Generalized Valence Bond Description of Simple Ylides

David A. Dixon,*[†,⊥] Thom H. Dunning, Jr.,[†] Robert A. Eades,[‡] and Paul G. Gassman*[‡]

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received March 21, 1983

Abstract: The electronic structures of the simplest ylides of nitrogen, oxygen, phosphorus, and sulfur have been determined from ab initio molecular orbital theory at the GVB + POL-CI level. The calculations were performed with double-ζ quality basis sets augmented by polarization (d) functions on the heavy atoms and a set of diffuse s and p functions on carbon. The energies for the internal proton-transfer reaction to form the ylide from its most stable isomer, $CH_3XH_n \rightarrow CH_2^-XH_{n+1}^+$, are 52.5, 66.3, 82.9, and 92.8 kcal/mol for X = P, N, S, and O, respectively, at the GVB + Pol-CI level. GVB orbitals for CH_3NH_2, CH_3OH, CH_3PH_2, and CH_3SH are presented. Differences in bonding, specifically for the lone pairs, between first- and second-row elements are discussed. The GVB orbitals for the ylides are discussed and are employed in a description of the bonding in these species.

The structures of ylides have been investigated by a number of workers because they are important intermediates in organic synthesis.[1] However, as intermediates, they are extremely difficult to characterize both in terms of structure and in terms of energetics. Thus, all of the studies on the structure of the simplest ylides with hydrogen as the substituent have been made by using molecular orbital theory. We[2] and others[3-12] have previously examined the conformations of these ylides at the Hartree–Fock level. The energetics of the ylides relative to their stable nonzwitterionic isomers as shown in reactions 1a and 1b have pre-

$$CH_3XH_2 \rightarrow CH_2^-XH_3^+ \quad (X = N, P) \qquad (1a)$$

$$CH_3XH \rightarrow CH_2^-XH_2^+ \quad (X = O, S) \qquad (1b)$$
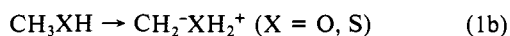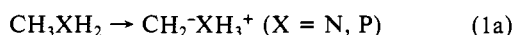
viously been investigated at the Hartree–Fock level.[2] At present there are two configuration interaction (CI) studies of ylides, one for $CH_2^-PH_3^+$ [6] and one for $CH_2^-OH_2^+$.[10] For the latter ylide, the energetics for reaction 1b have been obtained.

In this paper, we present results of calculations on the ylides and their isomers at both the generalized valences bond (GVB)[13] and configuration interaction (CI) level.[14] The GVB method was chosen to explore these ylides since (1) it accounts for important correlation effects involved in the making and breaking of bonds, (2) it can provide a simple chemical model for the description of the bonding in these novel systems, and (3) it provides an appropriate set of orbitals for the CI calculations. The bonding in both the nonzwitterionic isomers and the ylides is discussed in terms of the GVB orbitals.

Calculations

All calculations were performed with the computer codes operational at Argonne National Laboratory: BIGGMOLI (integrals), GVBTWO Version 2.0 (GVB calculations), and CITWO (CI calculations). The contracted Gaussian orbital basis sets were of double-ζ quality with polarization functions on the heavy atoms. The exponents and contraction coefficients were taken from Dunning and Hay.[15] The basis set for C was augmented by a set of diffuse s and p functions with exponents $\zeta(s) = 0.04548$ and $\zeta(p) = 0.034$, since the methylene group in the ylide is nominally a carbanion. It is well-known that diffuse functions are required to properly describe a negative ion.[15] This gives basis

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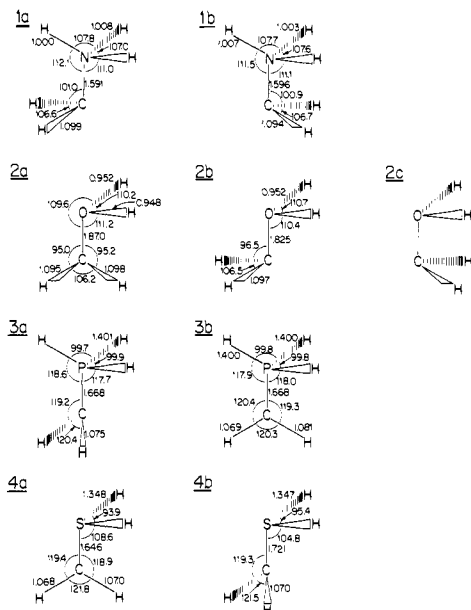
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[†] Argonne National Laboratory.

[‡] University of Minnesota.

[⊥] Address correspondence to this author at the Central Research and Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19898. A. P. Sloan Foundation Fellow, 1977–1981; Camille and Henry Dreyfus Teacher–Scholar, 1978–1983; Du Pont Young Faculty Grantee, 1978.

Figure 1. Conformations of the ylides. The **a** conformations are the most stable. **1**, $CH_2^-NH_3^+$; **2**, $CH_2^-OH_2^+$. **2c** represents the eclipsed conformation; **2b** represents a 180° rotation about the C–O bond of **2c**; and **2a** results from a 90° rotation about the C–O bond of **2c**. The geometric parameters for **2c** are taken from **2b**; **3**, $CH_2^-PH_3^+$; **4**, $CH_2^-SH_2^+$.

sets of the form: H, (4)/[2]; C, (10,6,1)/[4,3,1]; N and O, (9,5,1)/[3,2,1]; and P and S, (11,7,1)/[6,4,1]. The geometries were taken from our previously reported SCF structures obtained with the above basis sets.[2] The structures of the ylides were geometry optimized, and the geometries for the neutrals are from experiment. The conformations studied in this work are shown in Figure 1.

