A Comparative Quantum Chemical Investigation of the Bonding in First and Second Row Ylides

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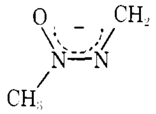
Abstract: Ab initio SCF-MO computations (4-31G) have been performed on the model ylides $^+PH_3CH_2^-$, $^+NH_3CH_2^-$, $^+SH_2CH_2^-$, and $^+OH_2CH_2^-$. In the first row ammonium and oxonium ylides, the $^+X{-}C^-$ bonds are longer than the X-C bonds of the stable tautomers of these ylides, methylamine and methanol. In the second row ylides, the $^+X{-}C^-$ bonds are shorter than the X-C bonds of the tautomers methylphosphine and methanethiol. The carbanionic centers of the second row ylides are more planar and more flexible than those of the corresponding first row ylides. Examination of charge distributions and overlap populations reveals that, in terms of both their covalent and ionic character, the $^+X{-}C^-$ bonds of the second row ylides are stronger than those of the corresponding first row ylides. These various findings are in agreement with experimental data, where these are available. The different structural characteristics of first and second row ylides can be rationalized in terms of group orbital interaction diagrams, which focus upon the stabilizing and destabilizing interactions between a carbon lone pair and π and π^* XH_n group orbitals. The destabilizing interaction dominates when X is a first row atom, and the stabilizing interaction dominates when X is a second row atom.

In 1955, Doering and Hoffmann[2] presented the results of a kinetic study of deuterioxide-catalyzed hydrogen-deuterium exchange of the methyl protons of tetramethylammonium, tetramethylphosphonium, and trimethylsulfonium cations. Since these reactions proceed via "onium" ylide intermediates, the objective of the work was to obtain information, in the form of rate constants and activation parameters, concerning the differing abilities of ammonium (N^+), phosphonium (P^+), and sulfonium (S^+) groups to stabilize (or destabilize) a developing adjacent carbanionic center. It was found that the enthalpies of activation were 32.2, 25.6, and 22.4 kcal/mol for the exchange of N^+, P^+, and S^+, respectively.

This work has since become a classic of its kind, and it is quoted extensively[3] to support the view that d-orbital conjugative effects are present in phosphonium and sulfonium ylides. Such an interpretation contains the implicit assumption that the activation parameters for the exchange of the ammonium cation are "normal", so that what is being observed is a *lowering* of the energy of the transition state in P^+ and S^+, i.e., a stabilizing effect in these cases.

However, there is an alternative explanation if it is supposed that P^+ and S^+ are the "normal" systems, and that, to take an extreme position, what is actually being observed is a *destabilizing* effect in N^+. This consideration developed in response to the interesting observations that the methyl groups of azoxymethane undergo exchange at different rates, and the more reactive site is the one *remote* from oxygen.[4] Since the stabilizing effects of conjugative interactions (e.g., **1**) in this system are not known, a permissive speculation is that both methyl groups are activated in this molecule, but the methyl protons proximate to oxygen exchange more slowly because the ammonium ylide intermediate is destabilized preferentially.



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Structural studies on phosphonium and sulfonium ylides (see Table I) suggest that some kind of stabilizing factor is operative in the $^-C{-}X^+$ region, because this bond is significantly shorter than a C-X single bond. However, no such stabilization is evident in the ammonium ylides shown in Table I. In the case of the molecules **9** and **10**, the $^+N{-}N^-$ bond is significantly *longer* than the N-N bond of hydrazine. Such findings are compatible with the speculation that destabilizing effects are substantial in ylides containing a positively charged first row atom.

The purpose of the present work is to examine, using ab initio SCF-MO theory, the static and dynamic stereochemical properties and the nature of the bonding, in particular the stabilizing and destabilizing effects present in the $^-C{-}X^+$ region, in a series of model ylide systems containing first and second row atoms. The compounds examined are $^+PH_3CH_2^-$, $^+NH_3CH_2^-$, $^+SH_2CH_2^-$, and $^+OH_2CH_2^-$. Although a number of semiempirical and ab initio theoretical studies of specific ylides have already been reported,[5] the novel feature of the present investigation is the attempt to ascertain and to analyze the effects of different heteroatoms.

