

A theoretical study of the CSH₄ and CPH₅ hypersurfaces. Geometries, tautomerization, and dissociation of sulfonium and phosphonium ylides

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Calculations have been performed at four basis set levels (STO-3G, STO-3G*, 4-31G, 4-31G*) on the model ylides methylenesulfurane (CH₂SH₂) and methylenephosphorane (CH₂PH₃), their stable tautomers (CH₃SH and CH₃PH₂), their dissociation products (SH₂, PH₃ and CH₂), and the protonated species CH₃SH₂⁺ and CH₃PH₃⁺. At each basis set level all geometries have been optimized fully, using the FORCE method. The conformational behaviour of the ylides as a function of C—X bond-stretching, C—X torsion, and CH₂ (or SH₂) bending has been examined in some detail. The experimental properties (i.e., geometries, relative stabilities, proton affinities, rotation-inversion behaviour) of sulfonium and phosphonium ylides are reproduced well by the model calculations with the 4-31G* basis set, which contains *d*-type functions on both carbon and sulfur (or phosphorus). All other basis sets are deficient in different ways and for different reasons, which are discussed in detail. The principal result of this work is the conclusion that *d*-type functions are essential for a proper description of the hypervalent species CH₂SH₂ and CH₂PH₃, but not for the normal-valent species SH₂, PH₃, CH₃SH, and CH₃PH₂. The conclusion concerning hypervalent species reverses our earlier views. The role of the *d*-type functions is to concentrate charge into the C—X region of the ylides, and thus to stabilize the system. Evidence for this effect has been obtained from quantitative perturbational molecular orbital (PMO) analyses of interactions associated with the carbon lone pair, as well as comparisons of electron density plots with and without the *d* AO's. A second conclusion is that the imposition of various geometrical constraints such as assumed C—X, C—H, or X—H bond lengths, and HCH or XH_n bond angles, as was necessary for computational reasons in all previous work on such systems, has major and previously unrecognized consequences. For example, the assumption that the CH₂ moiety is planar in CH₂SH₂ leads to very similar geometries with and without *d* AO's, although only in the latter case does such a geometry at carbon correspond to the true energy minimum; in the absence of *d* AO's the C—S bond length is maintained by a symmetry-enforced barrier to dissociation. These and other consequences of geometrical constraints at carbon, sulfur, or phosphorus are analyzed in detail.

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Utilisant quatre ensembles de base (STO-3G, STO-3G*, 4-31G, 4-31G*), on a effectué des calculs sur des modèles d'ylures de méthylènesulfurane (CH₂SH₂) et de méthylénephosphorane (CH₂PH₃), sur leurs tautomères stables (CH₃SH et CH₃PH₂), sur leurs produits de dissociation (SH₂, PH₃ et CH₂) et sur leurs espèces protonées CH₃SH₂⁺, CH₃PH₃⁺. Faisant appel à la méthode de FORCE, on a optimisé pleinement toutes les géométries pour tous les ensembles de base. On a examiné soigneusement le comportement conformationnel des ylures en fonction de l'élongation de la liaison C—X, de la torsion de cette liaison et de la déformation du CH₂ (ou du SH₂). On a reproduit convenablement les propriétés expérimentales (i.e. les géométries, les stabilités relatives, les affinités pour le proton, le comportement à la rotation-inversion) des ylures de sulfonium et de phosphonium en utilisant des calculs modèles de la base 4-31* qui contient les fonctions de type-*d* sur le carbone et le soufre (ou sur le phosphore). Tous les autres ensembles de base sont déficients de différentes façons et pour des raisons différentes que l'on discute en détail. Le résultat principal de ce travail permet de conclure que les fonctions-*d* sont essentielles pour une description adéquate des espèces hypervalentes CH₂SH₂ et CH₂PH₃ mais ne le sont pas dans le cas des espèces à valence normale SH₂, PH₃, CH₃SH et CH₃PH₂. La conclusion relative aux espèces hypervalentes renverse notre première idée. Les fonctions de type-*d* concentrent la charge dans la région de C—X des ylures et stabilisent alors le système. On a obtenu la preuve de cette action à partir des analyses quantitatives des perturbations d'orbitale moléculaires (POM) des interactions associées au doublet libre du carbone ainsi qu'à partir des comparaisons des courbes de densité électronique avec ou sans les OA *d*. On conclut également que l'imposition de contraintes géométriques variées telles qu'assumées par les longueurs de liaison C—X, C—H, ou X—H et par les angles HCH ou XH_n qui étaient nécessaires pour des raisons de calculs dans tous les travaux antérieurs portant sur de tels systèmes, ont des conséquences importantes et inconnues. Par exemple, l'hypothèse relative à la planéité de la portion CH₂ du CH₂SH₂ conduit à deux géométries très semblables avec ou sans les OA *d* bien que ce soit seulement dans le deuxième cas qu'une telle géométrie du carbone corresponde à l'énergie minimum réelle. En l'absence des OA *d*, la longueur de liaison C—S est maintenue par une barrière à la rotation induite par la symétrie. On analyse en détail ces faits et d'autres conséquences relatives aux contraintes géométriques au niveau du carbone, du soufre ou du phosphore.

