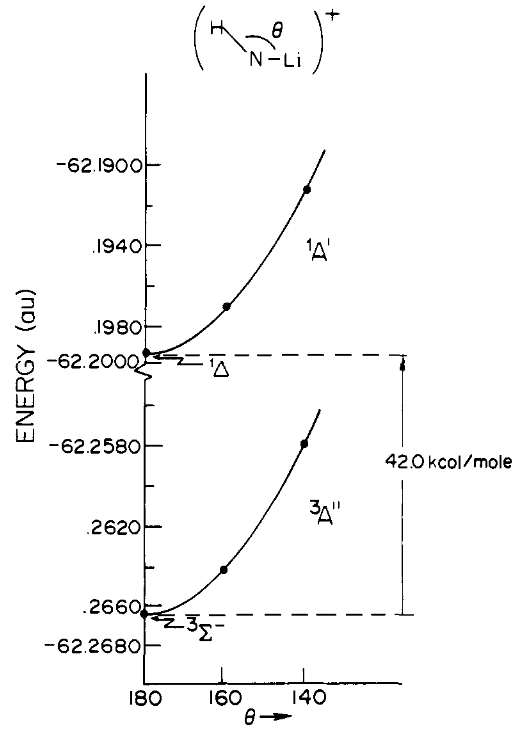


Figure 17. Configuration interaction prediction for the energy of the lowest singlet and triplet of $(LiNH)^+$ as a function of angle.

energies have been obtained using the same procedure discussed for the LiCH and Li_2C molecules. Briefly, the nitrogen basis set is Huzinaga's 9s, 5p set contracted to (6111/41), while the lithium and hydrogen basis is the one used in the corresponding carbene study. The energies of the triplet SCF calculation are shown in Figures 15 and 16 while the CI results for the lowest triplet and the lowest singlet at the SCF bond lengths of the triplet are shown as a function of angle in Figures 17 and 18. Because both the singlet and triplet states of the lithium substituted molecules are linear, we anticipate a smaller contribution from polarization functions than in the CH_2 case. Thus, while we anticipate that the singlet-triplet separation will be decreased slightly in an extended basis set calculation, we are confident, not only that the triplet will remain the ground state in both $^+NLi_2$ and ^+NHLi, but that the gap will be at least as large as in NH_2^+. The third class[12] consists of $^+NF_2$ and ^+NHF. Both of these molecules have been studied using a basis comparable to the corresponding lithium compounds but with considerably fewer configurations in the CI. We anticipate that a more extensive theoretical study will lower the singlets relative to the triplets and would not be surprised to see the $^1A'$ state of $(HNF)^+$ fall below the $^3A''$ state. Even with these recognized deficiencies, Figure 14 suggests strongly that NH_2^+ is more triplet than CH_2 and responds in the same way to Li and F substitutions as does CH_2.

A Model for the Effect of Substituents on the Multiplicity of the Ground State of Carbenes, Nitrenes, the Isoelectronic Silylenes, and Phosphenium Ions

Figures 12 and 14 suggest that it might be possible to un-

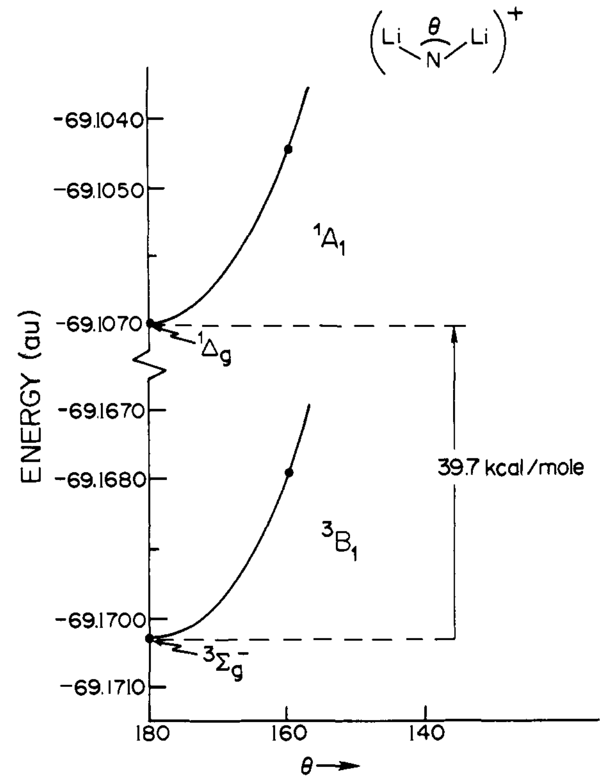
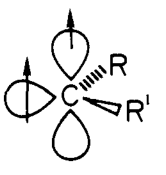