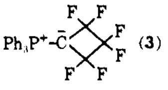
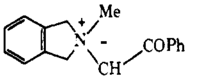
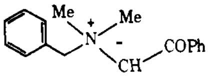
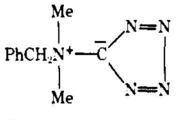
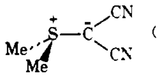
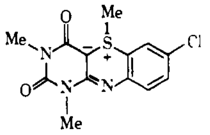
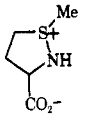
Calculations

The computations have been performed using the GAUSSIAN 70 program system[6] with the 4-31G basis set.[7] This basis set does not contain d-type functions on second row atoms. Consequently, no conclusion can be reached in this work concerning the relevance or irrelevance[5i,8,9] of d-orbital conjugation in these molecules. Nevertheless, as will be seen, the 4-31G basis set does reproduce the trends in the experimental geometries, where these are available, and a simple orbital interaction model can be constructed to rationalize these trends. The following bond lengths and valence angles were employed in the calculations: $r_{PH} = 1.424$; $r_{NH} = 1.014$; $r_{SH} = 1.323$; $r_{OH} = 0.96$; $r_{CH} = 1.091$ Å; $\angle HPH = 109.5$; and $\angle HNH = 109.5°$. All other geometrical parameters such as the $X^+{-}C^-$ bond lengths (X = P, N, S, O), the carbon valence angles, and the dihedral angles were optimized. The optimization of the carbon valence angles was performed using the constraint that $\angle HCH = \angle HCX$ and $\angle HXH = \angle HXC$.

Results and Discussion

A. Bond Lengths. The geometries of the most stable conformations of the four model ylides are summarized in Table II. The $X^+{-}C^-$ bond lengths ($r_{X^+C^-}$) are listed in the second column of this table. The numbers in parentheses refer to the X-C bond lengths (r_{XC}) in the tautomeric forms of these ylides, i.e., CH_3PH_2, CH_3NH_2, CH_3SH, and CH_3OH. Each of

Table I. Experimental Bond Lengths of Various Ylides and Related Molecules

Compd	Bond length, Å	Ref
$Ph_3P^+{-}CH_2^-$ (2)	$r_{P^+C^-} = 1.661$	*a*
 (3)	$r_{P^+C^-} = 1.713$	*b*
$(CH_3)_3P$	$r_{PC} = 1.841$	*c*
 (4)	$r_{N^+C^-} = 1.48$	*d*
 (5)	$r_{N^+C^-} = 1.47$	*d*
 (6)	$r_{N^+C^-} = 1.47$	*e*
CH_3NH_2	$r_{NC} = 1.474$	*f*
 (7)	$r_{S^+C^-} = 1.73$	*g*
 (8)	$r_{S^+C^-} = 1.721$	*h*
$(CH_3)_2S$	$r_{SC} = 1.809$	*i*
$Me_3N^+{-}{}^-NCOPh$ (9)	$r_{N^+N^-} = 1.471$	*j*
$Me_3N^+{-}{}^-NNO_2$ (10)	$r_{N^+N^-} = 1.470$	*j*
H_2NNH_2	$r_{NN} = 1.453$	*k*
 (11)	$r_{S^+N} = 1.679$	*l*

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these latter bond lengths was obtained by a geometry optimization using the 4-31G basis set.

Examination of these various bond lengths reveals that $r_{X^+C^-} < r_{XC}$ when X is a second row atom, but $r_{X^+C^-} > r_{XC}$ when X is a first row atom. That this observation is a genuine characteristic of first and second row ylides seems to be supported by the experimental bond lengths collected in Table I. Since the model systems are nonstabilized ylides,[3] the calculated trends should, in principle, be compared to experimental measurements on nonstabilized ylides. However, with the exception of the first entry of Table I, such measurements are not available.