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Introduction

The participation of low-lying virtual atomic *d*-orbitals ("outer" *d*-orbitals (1)) in molecular bonding has been studied extensively (2). Attention has focused, especially, upon hypervalent molecules (3), i.e., molecules having Lewis structures with more than eight valence electrons about a central atom (e.g., silicon, phosphorus, sulfur, chlorine) (4–12).

Included in the class of hypervalent molecules are the sulfonium and phosphonium ylides (13*a*), also known as methylenesulfuranes and methylenephosphoranes, which are isoelectronic with the corresponding sulfoxides (13*b*) and phosphine oxides. The importance of such ylides in organic synthesis (13*c*) has led to numerous theoretical investigations at both the semi-empirical (14) and *ab initio* levels (15, 16). All of the *ab initio* studies have employed either idealized geometries or have included a limited geometry optimization subject to some constraints.

One of the objectives of the present work is to re-examine the two model ylides methylenesulfurane (CH₂SH₂) and methylenephosphorane (CH₂PH₃) at the *ab initio* level, with complete geometry optimization. A second objective is to perform computations with and without *d*-atomic orbitals (*d* AO's) in the basis set, to evaluate the degree and manner of the participation of *d* AO's in the bonding in both ylides. Certain other points on the CSH₄ and CPH₅ hypersurfaces have also been examined, to assess the consequences of various geometrical constraints. The calculated relative energetics have been placed within the context of known experimental quantities by computation of the protonation energies and sulfur inversion barriers of selected species.

To facilitate the discussion, certain points will be highlighted using qualitative arguments based on the perturbational molecular orbital (PMO) method (17). As will be seen, the PMO treatment of these ylides is dominated by the presence of the lone pair on carbon.

Computational Details

The *ab initio* calculations were performed using either the GAUSSIAN 80 program system (18) or a modified version of GAUSSIAN 76 (19). All geometry optimizations were performed using the FORCE method (20), a gradient relaxation procedure now incorporated into GAUSSIAN 80. Setting the convergence on the RMS gradient at 0.0025 mdyne gave bond lengths accurate to 0.001 Å and bond angles accurate to 0.1°.

The basis sets used were the standard STO-3G (21), STO-3G* (10), 4-31G (22*a*), and 4-31G* (22*b*) basis sets of Pople. The 4-31G* basis set contains six second-order Gaussian functions (*xx*, *yy*, *zz*, *xz*, *yz*, *xy*) on all heavy atoms. The *d*-orbital exponents for sulfur and phosphorus were optimized variationally for the lowest energy conformations of CH₂SH₂ ($\alpha_d = 0.59$) and CH₂PH₃ ($\alpha_d = 0.51$), and were then used unchanged in subsequent calculations. The *d*-orbital set on carbon was not modified.