The GVB calculations were done with the constraints of perfect pairing and strong orthogonality. The GVB wave function properly describes the dissociation of a bond AB to A· and B·. The Hartree–Fock orbital for a bond AB is a doubly occupied orbital with paired electrons

$$[\phi_n(1)\phi_n(2)]\alpha\beta$$

At the bond dissociation limit, one obtains an ion pair, e.g., A⁻ and B⁺, since the orbital remains doubly occupied at all times. The GVB orbital pair

$$[\phi_a(1)\phi_b(2) + \sigma_a(2)\sigma_b(1)]\alpha\beta$$

can properly describe the bond dissociation process leading to the neutral radicals A· and B·. Thus each bond pair at the GVB level is composed of two one-electron orbitals that optimally describe the bond. For the ylides and neutrals with N and P as the substituent, the C_s structures (see Figure 1) are nominally the same. For these molecules, we split the electron pairs that are changing in the isomerization. For CH_3NH_2 and CH_3PH_2, this corresponds to splitting the C–X bond, the lone pair on X and the C–H bond in the plane. For the corresponding ylides, the C–X bond, the nominal "lone pair" on C, and the in-plane X–H bond were split. These orbitals remained reasonably well localized during the calculations (see the discussion below for $CH_2^-PH_3^+$). For the ylides of O and S, such calculations splitting only three pairs are not possible because of symmetry constraints. Furthermore, an attempt on CH_3OH to perform a similar three-pair calculation did not yield the same orbitals as were input as an initial wave function. For the neutrals and ylides with S or O as the substituent, all seven electron pairs in the valence space were split in the GVB calculations.

The CI calculations were done at the polarization–CI (POL–CI) level.[16] The POL–CI method is closely related to the first-order–CI method of Schaefer and co-workers.[17] The core orbitals are not included in the CI calculation and remain doubly occupied.

Table I. Total Energies (au)

molecule	SCF	GVB	POL–CI
CH_3NH_2	−95.228 11	−95.271 87[c]	−95.350 26
$CH_2^-NH_3^+$	−95.118 69	−95.164 00[c]	−95.244 64
CH_3OH	−115.063 63	−115.171 18[d]	−115.285 88
$CH_2^-OH_2^+(1)^a$	−114.925 84	−115.030 15[d]	−115.137 93
$CH_2^-OH_2^+(2)^b$	−114.924 27	−115.028 82[d]	−115.137 49
CH_3PH_2	−381.491 64	−381.526 10[c]	−381.586 49
$CH_2^-PH_3^+$	−381.400 02	−381.435 13[c]	−381.502 87
CH_3SH	−437.702 16	−437.787 17[d]	−437.890 53
$CH_2^-SH_2^+(1)^a$	−437.571 99	−437.653 57[d]	−437.758 45
$CH_2^-SH_2^+(2)^b$	−437.538 18	−437.621 25[d]	−437.724 43

^{a} Most stable form. ^{b} Rotated form. ^{c} Three pairs are split. ^{d} Seven pairs are split.

Table II. Energetics for Internal Proton Transfer and $\Delta H_f°$ for Ylides (kcal/mol)

ylide hetero-atom	ΔE-(SCF)	ΔE-(GVB(pp))	ΔE-(POL–CI)	$\Delta H_f°$-(ylide)
P	57.5	57.1	52.5	58.8
N	68.7	67.7	66.3	60.8
S	81.7	83.8	82.9	77.6
O	86.5	88.5	92.8	44.8

All single and double excitations are generated relative to the reference configurations of the GVB calculation with the restriction that no more than one electron can occupy an orbital outside the GVB space (GVB orbitals plus Hartree–Fock valence orbitals). The POL–CI method allows for the incorporation of important many-body effects neglected at the GVB level.

Results: Energetics

The total energies for each species are given in Table I at the SCF, GVB, and POL–CI levels. In Table II we present the isomerization energies for reactions 1a and 1b. As shown in Table II, the SCF values provide a reasonable estimate for the isomerization energy. The SCF and GVB values are in excellent agreement with the GVB energies, decreasing for the P and N substituents and increasing for the O and S substituents. The POL–CI calculations lower the isomerization energy for forming the phosphonium ylide by 4.6 kcal/mol but only change the energy for formation of the ammonium ylide by 1.4 kcal/mol in comparison with the GVB energies. The POL–CI calculations also lower the energy of the sulfonium ylide by 0.9 kcal/mol with respect to the GVB result. For the oxonium ylide, the CI actually increases the energy by 4.3 kcal/mol. We have also obtained energies for the rotated forms of the oxonium and sulfonium ylides. The energy difference at the SCF level for the two rotamers of the oxonium ylide is small (1 kcal/mol), and the difference becomes less at the POL–CI level (0.3 kcal/mol). The energy difference between the two rotamers of the sulfonium ylide is large (~20 kcal/mol) and is essentially independent of the level of calculation.