B. The Geometry at Carbon. It seems probable that the length of the X^+–C^- bond and the geometry at the ylide carbon are related observables because both depend upon the nature of the interaction between carbon and the adjacent heteroatom. Such an interrelationship is often implied in discussions of the short carbon–phosphorus bond of phosphonium ylides. Thus, Wittig states[10] that "*phosphorus . . . can expand its outer electron shell. This makes possible an energy-lowering resonance stabilization between ylide and ylene forms . . . with partial P═C bonding*". The effect of such bonding upon the geometry at carbon is uncertain because, as Ebsworth has pointed out,[11] the overlap between an sp^3 hybrid orbital and an adjacent d orbital is not much less than the p_π–d_π overlap. Nevertheless, according to Schmidbaur,[12] "*it seems to be well established that the phosphorus ylides are best described to be built up from sp^3 hybridized phosphorus atoms interacting with an sp^2 hybridized ylidic carbon atom.*"

Table II. Optimized Geometrical Parameters of the Model Ylides

Ylide	Bond length, Å	Valence angle, deg	Dihedral angle, deg[a]
$^+PH_3CH_2^-$	1.762 (1.922[b,c])	∠HCH = 117.7	180
$^+NH_3CH_2^-$	1.538 (1.451)	∠HCH = 103.6	180
$^+SH_2CH_2^-$	1.801 (1.885)	∠HCH = 109.2 ∠HSH = 105.4	90
$^+OH_2CH_2^-$	1.587 (1.429)	∠HCH = 96.7 ∠HOH = 120	90

[a] Dihedral angles of 0 and 180° refer to eclipsed and staggered (or antiperiplanar) conformations, respectively. [b] Numbers in parentheses refer to the X–C bond lengths of the stable tautomeric forms of the model ylides. [c] J. B. Collins, P. v R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

Schmidbaur's views were influenced by a crystallographic study of salt-free methylenetriphenylphosphorane (entry 1 of Table I), in which the methylene carbon was found to be planar. On the other hand, a study of the kinetic and thermodynamic acidities of fluoromethyl, methyl, and ethyltriphenylphosphonium salts[13] is more compatible with a pyramidal carbon atom in the derived ylides. Whether these latter observations are the result of salt effects[14] is not known. The ^{13}C NMR[15] and photoelectron spectra[16] of nonstabilized phosphonium ylides have been interpreted in terms of a planar configuration at carbon. However, the interpretation of these data is complicated by a lack of suitable model systems of known geometry.

The present computations are unable to resolve this problem because of the well-known sensitivity of computed carbon valence angles and barriers to pyramidal inversion to basis set variations.[17] For example, the optimized valence angles of CH_3^- are found to be 101 and 120° in STO-3G and 4-31G computations, respectively, for a C–H bond length of 1.091 Å. Similarly, the carbon valence angles of $^+PH_3CH_2^-$ are calculated to be 109 and 117.2° with the STO-3G and 4-31G basis sets, respectively;[5e] the corresponding results for $^+SH_2CH_2^-$ are 102 and 109°.

Despite the basis set dependence, the *trend* that carbon is more planar in the phosphonium ylide than in the sulfonium ylide is observed with both basis sets. The data shown in the third column of Table II have all been generated with the same carbon basis set. These indicate that the carbanionic center is more planar in the second row ylides than in the first row ylides and, within a row, more planar for the group 5 heteroatom than for the group 6 heteroatom. It is noteworthy that the azasulfonium salt **11**, which is isoelectronic with a nonstabilized sulfonium ylide, has a pyramidal configuration at nitrogen.

In the earlier, semiempirical studies,[5d] CNDO/2 computations predicted the carbanionic center of the phosphonium ylide to be planar when d orbitals are present on phosphorus, and pyramidal when d orbitals are absent. A very recent ab

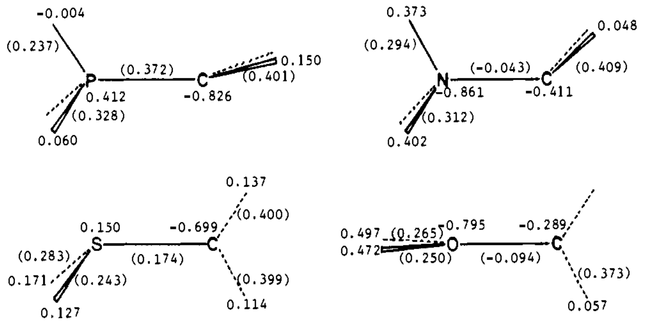

Figure 1. Net atomic charges and overlap populations (in parentheses) calculated for the model ylides.

