

to attack by neutral or other radical species, and so significant reaction stereoselectivity should be observed.<sup>16</sup> The 2-norbornyl radical is perhaps the clearest example of this type.

### Conclusion

The degree of pyramidalization of the *tert*-butyl radical is ~40% that of a perfect tetrahedron, and *tert*-butyl has a barrier to inversion on the order of 1 kcal/mol. The minimum energy inversion pathway involves simultaneous flattening of the radical center and rotation of the three methyl groups. The pyramidalization of *tert*-butyl arises from a simultaneous (and inseparable) minimization of torsional repulsions and maximization

of anti-periplanar hyperconjugative stabilization. In effect, the radical, like alkanes, has a tendency to adopt a staggered conformation. This effect joins electronegative substituent effects (e.g., CF<sub>3</sub>)<sup>17</sup> and angle strain effects<sup>18</sup> as an identified cause of pyramidalization of "normally" planar radicals.

**Acknowledgment.** We are grateful to the National Science Foundation for financial support of this work, and to Professor Jack Timberlake of the University of New Orleans for arousing our interest in radical calculations.

(16) Caramella, P.; Rondan, N. G.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2438.

(17) Pauling, L. *J. Chem. Phys.*, **1969**, *51*, 2767. Bernardi, F.; Cheng, W.; Shaile, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 1352 and references therein.

(18) Jemmis, E. D.; Russ, V.; Schleyer, P. v. R.; Allen, L. C. *J. Am. Chem. Soc.* **1976**, *98*, 6483.

## Carbene Singlet-Triplet Gaps. Linear Correlations with Substituent $\pi$ Donation

Paul H. Mueller,<sup>†</sup> Nelson G. Rondan,<sup>†</sup> K. N. Houk,<sup>\*†</sup> James F. Harrison,<sup>‡</sup> Dwight Hooper,<sup>§</sup> Barry H. Willen,<sup>§</sup> and Joel F. Liebman<sup>\*§</sup>

Contribution from the Departments of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, Michigan State University, East Lansing, Michigan 48824, and University of Maryland Baltimore County, Catonsville, Maryland 21228. Received December 15, 1980

**Abstract:** The singlet-triplet gaps from STO-3G calculations for methylene and 29 substituted methylenes correlate with theoretical and empirical measures of  $\pi$  donation by substituents. The  $\pi$  donors stabilize the singlet more than the triplet, while  $\pi$  acceptors have the opposite effect. Rough estimates of carbene singlet-triplet gaps can be made by using either calculated  $\pi$  charges in the corresponding substituted benzene or empirical  $\sigma_{R^0}$  constants.

Although the parent carbene, methylene, is a ground-state triplet, substituted methylenes often have singlet ground states.  $\pi$  donation to the vacant p orbital of the singlet state is generally believed to be the most effective mechanism for singlet stabilization,<sup>1,2</sup> and strong computational support for this  $\pi$  donor mechanism of singlet stabilization has been reported by Feller, Borden, and Davidson.<sup>3</sup> However, Bauschlicher, Schaefer, and Bagus noted that the stability of the singlet state of a halocarbene relative to the triplet increases as the halogen electronegativity increases,<sup>4,5</sup> and Harrison, Liedtke, and Liebman proposed more generally that electronegative substituents differentially stabilize singlet carbenes, while electropositive substituents stabilize triplet carbenes.<sup>6,7</sup> The relevance of electronegativity and  $\pi$  effects to the geometries of substituted singlet carbenes has also been argued,<sup>8,9</sup> and  $\pi$  effects have been shown to determine the electrophilic or nucleophilic character of substituted carbenes.<sup>10</sup>

We wish to show that for substituted carbenes, there is a remarkably simple relationship between the singlet-triplet (ST) gap and the substituent  $\pi$  donor or  $\pi$  acceptor propensity, assessed both theoretically and empirically. Thus, while the electronegativity arguments described above are relevant to ST gaps caused by central atom changes,<sup>7</sup> they are unnecessary in understanding substituent effects on ST gaps.