The only other calculation available at the CI level for an isomerization energy (reaction 1) is the work of Harding et al.[10] on the CH_4O surface. They employed a 6-31G** basis set with second-, third-, and fourth-order Møller–Plesset (MP) perturbation theory.[18] They find the isomerization energy for the oxonium ylide to be 94.8, 91.9, and 90.1 kcal/mol at the MP2, MP3, and MP4 levels, respectively. The geometries for these calculations were taken from HF/6-31G* optimized structures. If MP2/6-31G* geometries are employed, the relative energies are 91.8, 90.6, and 89.2 kcal/mol at the MP2, MP3, and MP4 levels, respectively. These values are in excellent agreement with our value of 92.8 kcal/mol considering the differences in basis set, geometry, and method of calculation. We note that these values represent ΔE and as such have not been corrected for zero-point effects. Harding et al.[10] have calculated zero-point energies for CH_3OH and $CH_2^-OH_2^+$ at the HF/6-31G* level. The difference in

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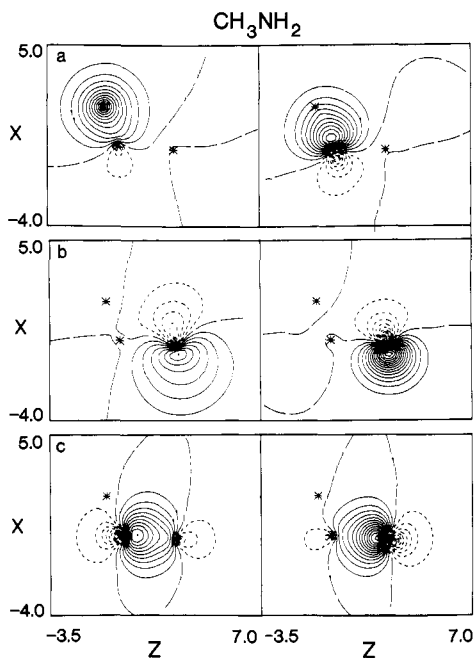
Figure 2. Generalized valence bond orbitals for CH_3NH_2. Contour intervals are in units of 0.05. Asterisks show atoms in the plane. The carbon is always on the left in the center. The heteroatom is on the right in the center. The remaining asterisks are hydrogens. The horizontal axis runs from −3.5 to 7.0 au while the vertical axis runs from −4.0 to 5.0 au. Solid lines indicate positive amplitude, and short dashed lines indicate negative amplitude. Long dashed lines show the nodal line. (a) C–H bond pair, (b) lone pair on N, (c) C–N bond pair.

zero-point energies is 4.6 kcal/mol, with the ylide having the smaller zero-point energy. Since the ylide is less stable than its isomer, the relative energy decreases to 84.6 kcal/mol at the MP4/6-31G**//MP2/6-31G* level. The zero-point difference will be the largest for the oxygen system since the structural differences are the greatest for this pair. The zero-point differences for the other pairs will be significantly smaller since the structures are more comparable. The main difference in zero-point energies for these compounds will be due to the difference in frequency between that of a C–H bond in the nonzwitterionic isomer and of an X–H bond in the ylide.

We can also estimate the energy difference obtained by Lischka[6] by combining his calculated value for the proton affinity of $CH_2^-PH_3^+$ and the corrected electronic component of the experimental value for the proton affinity (PA) of PH_2CH_3.[19,20] Lischka's method of calculation should adequately reproduce the experimental PA. Thus, Lischka's results yield an isomerization energy of 57 kcal/mol, in reasonable agreement with our result considering the approximations involved.

Bonding: Parent Molecules

In order to discuss the bonding in these molecules, we have plotted the GVB orbitals in Figures 2–5. As discussed previously, each GVB electron pair is composed of *two* one-electron orbitals. Let us first consider the C–H bond pair shown in Figure 2 for CH_3NH_2. The bond pair is split into two orbitals, one orbital predominatly localized on C and one orbital predominantly
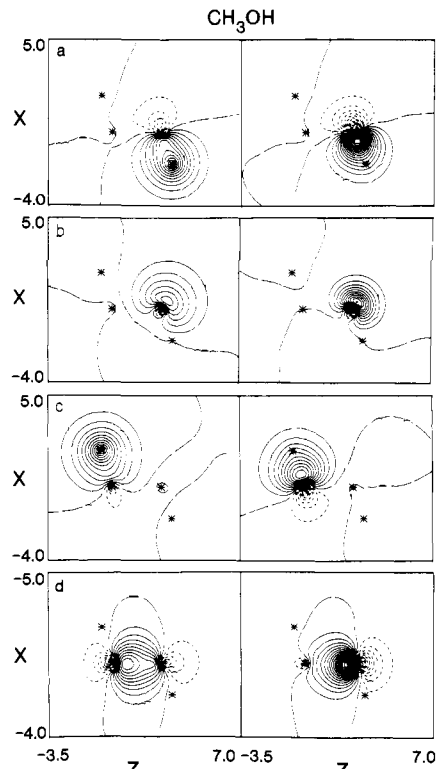
(19) The proton affinity (PA) of CH_3PH_2 is 204.8 kcal/mol using a value for PA(NH_3) of 205.0 kcal/mol (ref 20). The electronic component at 0 K, ΔE_0, for PA(B) is given by $\Delta E_0 = -PA(B) - \Delta ZPE + \frac{5}{2}RT$ where ΔZPE is the difference in zero-point energies between B and BH^+ and the $\frac{5}{2}RT$ term is a conversion factor for going between ΔH and ΔE (ref 21). The ΔZPE term has been calculated to be 6.6 kcal/mol at the STO-3G level (ref 22). This gives $\Delta E_0(CH_3PH_2) = -209.9$ kcal/mol. The CEPA value for PA(CH_2PH_3) from ref 3 is −267.9 kcal/mol.