Table III. Rotation and Inversion Barriers of the Model Ylides[a]

Ylide	Rotational barrier	Inversion barrier[b]
$^+PH_3CH_2^-$	0.40	0.13 (C)
$^+NH_3CH_2^-$	2.30	12.4 (C)
$^+SH_2CH_2^-$	11.0[c]	4.40 (C)
	7.60[d]	13.4 (S)[e]
$^+OH_2CH_2^-$	2.9	21.0 (C)

[a] Energies are in kcal/mol. [b] The site of inversion is shown in parentheses. [c] This number refers to the gauche → cis (eclipsed) barrier. [d] This number refers to the gauche → anti barrier. [e] With the 4-31G basis set and r_{SH} = 1.323 Å, the pyramidal inversion barrier of $^+SH_3$ is calculated to be 17.7 kcal/mol. The 4-5 kcal/mol lower sulfur inversion barrier in the ylide agrees well with experimental findings. See, e.g., D. Darwish and R. L. Tomilson, *J. Am. Chem. Soc.*, **90**, 5938 (1968); S. Wolfe, P. Chamberlain, and T. F. Garrard, *Can. J. Chem.*, **54**, 2847 (1976).

initio calculation[5i] indicates only slight distortion from planarity at carbon in PH_3CH_2. In ammonium ylides,[5d,f] the carbanionic center has been found to be pyramidal by both the CNDO/2 and MINDO/3 procedures. These various results are compatible with the trends found in the present work.

C. Rotation and Inversion Barriers. Table III lists the barriers to rotation about the X^+-C^- bonds and the barriers to pyramidal inversion at X^+ and C^-. The rotational barriers were obtained by rigid rotation of the most stable conformation of each ylide; the inversion barriers refer to a single inversion process at X or C.

The carbanion inversion barriers of the model ylides increase in the order $^+PH_3CH_2^- < {}^+SH_2CH_2^- \ll {}^+NH_3CH_2^- < {}^+OH_2CH_2^-$. This trend parallels the pyramidalities of the ylide carbon atoms, and it can be concluded that the carbanionic centers of second row ylides are both more planar and more flexible than those of the corresponding first row ylides.

D. Charge Distribution. We employ the Mulliken population analysis[18] to discuss the charge distribution in the model ylides. Figure 1 shows the overlap populations of each bond and the net atomic charges on the atoms of these systems in their most stable conformations.

In the second row ylides, the net charges on X and C are positive and negative, respectively. However, in the first row ylides, both X and C have net negative charges and, in addition, the X atom accumulates more negative charge than does carbon.

The ionic bond order, p'_{AB}, is defined by

$$p'_{AB} = -q_A q_B / r_{AB} \qquad (1)$$

in which q_A and q_B are the net charges on the atoms A and B, respectively.[19] The ionic bond order of the X-C bond is thus positive in the second row ylides and negative in the first row ylides. The overlap population of the X-C bond is also positive in the second row ylides and negative in the first row ylides.[20] Thus in terms of both their covalent and ionic character, the X-C bonds of the second row ylides are stronger than those of the corresponding first row ylides.

Figure 2. Schematic representation of the nodal properties of the HOMO's. In each case, carbon is on the left and XH_n is on the right. Top left, P^+; top right, S^+; lower left, N^+; lower right, O^+.

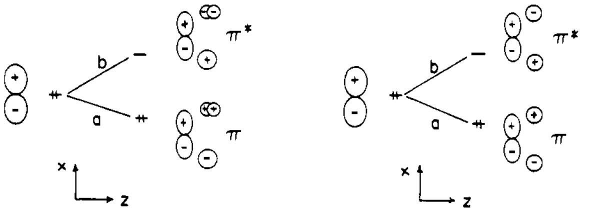

Figure 3. (A) A qualitative group orbital interaction diagram for $^+PH_3CH_2^-$ and $^+NH_3CH_2^-$. The left hand side of the diagram represents the CH_2^- group and the right hand side represents the $^+XH_3$ group. (B) A qualitative group orbital interaction diagram for $^+SH_2CH_2^-$ and $^+OH_2CH_2^-$.

This result leads to the expectation that the stability of ylides with respect to dissociation into carbenes will be greater for the second row systems. It is known that ammonium ylides dissociate readily in this way.[21] Sulfonium ylides sometimes undergo this reaction,[22] but phosphonium ylides dissociate only upon heating at high temperatures or upon photolysis.[23]

E. Perturbational Molecular Orbital Analysis. In this section, the differences in the bonding of the first and second row ylides are discussed in terms of a fragment orbital interaction analysis. The nodal properties of the highest occupied molecular orbitals (HOMO's) of the model ylides are represented schematically in Figure 2. In each case, the dominant contributor to the HOMO is the carbon lone pair.[5h,i] However, closer examination of Figure 2 reveals that, in the HOMO's of the second row ylides, the X-C region is π bonding and the X-H region is π antibonding. In the first row ylides, the X-C region is π antibonding and the X-H region is π bonding. This is a most important observation, as can be seen upon consideration of the qualitative fragment orbital interaction diagrams shown in Figure 3.