### Models for Singlet or Triplet Carbene Stabilization

The valence orbitals of singlet and triplet states of carbenes are represented schematically in Figure 1. Both species are bent

(~102° and 136°, respectively) and have a relatively low-lying  $\sigma$  lone-pair orbital and higher-lying  $\pi$  (p in methylene) orbital. The dominant configuration of a singlet methylene is  $\sigma^2p^0$ , while that of a triplet is  $\sigma^1p^1$ . A relatively high-lying  $\pi$  orbital of a substituent will mix with the carbene  $\pi$  (p) orbital. This will stabilize the singlet more than the triplet, since two  $\pi$  electrons from the donor are stabilized through this mixing. The triplet will be stabilized less because the stabilization of the two  $\pi$  electrons of the donor will be partially counteracted by destabilization of one  $\pi$  electron of the carbene.

The influence of  $\pi$  acceptors depends on the geometry of the carbene. If the carbene geometry is like that shown for the donor substituent in Figure 1a, then the acceptor can only stabilize the triplet, while rotation of the acceptor group so that the  $\pi$  orbital is in-plane permits greater stabilization of the singlet than the triplet. This arises due to the two-electron interaction involving the singlet  $\sigma$  orbital and the acceptor in-plane  $\pi^*$  orbital for the

(1) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. Gleiter, R.; Hoffmann, R. *Ibid.* **1968**, *90*, 5457.

(2) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333. (3) (a) Feller, D.; Borden, W. T.; Davidson, E. R. *J. Chem. Phys.* **1979**, *71*, 4987. (b) *Chem. Phys. Lett.* **1980**, *71*, 22.

(4) Bauschlicher, C. W.; Schaefer, H. F., III; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106.

(5) Bauschlicher, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 5492.

(6) Harrison, J. F.; Liedtke, R. C.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 7162.

(7) These arguments<sup>6</sup> were also applied to species which are isovalent with carbenes: SiH<sub>2</sub>, \*NH<sub>2</sub>, and \*PH<sub>2</sub>. Here, electropositive central atoms favor the singlet state and electronegative the triplet state;  $\pi$ -donor effects are obviously absent in this series.

(8) Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1980**, 124.

(9) Pauling, L. *J. Chem. Soc., Chem. Commun.* **1980**, 688.

(10) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.

\* Address correspondence to K.N.H. at the University of Pittsburgh.

† Louisiana State University and University of Pittsburgh.

‡ Michigan State University.

§ University of Maryland.

Table I. Carbene Singlet-Triplet Energy Gaps (STO-3G RHF for Singlets, STO-3G UHF for Triplets)<sup>a</sup>