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Figure 3. Generalized valence bond orbitals for CH_3OH (see Figure 2): (a) O–H bond pair, (b) lone pair on O, projection on molecular symmetry plane, (c) C–H bond pair, (d) C–O bond pair.
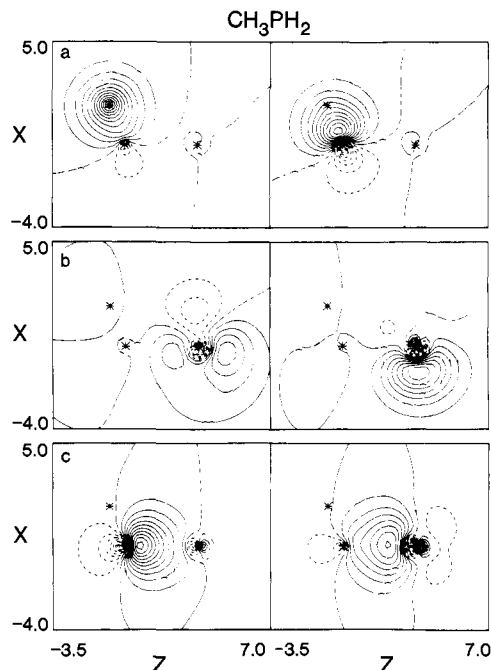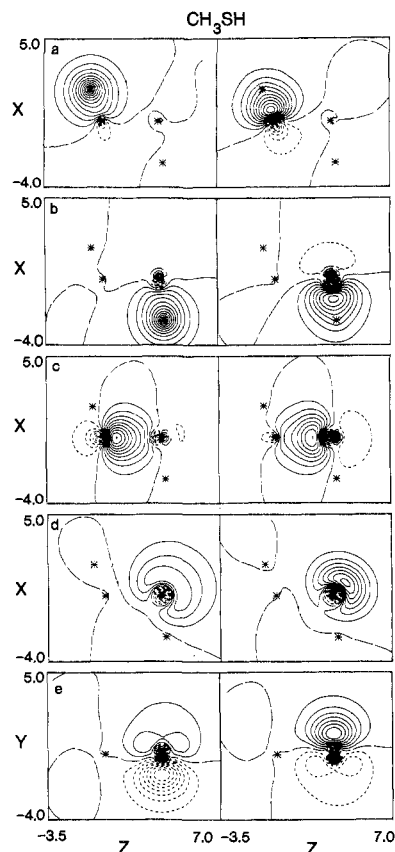

Figure 4. Generalized valence bond orbitals for CH_3PH_2 (see Figure 2): (a) C–H bond pair, (b) lone pair on P, (c) P–C bond pair.

localized on H. The C–N bond follows a similar pattern with one orbital localized on C and one orbital localized on N. Since the N is more electronegative, the orbital on N has its density more highly localized near the atom than does the corresponding orbital on C. The C–H and C–N bond pairs provide an example of the left–right correlation expected for a chemical bond. The lone pair is localized on N and exhibits in–out correlation with one tight orbital and one diffuse orbital rather than the left–right correlation observed for the bond pairs. The C–O, C–H, and O–H orbitals for CH_3OH (Figure 3) are similar to those in CH_3NH_2. The orbital localized on O in the C–O bond is even tighter than the

CH₃SH

Figure 5. Generalized valence bond orbitals for CH_3SH (see Figure 2): (a) C–H bond pair, (b) S–H bond pair, (c) C–S bond pair, (d) lone pair on S in molecular symmetry plane, (e) lone pair on S perpendicular to molecular symmetry plane.

orbital on N in the C–N bond following the predictions made on the basis of electronegativity. There are two equivalent lone pairs on O, which reside on each side of the molecular plane. We show the projection of one orbital onto the molecular symmetry plane in Figure 3. This lone pair shows the expected in–out correlation with one tight orbital and one more diffuse orbital.

The C–H and C–P bonds in CH_3PH_2 (Figure 4) show the typical left–right correlation expected for bond pairs. The orbital on P is more diffuse than the orbital on C in the P–C bond, as would be expected since the electronegativity of P is less than that of C. The surprising result is the lone pair on P. The inner part of the orbital follows the general shape expected for a lone pair and is somewhat more diffuse than the comparable orbital in CH_3NH_2. However, the outer, more diffuse orbital shows a striking difference in comparison with its nitrogen counterpart. The orbital is significantly broadened and no longer has its maximum density along the same vector as does the maximum of the inner orbital of the lone pair. Rather, the maximum lies almost directly behind the P–C bond. There is also some density over the P–C bond. This latter concentration of density shows the d-orbital character in the lone pair. A similar difference is noted between the lone pairs of NH_3 and PH_3, which are shown in Figure 6.[23] The lone pair on PH_3 is, of course, symmetric about the axis but is quite similar to the lone pair on P in CH_3PH_2. The presence of the CH_3 group is a significant perturbation on the lone pair, and the lone pair moves away from the CH_3 group to decrease the interaction. The change in the lone pairs in going from N to P is strongly dependent on the geometry change in going from a central N to a central P, e.g., NH_3 to PH_3. The angles are approximately tetrahedral in NH_3 (106°)[24] and approximately
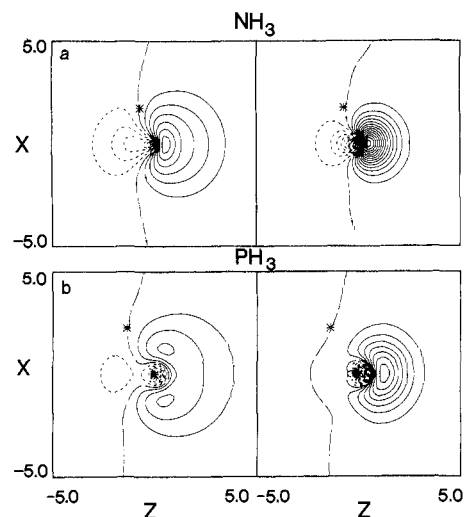
NH₃