In each ylide, the HOMO shown in Figure 2 is derived mainly by the sum of the out-of-phase combination of interaction a and the in-phase combination of interaction b. A comparison of Figures 2 and 3 shows clearly that the four-electron *destabilizing* interaction a dominates in the first row ylides, and that the two-electron *stabilizing* interaction b dominates in the second row ylides. When three orbitals and four electrons interact in the manner shown in Figure 3, dominance of a leads to π antibonding, and dominance of b leads to π bonding in the X-C region. That this is the case here is evident from the X-C overlap populations that result from the p_x orbitals of X and C (Table IV).

From an energetic point of view the two-orbital two-electron interaction b leads to a net energy stabilization given by the following expression

$$\Delta E_{ij}{}^2 = \frac{(K - \epsilon_i)^2}{\epsilon_i - \epsilon_j} S_{ij}{}^2 \qquad (2)$$

Table IV. Computed Overlap Populations between the p_x Orbitals on X^+ and C^- in the Model Ylides

Ylide	Overlap population
$^+PH_3CH_2^-$	0.119
$^+NH_3CH_2^-$	−0.019
$^+SH_2CH_2^-$	0.064
$^+OH_2CH_2^-$	−0.011

while the two-orbital four-electron interaction a leads to a net destabilization energy given by the following expression[24]

$$\Delta E_{ij}{}^4 = \frac{4S_{ij}{}^2}{1 - S_{ij}{}^2}(\epsilon - K) \qquad (3)$$

In eq 2 and 3 ϵ_i and ϵ_j are the orbital energies of the interacting orbitals, ϵ the mean of such energies, S_{ij} their overlap integral, and K is a constant.

Thus, dominance of b in the second row ylides explains the shortening of the X–C bond and the tendency of the ylide carbon to be more planar, since these geometrical changes are accompanied by an increase in the overlap integral, a decrease in the energy gap, and therefore a greater stabilization.

On the other hand, when a dominates, the destabilization associated with this interaction is lessened by a lengthening of the X–C bond and concomitant pyramidalization of the carbanionic center, since these geometrical changes are accompanied by a decrease in the overlap integral and by a more negative value of ϵ, which in turn leads to a smaller $(\epsilon - K)$ value.

The discussion just presented has ignored the possibility that $(p \rightarrow d)_\pi$ conjugative effects are present in the second row ylides, because the ab initio SCF-MO calculations upon which it is based did not employ d-type functions in the basis set. Despite this computational choice, the experimental trends in the X–C bond lengths of phosphonium, sulfonium, and ammonium ylides were reproduced acceptably. In terms of the interaction model of Figure 3, the dominance of b in the second row ylides is the result of an availability of low-lying π^* orbitals of the $^+PH_3$ and $^+SH_2$ groups;[25] within the framework of this model, these fragment orbitals fulfill the role otherwise attributed to 3d orbitals.

A particularly pleasing feature of the interaction analysis is that it contains contributions from both attractive (stabilizing) and repulsive (destabilizing) effects; and it provides a qualitative understanding of the interplay between these effects as the heteroatom is changed. Thus the stabilization envisaged for P^+ and S^+ by Doering[2] has been traced to the dominating effect of interaction b; and the destabilization postulated for N^+ has also been found, in the dominating effect of a in this case.

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(20) The finding of a negative $X^+–C^-$ overlap population in the first row ylides does not mean that no bonding orbital exists in this region. Rather, it indicates that the positive overlap population associated with the $\sigma_{X^+C^-}$ bonding orbital is outweighed by the net negative overlap populations resulting from the π-type molecular orbitals of these systems (vide infra).
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(24) This result is obtained by application of the variational method to the case of a two-orbital interaction and involves no additional assumptions other than the usual approximation of the interaction matrix element as a linear function of the overlap integral; for details, see L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968).
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