carbene	$E(S) - E(T)$ , kcal/mol	$\Delta E$		notes on geometries	ref
		singlet	triplet		
C(CN) <sub>2</sub>	79.5	109.7	180.0	S: $\angle$ CCN fixed at 180°	2, 20
HCCHO	64.1	104.4	128.6	S: dihedral $\angle$ HCCO = 90°; T: planar	2
HCCN	58.7	104.1	134.4		2
HCCONH <sub>2</sub>	54.7	103.6	126.9	S: dihedral $\angle$ HCCO = 90°; T: planar	
HCB <sub>2</sub> H	52.9	180.0	180.0		
CLi <sub>2</sub>	47.9	180.0	77.9		6
HCLi	45.2	180.0	180.0		6
CH <sub>2</sub>	40.1	100.4	125.5		2, 4, 6, 17, 19
HCCF <sub>3</sub>	39.9	101.3	125.6	S, T: dihedral $\angle$ HCCF fixed at 60, 180, and 300°	
HCCH <sub>3</sub>	35.1	104.0	127.3	S, T: dihedral $\angle$ HCCH fixed at 60, 180, and 300°	2, 17
C(CH <sub>3</sub> ) <sub>2</sub>	32.2	107.6	127.2	S, T: dihedral $\angle$ HCCC fixed at 60, 180, and 300°	2
FCCN	29.1	105.2	134.4	S, T: $\angle$ CCN = 180°	
HCNC	28.1	103.3	125.3	S: $\angle$ CNC = 173.0°; $\angle$ HCNC = 180° T: $\angle$ CNC = 174.3°; $\angle$ HCNC = 180°	
HCCI	25.4	100.2	122.1		4
HCBH <sub>2</sub>	24.3	180.0	134.2	S, T: planar	
ClCCH <sub>3</sub>	21.6	105.4	124.0	S, T: dihedral $\angle$ ClCCH fixed at 60, 180, and 300°	
NCCOH	19.3	104.4	135.6	S, T: dihedral $\angle$ CCOH fixed at 180°	
NCCNH <sub>2</sub>	16.4	107.8	138.7	S: planar; T: dihedral $\angle$ CCNH fixed at 120 and 240°	2
HCF	12.2	100.4	121.9		2, 4, 6, 17, 19
HCOCH <sub>3</sub>	2.0	114.0	123.0	S: $\angle$ HCOC = 180°; dihedral $\angle$ COCH fixed at 60, 180, and 300° T: $\angle$ HCOC = 90°; dihedral angles $\angle$ COCH fixed at 60, 180, and 300°	2
HCOH	1.2	100.9	123.3	S: dihedral $\angle$ HCOH = 180° T: dihedral $\angle$ HCOH = 90°	2, 19
HCNH <sub>2</sub>	-3.1	103.4	126.6	S: planar T: dihedral $\angle$ HCNH = 127.1 and 232.9°	2, 19
HCNHCH <sub>3</sub>	-4.6	103.7	124.9	S: HCNHC planar T: $\angle$ CNH = 111.1°, $\angle$ CNC = 113.0°, $\angle$ HNC = 107.6°	
FCCI	-7.4	104.2	121.8		
CCl <sub>2</sub>	-11.8	106.7	124.5		
CF <sub>2</sub>	-21.2	102.6	119.2		4
FCOH	-23.7	102.4	120.9	S: planar; T: dihedral $\angle$ FCOH = 90°	4
C(OCH <sub>3</sub> ) <sub>2</sub>	-24.7	100.7	121.9	S: $\angle$ COC = 112.5°; dihedral $\angle$ OCOC = 180° T: $\angle$ COC = 111.4°; dihedral $\angle$ OCOC = 90°	
C(NH <sub>2</sub> ) <sub>2</sub>	-25.8	109.1	125.0	S: $\angle$ CNH = 119.5°, 125.6°, planar T: $\angle$ CNH = 109.5°; dihedral $\angle$ CNH fixed at 120 and 240°; 60 and 300°	3b
C(OH) <sub>2</sub>	-26.3	102.0	122.0	S: $\angle$ COH = 106.2°; dihedral $\angle$ OCOH = 180° T: $\angle$ COH = 106.0°; dihedral $\angle$ OCOH = 90°	3a, 3b

<sup>a</sup> Partial geometrical descriptions and references to other works which contain calculations on these carbenes are also given.

singlet, whereas this interaction is a less-stabilizing one-electron interaction in the case of the triplet.

### Results and Discussion

As a theoretical index of  $\pi$  donation, or acceptance by a substituent, X, we have used the change in total  $\pi$  electron density of benzene, PhH, caused by substitution to form PhX. This theoretical index,  $\sum \Delta q_\pi$ , calculated at the ab initio minimal basis set (STO-3G) level,<sup>11</sup> has been shown to correlate with empirical measures of electron donation or acceptance,<sup>12</sup> such as  $\sigma_R$ .<sup>13</sup> The  $\pi$  charges ( $q_\pi$ ) calculated at the STO-3G level for a variety of substituted benzenes are already available.<sup>12,14</sup>

When the singlet-triplet gaps calculated by Baird and Taylor<sup>2</sup> for 12 carbenes, HCX, without or with Cl, are plotted vs.  $\sum \Delta q_\pi$  for PhX, the following correlations result ( $E$  in kcal/mol;  $q_\pi$  in electrons;  $r$  is the correlation coefficient):<sup>15</sup> no Cl:

$$E(S) - E(T) = 290.0 \sum \Delta q_\pi + 24.5 \quad (r = 0.974)$$

with Cl:

$$E(S) - E(T) = 289.2 \sum \Delta q_\pi + 14.5 \quad (r = 0.975)$$

(11) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(12) Taft, R. W.; Hehre, W. J.; Topsom, R. O. *Prog. Phys. Org. Chem.* **1976**, *12*, 159.