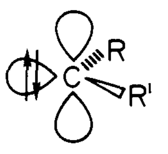
Figure 18. Configuration interaction prediction for the energy of the lowest singlet and triplet of Li_2N^+ as a function of angle.

derstand the effect of substituents in determining the ground-state multiplicity of carbenes and nitrenes with an electronegativity-based theory.[13] Briefly, in the limit of a very electronegative substituent (i.e., one which would remove the electron completely) the carbon atom in RCR′ will be "C^{2+}-like" or isoelectronic with Be and therefore prone toward a ^1S state. We therefore anticipate that electronegative substituents will favor a singlet ground state. At the other extreme a very electropositive substituent (for example, the electron) will, in the limit, result in an in situ C^{2-} which, being isoelectronic with ^3P oxygen, will favor a triplet ground state.

When the substituents are such that the bonds are more covalent, a somewhat modified argument is required. Consider an arbitrary acyclic carbene in the lowest triplet state (i) and



i



ii

in the lowest singlet state (*ii*). Which of these represents the ground state depends on the relative energies of the σ and p orbitals. If they are comparable in energy then the triplet will be the ground state. If, however, the σ orbital is sufficiently low so that the increase in electron repulsion associated with going from σp to σ^2 is more than compensated for, then a singlet ground state will obtain. When the electronegativity of the ligands increases, the s character of the σ orbital increases and thus its energy decreases, favoring the singlet state. In the limit the carbon is $C^{2+}(1s^22s^2)$ as inferred previously. Conversely, as the ligands become more electropositive and electrons are transferred from the ligands to the central atom the σ orbital loses s character and the RCR^1 angle opens. At some point the σ and p orbitals are close enough in energy that the triplet state

ELECTRONEGATIVE
SUBSTITUENTS

$R{-}C{-}R \longrightarrow R^- \; C^{++} \; R^-$
$C^{++} = 1S^2 \; 2S^2 \equiv Be\,(^1S)$
∴ <u>SINGLET PRONE</u>

ELECTROPOSITIVE
SUBSTITUENTS

$R{-}C{-}R \longrightarrow R^+ \; C^= \; R^+$
$C^= \; 1S^2 \; 2S^2 \; 2P^4 \equiv O(^3P)$
∴ <u>TRIPLET PRONE</u>

Figure 19. Model for the multiplicity of the ground state of carbenes.

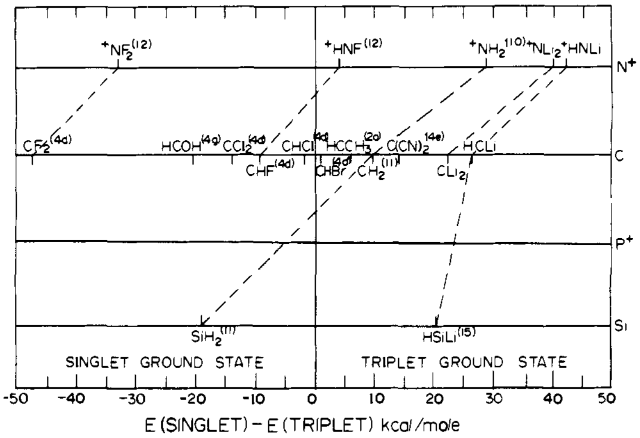


Figure 20. Approximate singlet-triplet gap in various carbenes and isoelectronic molecules. References from which data were obtained are noted as superscripts.

obtains as the ground state. In the limit one arrives at $C^{2-}(1s^22s^22p^4)$ as the ionic model. This model, summarized in Figure 19, then predicts that as the substituent takes the carbon from C^{2-} through C^0 to C^{2+} the singlet state becomes more stable than the triplet. Implicit in this rationalization is the requirement that the carbene carbon and the ligands do not form multiple bonds to one another.

The effect of substituents on the nitrenium ion S-T separation can be understood by noting that the limiting configurations of the in situ N atoms are $N^{3+}(^1S)$ and $N^-(^3P)$, once again suggesting that as the electronegativity of the ligands is increased the singlet nitrenium ion will be stabilized. In addition, since N^+ is much more electronegative than carbon, a substituent of a given electronegativity will be less effective in removing an electron from N^+ than from C, resulting in the triplet nitrenium ion being more stable relative to the singlet than its carbene analogue. As can be seen from Figure 20 the entire pattern of nitrenium ion singlet–triplet separations shifts accordingly.