PH₃

Figure 6. Generalized valence bond orbitals for the lone pairs on pyramidal NH_3 and PH_3. The asterisks show the N or P at the center and one H atom. The horizontal and vertical axes both run from –5.0 to 5.0 au. Contour levels are in units of 0.05. (a) NH_3, (b) PH_3.
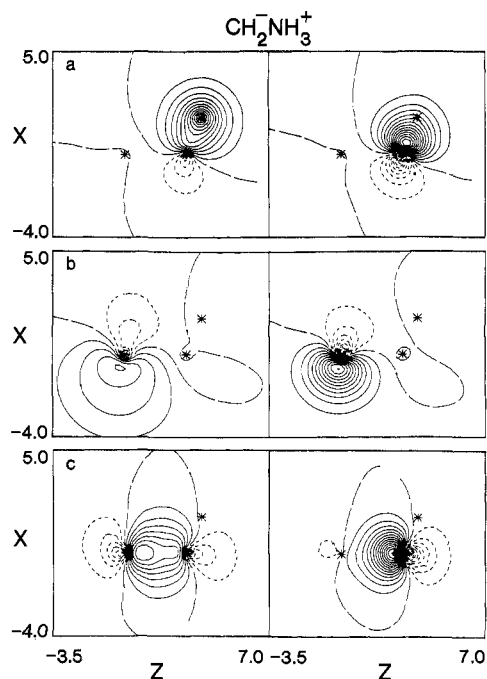
CH₂⁻NH₃⁺

Figure 7. Generalized valence bond orbitals for $CH_2^-NH_3^+$ (see Figure 2): (a) N–H bond pair, (b) lone pair on C, (c) N–C bond pair.

95° in PH_3.[25] In NH_3 one would expect four orbitals (three N–H bonds and a lone pair) with approximately sp^3 hybridization. For PH_3, one would expect three P–H bonds with pure p hybridization at P and a 3s lone pair. However, this arrangement of orbitals in PH_3 would lead to significant electron repulsions between the lone pair and the P–H bond orbitals. Thus the lone pair acquires some p and d hybrid character to move the center of the lone pair away from the P.

The GVB bond orbitals for CH_3SH (Figure 5) follow the expected trends. The two orbitals for the C–S bond are of comparable size, which is consistent with predictions based on electronegativity values. The two lone pairs are quite different, in contrast to the equivalent lone pairs found in CH_3OH. One lone pair is very s-like, with only a small amount of p character. This orbital is hybridized away from the C–H and S–C bonds in order

(23) These calculations were performed on NH_3 and PH_3 by using the basis sets reported in this paper and with a set of p orbitals (ζ = 1.0) on H. All valence orbitals were split in the GVB calculations. The geometry for NH_3 was taken from experiment 24 while that for PH_3 was taken from the SCF optimized geometry.[25]

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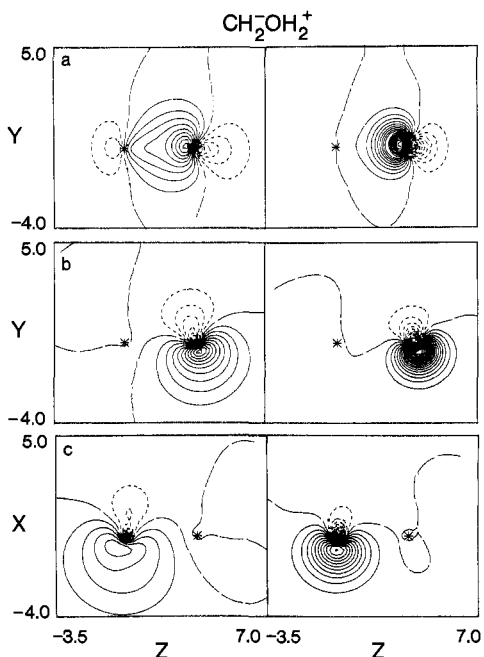(25) Marynick, D. S.; Dixon D. A. *J. Phys. Chem.* **1982**, *86*, 914.

Figure 8. Generalized valence bond orbitals for $CH_2^-OH_2^+$ (see Figure 2): (a) Lone pair on O (donating toward C), (b) lone pair on O, (c) lone pair on C.
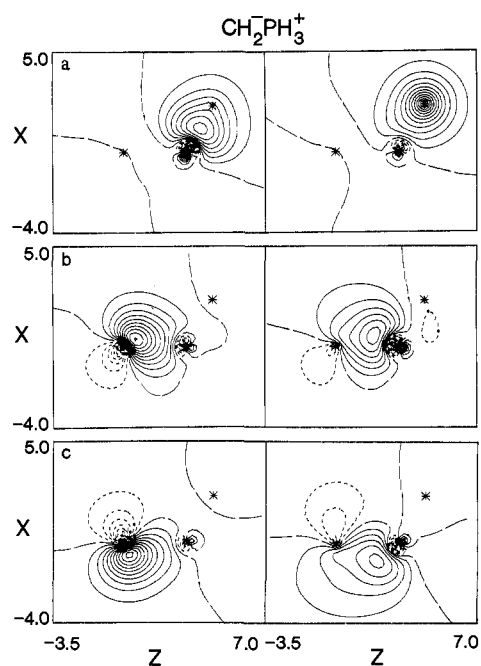

Figure 9. Generalized valence bond orbitals for $CH_2^-PH_3^+$ (see Figure 2): (a) P–H bond pair, (b) P–C τ (bent) bond pair, (c) P–C τ (bent) bond pair.