(13) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

(14) Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496. Dill, J. D. Ph.D. Dissertation, Princeton University, 1976.

(15) Statistical analyses and graphs were produced on the PROPHET computer system, a biomedical computing facility sponsored by the National Institutes of Health, Division of Research Resources.

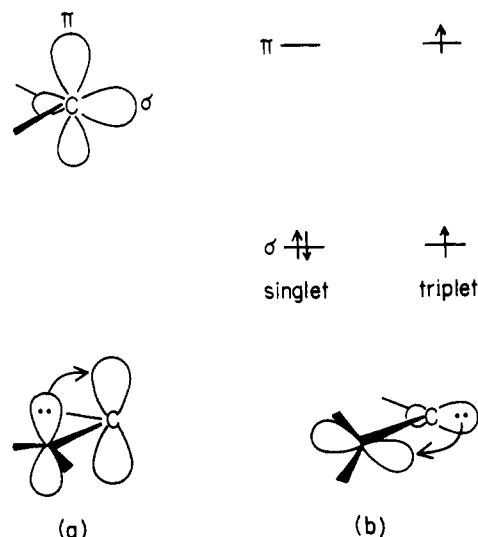
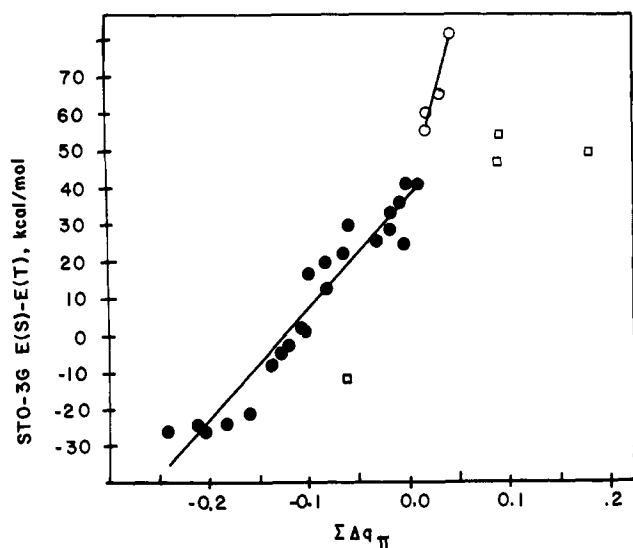


Figure 1. Frontier MOs of singlet and triplet methylenes. (a) Interaction of  $\pi$  donor with carbene  $\pi$  orbital. (b) Interaction of in-plane  $\pi$  acceptor orbital with carbene  $\sigma$  orbital.

The intercepts of these two equations are too high, based on the 9 kcal/mol ST gap of methylene,<sup>16</sup> but the nearly identical slopes indicate that predictions of relative ST gaps can be made

(16) For references to this controversial number, see ref 6.



**Figure 2.**  $E(S) - E(T)$  for substituted carbenes vs.  $\Sigma\Delta q_\pi$ , using carbene geometries optimized by STO-3G, and  $q_\pi$  from STO-3G calculations on standard PhX models:<sup>14</sup> ●, donor substituted carbenes; ○, acceptor substituted carbenes; □, LiCH, Li<sub>2</sub>C, HBeCH, and CCl<sub>2</sub>.

even without CI. Plots of a similar nature for smaller sets of carbenes, calculated by more sophisticated methods,<sup>4,17</sup> produce similarly good correlations. For CH<sub>2</sub>, CHX, and CX<sub>2</sub>, where X = F or Cl,<sup>4</sup>  $E(S) - E(T) = 342.7\Sigma\Delta q_\pi + 11.6$  ( $r = 0.981$ ).