The effect of replacing carbon (carbenes) with silicon (silylenes) holding the ligands constant is easily predicted to result in a stabilization of the singlet relative to the triplet. The experimental results for SiH_2[14] (singlet ground state, singlet-triplet gap less than 13.8 kcal/mol), as well as the theoretical results for SiH_2[11] (singlet ground state, S-T gap of 18.6 kcal/mol) and HSiLi[15] (triplet ground state, S-T gap of less than 21 kcal/mol), are consistent with our expectations. The suggestion[16] that SiF_2 is a ground-state singlet is also consistent with our model.

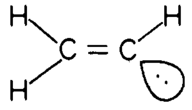
There are no data for the phosphenium ions. However, since we anticipate that the phosphenium ion pattern will be shifted to the left relative to the carbenes and to the right relative to the silylenes, the parent compound PH_2^+ will be less triplet than CH_2 but not as singlet as SiH_2. Furthermore, while compounds of the form X-A-Y, where X and Y are alkali atoms and A is one of the species C, N^+, Si and P^+, will have triplet ground states, compounds of the form H-Si-X and X-Si-Y, where X and Y are halogen, will undoubtedly have singlet ground states. Also, while H-Si-OH should be more singlet than H-C-OH, it is difficult to say whether $(H\text{-}N\text{-}OH)^+$ will be a singlet or triplet. Finally, while our model suggests that $(FNLi)^+$ will have a triplet ground state, it is not clear where FSiLi will fall.

The reliability of these predictions and the many others which are possible depends, of course, on the extent to which Figure 20 faithfully tracks the response of the singlet-triplet gap to substitution. The widely divergent accuracy of the data plotted in Figure 20 precludes our claiming quantitative reliability for the predictions. Rather, we believe that the available data reflects a qualitative trend in the splitting which may become more quantitative as more accurate experiments and calculations become available.

Conclusion

We have suggested that the electronegativity of the substituents is an important, perhaps decisive, factor in determining the multiplicity of the ground state of substituted acyclic carbenes and related isoelectronic molecules. In particular we find that very electronegative substituents (e.g., F) favor a singlet ground state while very electropositive substituents (e.g., Li) favor the triplet. This conclusion extends the suggestion of Schaefer[5d] et al. that the singlet-triplet separation in the halogenated carbenes correlates with the electronegativity of the ligand. In particular we note that our model permits us to correlate the magnitude of the singlet-triplet separation in isoelectronic molecules with the appropriate separation for the corresponding carbene.

In a similar study Baird and Taylor[5f] conclude that the singlet is "... the ground state of acyclic carbenes H$\ddot{\mathrm{C}}$X and X$\ddot{\mathrm{C}}$X whenever X has a lone-pair donor atom bonded directly to $\ddot{\mathrm{C}}$ (i.e., when X = F, OR, NR_2, CR_2^-)". The model we propose can accommodate the singlet nature of HCF, HCOR, and perhaps $HCNH_2$ but certainly not $HCCH_2^-$. However, since the ground state of $HCCH_2^-$ is best represented as iii,



iii

we believe that it is not really a carbene. In addition, although Baird and Taylor's model predicts HCF, CCl, and HCBr to be singlet ground states, it does not rank them according to the magnitude of the singlet-triplet separation and in particular does not allow for the possibility of HCl being a triplet. Finally, note that the calculated gaps in the sequence HCF, HCOH, and $HCNH_2$ are the reverse order to that expected in the electronegativity model. We believe that this is due to our neglecting "secondary" effects in the proposed model, the "secondary" effect in this instance being the stabilization of the carbon p_π orbital by the electronegative substituent with the resulting stabilization of the triplet (in which this orbital is fully occupied) relative to the singlet (in which it is negligibly occupied). The more electronegative substituent should have the greatest influence on the carbon p_π orbital. In Figure 20, HCF and HCOH have been shifted to the right (HCF more than HCOH) relative to where they would fall if the effect were not operative. Although not shown in Figure 20, a similar scenario obtains for $HCNH_2$.

References and Notes

(1) (a) Michigan State University; (b) University of Maryland Baltimore County.

(2) (a) J. F. Harrison, *Acc. Chem. Res.*, 7, 378 (1974); (b) P. P. Gaspar and G. S. Hammond in "Carbenes", Vol. II, R. A. Moss and M. Jones Jr., Eds., Wiley, New York, 1975, pp 207-362; (c) J. F. Harrison in "Carbene Chemistry", W. Kirmse, Ed., Academic Press, New York, 1971.