Figure 10. Generalized valence bond orbitals for $CH_2^-SH_2^+$, stable form (conformation d in Figure 1) (see Figure 2): (a) C–H bond pair, (b) C–S bond pair, (c) C–S bond pair, (d) lone pair on S.

Figure 11. Generalized valence bond orbitals for $CH_2^-SH_2^+$, unstable rotamer (see conformation e, Figure 1) (see Figure 2): (a) C–S bond pair, (b) lone pair on C, (c) lone pair on S.

to lower electron repulsion. The other lone pair is essentially pure p and is perpendicular to the molecular plane. There is some d character in this orbital, as evidenced by the regions of increased density to either side of the s on the low intensity part of the orbital.

Bonding Orbitals: Ylides

The orbitals for the ylides are shown in Figures 7–11. The orbitals for the ammonium ylide (Figure 7) are similar to those found in CH_3NH_2. The C–N bond exhibits left–right correlation, and the orbital on N has its maximum density closer to the nucleus than does the orbital on C as found for CH_3NH_2. In fact, the C–N bond exhibits only small changes in the ylide as compared to CH_3NH_2. The lone pair on the ylide, of course, has now moved to the carbon atom from the nitrogen atom. The outer orbital of the lone pair on C in the ylide is significantly more diffuse than
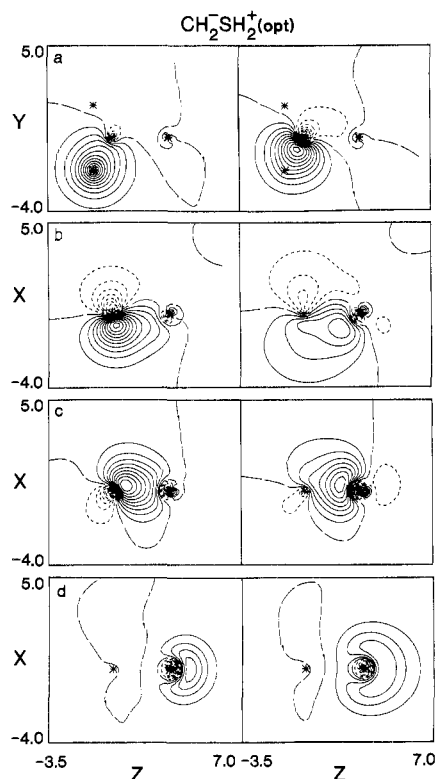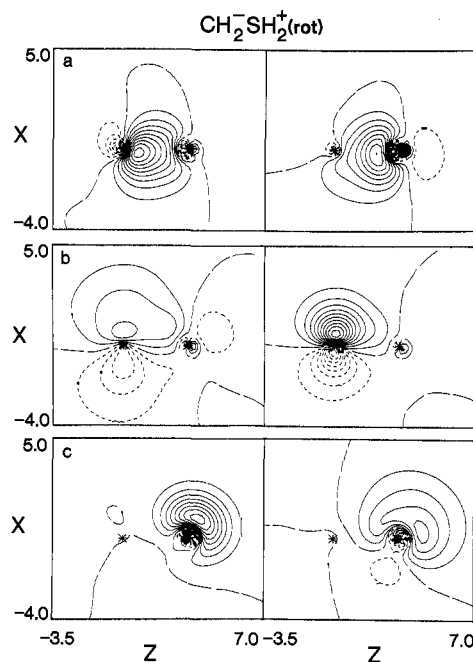
the outer orbital of the lone pair on N in CH_3NH_2, showing the anionic character of the carbon atom. However, there is essentially no "back-bonding" to the nitrogen. The inner orbital on the C lone pair in the ylide is similar to the inner orbital on N in CH_3NH_2; the inner orbital on C is slightly more diffuse following predictions based on electronegativities.

The orbitals for the oxonium ylide (Figure 8) are quite different from those of the ammonium ylide. The C–O bond pair now consists of two orbitals which are highly localized on the oxygen and can be compared with the lone pair on the oxygen (to which

it is similar). The C–O bond is best described as an oxygen lone pair donating into a vacant orbital on the carbon. The lone pair on carbon is in a plane perpendicular to the plane containing the two oxygen lone pairs and exhibits the expected in–out correlation. The diffuse orbital is somewhat less diffuse than the comparable orbital in $CH_2^-NH_3^+$. The diffuse orbital of the C lone pair is bent somewhat further from the C–O bond than its tighter partner.
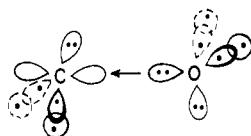

The orbitals clearly demonstrate that the oxonium ylide strongly resembles a $CH_2(^1A_1)$ strongly solvated by H_2O. The $^1A_1$ state of CH_2 has the appropriate vacant orbital needed for solvation by the H_2O. As expected, the orbitals for the oxonium ylide do not show a strong dependence on rotational conformation. There is also, as observed for $CH_2^-NH_3^+$, no back-bonding from the C lone pair to the O.