To test this relationship more generally, we have optimized all important geometrical parameters of the singlet and triplet states of 30 carbenes, using the STO-3G basis set.<sup>18</sup> Some values for simple carbenes were taken from the Carnegie-Mellon Archive.<sup>19</sup> The singlet and triplet energy gaps and optimized geometries are given in Table I. The plot of  $E(S) - E(T)$  vs.  $\Sigma\Delta q_\pi$  (PhX) is given in Figure 2. Two lines are drawn on the graph. For methylene and 21  $\pi$  donor substituted derivatives:

$$\pi \text{ donors: } E(S) - E(T) = 298.1\Sigma\Delta q_\pi + 36.1 \quad (r = 0.968)$$

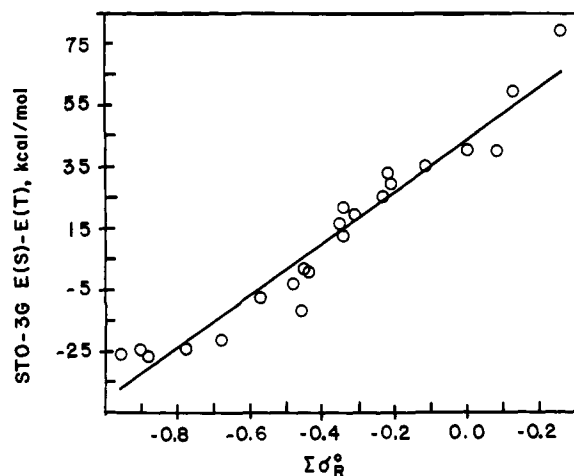
Increasing  $\pi$  donation to the methylene vacant orbital preferentially stabilizes the singlet state. The four  $\pi$  acceptor substituted methylene fall on a much steeper line:

$$\pi \text{ acceptors: } E(S) - E(T) = 977.8\Sigma\Delta q_\pi + 35.4 \quad (r = 0.984)$$

For the CN, CHO, and CONH<sub>2</sub> substituted species, the ST gap increases as more potent electron withdrawers are attached to the carbene. This observation can be explained simply as a result of greater stabilization of the triplet than of the singlet by  $\pi$  acceptor substituents.<sup>2</sup> For example, the singlet state of formylmethylene, HCCHO, prefers a geometry with the CHO plane perpendicular to the HCC plane. This geometry allows some overlap of the occupied lone-pair HOMO of the carbene with the  $\pi^*_{CO}$  LUMO of the formyl group. The triplet prefers a planar geometry, since overlap of the formyl  $\pi$  orbital with the singly occupied p orbital of the triplet is maximized.<sup>21</sup> Additional indications that the formyl group stabilizes the triplet by a  $\pi$  acceptor interaction is that the C-C bond length is shortened and the C-O bond length lengthened in the triplet as compared to the singlet. Similar indications of increasing C-C bond order and/or

**Table II.** Singlet-Triplet Gaps in Two Isoelectronic Carbene Series

carbene	$E(S) - E(T)$ , kcal/mol
Series 1	
H-C <sup>+</sup> FH	30.3
H-C-OH	-1.2
H-C <sup>-</sup> NH	-17.1
Series 2	
H-C <sup>+</sup> NH <sub>3</sub>	33.8
H-C-CH <sub>3</sub>	35.1
H-C <sup>-</sup> BH <sub>3</sub>	35.7



**Figure 3.**  $E(S) - E(T)$  by STO-3G vs. the empirical substituent constant,  $\Sigma\sigma_R^\circ$ .

decreasing C-X bond order are evident in all the geometries of the triplet states with the electron-withdrawing substituents.

Four carbenes do not fit on either of these lines. The substituents Li and BeH are  $\sigma$  donors, but have no  $\pi$  electrons. CLi<sub>2</sub>, CHLi, and CHBeH have ST gaps approximately equal to that of CH<sub>2</sub>. No electronegativity effect is manifested here. CCl<sub>2</sub> inexplicably deviates from the appropriate  $\pi$  donor line at this level of theory.