(3) For references prior to 1973 see ref 2a. Work subsequent to 1974 includes: (a) V. Staemmler, *Theor. Chim. Acta*, **35**, 309 (1974); (b) M. J. S. Dewar, R. C. Haddon, and P. K. Weiner, *J. Am. Chem. Soc.*, **96**, 254 (1974); (c) A. H. Pakiari and N. C. Handy, *Theor. Chim. Acta*, **40**, 17 (1975); (d) V. V. Dudorov, *Russ. J. Phys. Chem. (Engl. Transl.)*, **49**, 607 (1975); (e) J. Lieven and G. Verhaegen, *Theor. Chim. Acta*, **42**, 47 (1976); (f) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem., Symp.*, **10**, 1 (1976); (g) R. R. Lucchese and H. F. Schaefer III, *J. Am. Chem. Soc.*, **99**, 6765 (1977); (h) B. O. Roos and P. M. Siegbahn, *ibid.*, **99**, 7716 (1977); (i) D. Gervy and G. Verhaegen, *Int. J. Quantum Chem.*, **12**, 115 (1977); (j) L. B. Harding and W. A. Goodard III, *J. Chem. Phys.*, **67**, 1777 (1977); (k) C. W. Bauschlicher, Jr., and I. Shavitt, *J. Am. Chem. Soc.*, **100**, 739 (1978); (l) M. J. S. Dewar and H. S. Rzepa, *ibid.*, **100**, 784 (1978); (m) H. L. Hase, G. Lauer, K. W. Schutte, A. Schwirg, and W. Thiel, *Chem. Phys. Lett.*, **54**, 494 (1978); (n) S-K. Shih, S. D. Peyerimhoff, R. J. Buenker, and M. Peric, *ibid.*, **55**, 206 (1978); (o) L. B. Harding and W. A. Goddard III, *ibid.*, **55**, 217 (1978).

(4) Although the reliability of the singlet-triplet separation is unprecedented, it is not uncontested. The 1978 Boulder Conference on the Spin States of Carbenes failed to reconcile the discrepancy between the experimental value of 19.5 ± 0.7 kcal/mol [P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3731 (1976)] and the 10 kcal/mol prediction of theory (ref 3) and the comparable prediction of several other experiments. See, for example, R. K. Lengel and R. N. Zare, *J. Am. Chem. Soc.*, **100**, 7495 (1978), and references cited therein.

(5) (a) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974); (b) J. B. Moffatt, *J. Chem. Soc., Chem. Commun.*, 888 (1975); (c) W. J. Hehre, J. A. Pople, W. A. Latham, L. R. Radom, E. Wasserman, and Z. R. Wassermann, *J. Am. Chem. Soc.*, **98**, 4378 (1976); (d) C. W. Bauschlicher, H. F. Schaefer III, and P. S. Bagus, *ibid.*, **99**, 7106 (1977); (e) R. R. Lucchese and H. F. Schaefer III, *ibid.*, **99**, 7106 (1977); (e) R. R. Lucchese and H. F. Schaefer, *ibid.*, **99**, 13 (1977); (f) N. C. Baird and K. F. Taylor, *ibid.*, **100**, 1333 (1978); (g) R. R. Lucchese and H. F. Schaefer III, *ibid.*, **100**, 298 (1978).

(6) (a) J. F. Harrison, *J. Am. Chem. Soc.*, **93**, 4112 (1971); (b) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); Technical Report from the Theoretical Chemistry Division, University of Alberta, 1971.

(7) J. E. Williams, Jr., and A. Streitwieser, Jr., *Chem. Phys. Lett.*, **25**, 507 (1974).

(8) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

(9) G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).

(10) C. F. Bender, J. H. Meadows, and H. F. Schaefer III, *Faraday Discuss. Chem. Soc.*, **62**, 59 (1977).

(11) J. H. Meadows and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **98**, 4383 (1976).

(12) J. F. Harrison and C. W. Eakers, *J. Am. Chem. Soc.*, **95**, 3467 (1973).

(13) J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976). See especially section XVI-C. See also J. F. Liebman, P. Politzer, and W. A. Sanders, *J. Am. Chem. Soc.*, **98**, 5115 (1976).

(14) A. Kasdan, E. Herbst, and W. C. Lineberger, *J. Chem. Phys.*, **62**, 541 (1975).

(15) W. B. Mueller and J. F. Harrison, unpublished work.

(16) J. W. E. Johns, G. W. Chantry, and R. F. Barrow, *Trans. Faraday Soc.*, **54**, 1589 (1958); D. R. Rao and P. Venkateswarlu, *J. Mol. Spectrosc.* **7**, 287 (1961); D. R. Rao, *ibid.*, **34**, 284 (1970); R. N. Dixon and M. Halle, *ibid.*, **36**, 192 (1970); O. F. Zeck, Y. Y. Su, G. P. Gennaro, and Y. N. Tang, *J. Am. Chem. Soc.*, **96**, 5967 (1974).