The orbitals for the phosphonium ylide (Figure 9) exhibit a different type of bonding scheme from that observed in the ammonium and oxonium ylides. In this case, no lone pair on C is observed. Rather there are two strongly polarized τ (banana) bond pairs between P and C. Each τ bond pair is composed of a tight orbital centered on C and a more diffuse orbital centered on P. This pattern of orbitals is similar to the result found for the P–C σ bond in CH_3PH_2. The two bond pairs are not equivalent, as expected from the C_s molecular symmetry. The pair with the most diffuse orbital on P lies on the side of the P–C axis where there are two hydrogens on either side of the plane, presumably to lower electron repulsions. The GVB orbitals are similar to the localized molecular orbitals (LMO's) obtained by Lischka (see his Figure 5)[6] using the Boys criterion.[26] However, we note that the GVB orbitals are obtained by a rigorous energetic "localization" technique whereas the Boys LMO's are obtained by a maximal separation of centroids of charge.

The orbitals for $CH_2^-SH_2^+$ strongly depend on the molecular conformation, as shown in Figures 10 and 11. The S–C bond orbitals for the optimum configuration (Figure 10) consist of two very nonequivalent bent bonds. One orbital can best be considered as a somewhat bent C–S σ bond. The other bond pair, derived from the nominal C lone pair, has partially π-type character. It consists of a tight orbital centered on C and a more diffuse orbital centered on S. Thus the bonding between the heavy atoms in $CH_2^-SH_2^+$ lies intermediate between the bonding in $CH_2^-NH_3^+$ (a C–N σ bond and a C^- lone pair) and the bonding in $CH_2^-PH_3^+$ (a P–C double bond), and there is some double-bond character in the C–S bond. The lone pair on S retains its s-like character and is very similar to the inner shell lone pair found for CH_3SH. This orbital is now directly behind the S atom along the C–S bond axis. We show the three most important orbitals for the high energy form of $CH_2^-SH_2^+$ in Figure 11. The C–S bond now consists of a σ-bond essentially along the C–S axis. The π-type C–S bond in the more stable ylide now becomes essentially a lone pair localized on C. The lone pair shows in–out correlation and some amount of delocalization toward the S. Indeed the tight orbital on C is similar for both conformers. However, the diffuse orbital is now located on the C and the orbitals more closely resemble those for the lone pair on C in $CH_2^-NH_3^+$. Because of the positions of the H atoms and the CH_2^- group, the lone pair on S increases its amount of p-orbital character. The lone pair on S shows definite in–out correlation and is similar to the lone pair on P in CH_3PH_2. The maximal density in the outer orbital has now moved behind the C–S bond. It does this since the two lone-pair orbitals are now on the same side of the bond and are strongly repulsive. The lone pair on S must move away from the lone pair on C, which is attempting to back-bond to S in order to gain additional stabilization.
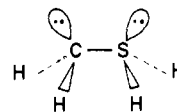
Discussion

The energetics of ylides can be discussed from several view points. We[2] have previously discussed the isomerization energy of the ylides in terms of the relative proton affinities of NH_3, PH_3, H_2O, and H_2S. There are additional features to be considered. For example, the average bond strengths are C–H = 98.8, P–H = 76.4, N–H = 93.4, O–H = 110.6, and S–H = 81.1 kcal/mol.[27] Thus transfer of a hydrogen atom from C to a heteroatom X leaving two radical centers would be a possibility (reaction 2).

$$H_3C-XH_n \rightarrow H_2\dot{C}-\dot{X}H_nH \qquad (2)$$

This of course presumes that the X center can extend its valence shell beyond the octet. For first-row atoms this is unlikely, and so reaction 2 is an unlikely model. However for second-row atoms it is possible to form a hypervalent species (see Figure 9 for $CH_2^-PH_3^+$), and this can serve as part of a model. Formation of the phosphonium ylide requires a loss of 22 kcal/mol due to bond strength differences alone. To this value must be added the energy required to rehybridize the phosphorus while the energy gained from forming the double bond must be subtracted. A similar analysis can be carried out for the sulfonium ylide. Here the bond strength difference between the C–H and S–H bonds is 18 kcal/mol.

The heats of formation of the various ylides are given in Table II by adding the value of $\Delta E(POL-CI)$ to the experimental value for $\Delta H_f°_{298}$ of the nonzwitterionic isomer.[28] We note that these are gas-phase values and do not include any effects of solvation. Solvation should dramatically change the values for ΔH_f and as is well-known for basicities for substituted amines[29] can alter relative energy orderings. We further point out that these values do not reflect relative stabilities of the ylides. As examples, the highest value for ΔH_f is for the sulfonium ylide, yet, the ylide $CH_2^-S(CH_3)_2^+$ is a remarkably stable intermediate. Furthermore, the oxonium ylide has the lowest ΔH_f, yet it resembles a solvated CH_2:, and indeed no oxonium ylides have been observed experimentally.