At the STO-3G level, the triplet is much too stable relative to the singlet. For example, for methylene, the triplet is calculated to be 40.1 kcal/mol more stable than the singlet, whereas the experimental and best calculated value is 9-10 kcal/mol; for the parent, there is a 30 kcal/mol overestimate of the stability of the triplet state relative to the singlet. For most of these species, there is a 20-30 kcal/mol overestimate of the triplet stabilities. For example, to convert our values of  $E(S) - E(T)$  to those obtained by Schaefer et al.<sup>4</sup> requires subtraction of 27.3, 21.4, 27.0, 23.3, and 1.7 kcal/mol for CH<sub>2</sub>, CHF, CHCl, CF<sub>2</sub>, and CCl<sub>2</sub>, respectively. Except for the anomalous CCl<sub>2</sub>, a correction factor of 20-30 kcal/mol is adequate. In the general case, however, the values may deviate more substantially from this. Considering the extreme cases for which more reliable calculations are available in the literature, we calculate  $E(S) - E(T)$  to be -26.3 and 79.5 kcal/mol respectively for C(OH)<sub>2</sub> and C(CN)<sub>2</sub>, whereas the best literature values from calculations with substantial inclusion of correlation energy are 26.3<sup>3</sup> and ~14<sup>20</sup> kcal/mol, respectively. For these two cases, correction factors of ~0 and ~66 kcal/mol are required for our calculations. This is a rather enormous range of errors, and the corrected STO-3G ST gaps are best used only to estimate experimental values for mild donors.

Performing 3 × 3 CI calculations on the singlet decreases the overestimate of triplet stability somewhat, and the linear correlation improves for the ST gaps of HCX, where X = Li, BeH, BH<sub>2</sub>, CH<sub>3</sub>, NH<sub>2</sub>, OH, and F:  $E(S) - E(T) = 273.9\Sigma\Delta q_\pi + 34$  ( $r = 0.992$ ).

The dominant influence of  $\pi$  donation on carbene ST gaps is further supported by calculations on two isoelectronic series, shown

(17) Staemmler, V. *Theor. Chim. Acta* **1974**, *35*, 309.

(18) Full details of these calculations will be made available on request.

(19) Whiteside, R. A.; Binkley, R. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University, 1980.

(20) Lucchese, R. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1977**, *99*, 13.

(21) Similar results on carboxyhydroxycarbene have been reported recently: Kim, K. S.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 5391.

in Table II. In the first set, substituent  $\pi$  donation increases, and electronegativity decreases, from top to bottom. Only the  $\pi$  donor hypothesis can explain the increasing stability of the singlet relative to the triplet in this series. In the second series, substituent electronegativity decreases to a large extent, from top to bottom, while  $\pi$  donation is expected to be small and constant in the whole series. The near constancy of the ST gap in series 2 attests to the insignificance of electronegativity as an influence on the carbene ST gap.

Since  $\sum \Delta q_r$  has been shown to correlate satisfactorily with the empirical resonance substituent constant,  $\sigma_R^\circ$ ,<sup>12</sup> it is not surprising that the calculated ST gaps correlate with  $\sigma_R^\circ$ 's as well. For the Schaefer-Bauschlicher series of halocarbenes in which ST gaps were calculated with double- $\zeta$  basis sets plus polarization functions<sup>4,20</sup> ( $\text{CH}_2$ ,  $\text{CHX}$ , and  $\text{CX}_2$ , where  $X = \text{F, Cl, or Br}$ );  $E(\text{S}) - E(\text{T}) = 79.5 \sum \sigma_R^\circ + 17.0$  ( $r = 0.962$ ). For our STO-3G calculations on 22 carbenes, a remarkably good correlation is obtained as shown in Figure 3:  $E(\text{S}) - E(\text{T}) = 84.5 \sum \sigma_R^\circ + 43.9$

( $r = 0.969$ ).

If we assume that the STO-3G ST gaps used in this correlation are consistently overestimated by about 31 kcal/mol, this last equation can be recast into an astonishingly simple relationship for the prediction of carbene ST gaps:  $E(\text{S}) - E(\text{T}) = 84.5 \sum \sigma_R^\circ + 13$ . The empirical resonance substituent constants,  $\sigma_R^\circ$ , are available for a large number of substituents.<sup>13</sup>

In conclusion, the ST gaps of substituted carbenes are determined by  $\pi$  donation or acceptance by the substituents. The electronegativity of the central atom of isoivalent species,  $\text{AH}_2$ , influences the ST gap of the parent,<sup>6</sup> and provides a "scaffold" from which substituents modulate the singlet-triplet gap by  $\pi$  donor or  $\pi$  acceptor effects.