The bonding in the neutral compounds follows the general ideas of Goddard and Harding[30] derived for simple hydrides, especially for CH_3PH_2 and CH_3SH. Indeed our orbitals for CH_3SH follow the general prediction for H_2S of an inner lone-pair 3s orbital and a pure p lone pair while for PH_2CH_3 a distorted 3s-like lone pair is found. Goddard and Harding ascribe the differences in bond angles between first- and second-row hydrides to hydrogen–hydrogen repulsions. Although this exists, there are also significant differences in the lone pairs between the first and second row. Two equivalent lone pairs are found for CH_3OH, in contrast to the result found for CH_3SH where the lone pairs are different. Furthermore, we note that this difference is based on a rigorous energetic criteria since we have solved for the optimal GVB-valence orbitals in a self-consistent fashion. The other difference between the first- and second-row lone pairs occurs because of the valence d-orbitals in the second row. These d-orbitals play a significant role in determining the nature of the lone pairs in the second row while only a very small role is found for d-orbital participation with the first row. This is best seen by comparing the lone pairs on PH_3 and NH_3 and on CH_3NH_2 and CH_3PH_2.

Knowledge of the GVB orbitals of the ylides is an important aid in understanding the bonding patterns. In contrast to the conclusions of both Lischka[6] and Mitchell et al.,[7b] our results

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suggest that there is significant back-bonding from the carbon to the heteroatom for P and S leading to partial double-bond character. For the phosphonium ylide a reasonable amount of double-bond character is expected, with less double-bond character expected for the sulfonium ylide. This is consistent with the decrease in bond lengths over normal C–P and C–S single bonds observed for the ylides.[2] The bonding in the phosphonium ylide
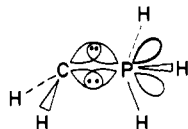
is surprising in light of the low rotation barrier. However, the significant contribution of the d orbitals on P to the bonding leading to a hypervalent P causes this to occur. The CH_2 can approximately freely rotate about the P and as it rotates, builds in character from a different d orbital. It is the general angular

form of the d orbitals that are oriented toward the two lobes of the CH_2 group that lead to the low rotation barrier. The results of Mitchell et al.[7b] suggest that $CH_2^-SH_2^+$ is best described as a $CH_2(^1A_1)$ solvated by H_2S. However, our results for the optimum form of $CH_2^-SH_2^+$ show the presence of a partial double bond, and even for the unstable rotamer there is still an S–C σ bond. The bonding in $CH_2^-SH_2^+$ is thus significantly different from that on $CH_2^-OH_2^+$.

Radical Anions and Radical Trianions of Tetracyanoarenoquinodimethanes. An ESR and ENDOR Study

Fabian Gerson,[*1a] **René Heckendorn,**[1a] **Dwaine O. Cowan,**[1b] **Aravinda M. Kini,**[1b] and **McRae Maxfield**[1b]

Contribution from Physikalisch-Chemisches Institut der Universität Basel, 4056 Basel, Switzerland, and Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. Received March 28, 1983

Abstract: The ESR spectra of the radical anions of 7,7,8,8-tetracyano-2,3,5,6-tetrafluorobenzo-1,4-quinodimethane (**2**), 9,9,10,10-tetracyanonaphtho-1,4-quinodimethane (**3**), 9,9,10,10-tetracyanonaphtho-2,6-quinodimethane (**4**), 7,7,7′,7′-tetracyanodipheno-4,4′-quinodimethane (**5**), 11,11,12,12-tetracyano-4,5,9,10-tetrahydropyreno-2,7-quinodimethane (**6**), and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (**7**) have been reexamined under higher resolution. Their analysis has been assisted by the ENDOR technique. Reliable hyperfine data, thus far missing in the literature, have been obtained. The radical trianions of **3**, **4**, and **7**, prepared by both chemical and electrolytic methods, have also been characterized by ESR spectroscopy. The π spin and/or π charge distribution in the radical anions, the dianions, and the radical trianions are discussed in terms of simple MO models. The electronic structure and the ease of formation of the radical trianions are related to those of the radical anions of the corresponding dialkyl-substituted aromatic hydrocarbons.

The recent search for organic metals and superconductors[2] has provided the impetus for the syntheses of numerous organic electron donors and acceptors. This research was initiated by the Du Pont group's observations of electrical conductivity in organic salts of 7,7,8,8-tetracyanobenzo-1,4-quinodimethane (tetracyanoquinodimethane = TCNQ).[3] Donor–acceptor complexes, such as tetrathiofulvalene–tetracyanoquinodimethane (TTF–TCNQ), display metal-like conductivity ($\sim 10^3$ Ω^{-1} cm^{-1});[2] on the other hand, some metal salts of TCNQ, e.g., Cu and Ag, exhibit electrical or optical field induced switching phenomena on a nanosecond time scale.[4]

One particular aspect of the syntheses of tetracyanoarenoquinodimethanes other than TCNQ was to extend the π-system of the acceptor. Such an increase, which reduces the intramolecular Coulomb interactions in the radical anion of the acceptor, was thought to be of great importance for attaining high electrical conductivity. In addition to TCNQ (**1**),[3] the following tetracyanoarenoquinodimethanes have been synthesized in the last two decades: 7,7,8,8-tetracyano-2,3,5,6-tetrafluorobenzo-1,4-quinodimethane (TCNQF₄) (**2**),[5] 9,9,10,10-tetracyanonaphtho-1,4-quinodimethane (benzo-TCNQ) (**3**),[6] 9,9,10,10-tetracyanonaphtho-2,6-quinodimethane (TNAP) (**4**),[7] 7,7,7′,7′-tetracyanodipheno-4,4′-quinodimethane (TCNDQ) (**5**),[8,9] 11,11,12,12-

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