**Acknowledgment.** We are grateful to the National Science Foundation (K.N.H.) and the Department of Energy, Office of Environment, under contract No. 80EV10373.000 (J.F.L.) for financial support of this research.

## Delocalized Dicarbanions and Higher Delocalized Carbanions

Robert B. Bates,\*<sup>1a</sup> B. Andes Hess, Jr.,\*<sup>1b</sup> Craig A. Ogle,<sup>1a</sup> and L. J. Schaad\*<sup>1b</sup>

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721, and Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.

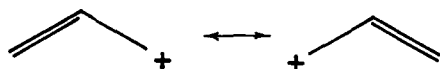
Received February 25, 1981

**Abstract:** Simple routes to four new dianions with high resonance energy per atom (REPA) and improved preparations for several other di- and trianions are given. REPA is calculated for delocalized dicarbanions and higher delocalized carbanions which have been prepared and many which have not. Most low molecular weight anions with a charge of less than 0.5 e per atom have REPA's indicating stabilization and most with 0.5 e or more do not. Simple monocyclic anions are calculated to be stabilized or destabilized relative to the corresponding acyclic anions in accordance with the Hückel rule, except that when the charge per atom is large, all of the cyclic anions are destabilized. For linear acyclic and monocyclic systems, REPA is calculated to be maximum at a charge of about 0.17 e per atom. Cyclopentadienyl anion has the largest REPA, and the 13 next highest REPA's belong to some of its di- and trianion derivatives. The calculated values correlate well with the experimental ease of preparation and stabilities of these anions.

Due largely to their bond-forming reactions with a great variety of electrophiles, carbanions are among the most important intermediates in organic synthesis. We report here the synthesis of several new dianions together with calculations of their resonance energies. Calculated resonance energies of many other recently prepared<sup>2</sup> as well as of yet-to-be-prepared dicarbanions and higher carbanions are also given. These calculations correlate well with earlier and new experimental findings on those whose preparation has been attempted. They should help to indicate which new members of this class are worthwhile synthetic goals.

### Theory

We have recently shown that the resonance stabilization of ions and radicals can be computed by using the Hückel method in conjunction with a localized reference structure.<sup>3</sup> One of the major difficulties in obtaining a localized reference for ions and radicals was that they, unlike acyclic molecules (e.g., butadiene), have more than one resonance structure as in the allyl cation.



(1) (a) University of Arizona. (b) Vanderbilt University.

(2) Bates, R. B. In "Comprehensive Carbanion Chemistry"; Buncl, E., Durst, T., Eds.; Elsevier: New York, 1980; pp 1-53.

(3) Hess, B. A., Jr.; Schaad, L. J. Plenary Lecture, International Symposium on Aromaticity, Dubrovnik, Yugoslavia, Oct 1979; *J. Pure Appl. Chem.* 1980, 52, 1471.

Table I. Ion and Radical Bond Energy Terms

bond type <sup>a</sup>	designation	bond energy, $\beta$
HC-CH <sub>2</sub> *	$E_3^*$	0.6632
HC-CH*	$E_2^*$	0.5996
C-CH <sub>2</sub> *	$E_2'^*$	0.5950
HC-C*	$E_1^*$	0.5480
C-CH*	$E_1'^*$	0.5697
C-C*	$E_0^*$	0.5430
HC*-CH <sub>2</sub> *	$E_3^{**}$	0.7967
HC*-CH*	$E_2^{**}$	0.7330
C*-CH <sub>2</sub> *	$E_2'^{**}$	0.7067
C*-CH*	$E_1'^{**}$	0.6815
C*-C*	$E_0^{**}$	0.6570

<sup>a</sup> The asterisks refer to positive or negative charges or in the first six bond energy terms to single electrons. We have treated only monoradicals, and the last five bond energies do not apply to these systems.

This problem was overcome by adopting a reference structure containing long (single) and short (double) bonds patterned after that of Mulliken and Parr.<sup>4</sup> Having defined this reference and obtained the reference energy and the resonance energy of the allylic system, all bond energy terms for computing localized

(4) Mulliken, R. S.; Parr, R. G. *J. Chem. Phys.* 1951, 19, 1271.