The program used to plot electron density difference maps was adapted from Jorgensen's PSI/77 (23). Energy surfaces were generated using the program 3DPLOT (20).

In those sections of the discussion which deal with a quantitative PMO analysis, the fragment orbital energies and the properties of these orbitals necessary for the computation of orbital interaction energies were obtained by the procedure described earlier (24). The two-orbital, four-electron interaction energies were calculated using eq. [1] where e_i^0 and e_j^0 are the energies of the fragment orbitals ϕ_i^0 and ϕ_j^0 , and S_{ij} and Δ_{ij} are the overlap integral and the interaction matrix element between them, respectively. The two-orbital, two-electron interaction energies were calculated by direct solution of the appropriate secular determinant (eq. [2]).²

$$[1] \quad \Delta e_{ij} = 2S_{ij}[-2\Delta_{ij} + (e_i^0 + e_j^0)S_{ij}]/(1 - S_{ij}^2)$$

$$[2] \quad \begin{vmatrix} e_i^0 - e & \Delta_{ij} - S_{ij}e \\ \Delta_{ij} - S_{ij}e & e_j^0 - e \end{vmatrix} = 0$$

Results and Discussion

1. *Ab initio* Calculations

Thermodynamic Aspects of the CSH₄ and CPH₅ Hypersurfaces

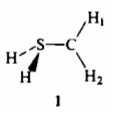
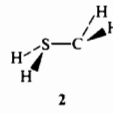
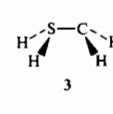
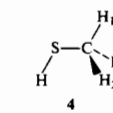
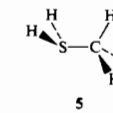
Calculations with full geometry optimization were performed at the four different basis set levels for selected conformations of the two ylides CH₂SH₂ and CH₂PH₃, the staggered conformations of the stable tautomers CH₃SH and CH₃PH₂, and the dissociation products H₂S, PH₃, and CH₂. Calculations are also reported for the staggered conformations of the protonation products CH₃SH₂⁺ and CH₃PH₃⁺. The various geometries and total energies of the two heavy-atom sulfur and phosphorus

²The usual equation [3], which approximates the solution to [2],

$$[3] \quad \Delta e_{ij} = 2(\Delta_{ij} - e_i^0 S_{ij})^2 / (e_i^0 - e_j^0)$$

could not be used because of the unusually large stabilizing interactions in these molecules.

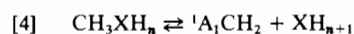
TABLE 1. Geometries^a and total energies^b of selected CSH₄ Systems and CH₃SH₂⁺

Molecule	Parameter	Basis set			
		STO-3G	STO-3G*	4-31G	4-31G*
 1	$r(\text{CS})$	1.690	1.596	1.732	1.627
	$r(\text{CH}_1)$	1.057	1.069	1.062	1.067
	$r(\text{CH}_2)$	1.059	1.069	1.062	1.068
	$r(\text{SH})$	1.361	1.354	1.376	1.355
	$\angle(\text{SCH}_1)$	114.7	115.3	113.6	114.7
	$\angle(\text{SCH}_2)$	119.1	124.2	119.1	122.9
	$\angle(\text{CSH})$	109.2	111.5	112.5	113.2
	$\angle(\text{HSH})$	90.7	88.9	93.4	90.4
E_T		-432.68254	-432.79874	-437.00816	-437.11947
 2	$r(\text{CS})$	2.060	1.812	2.451	2.049
	$r(\text{CH})$	1.111	1.105	1.100	1.097
	$r(\text{SH})$	1.333	1.332	1.349	1.327
	$\angle(\text{SCH})$	94.1	97.6	91.3	95.6
	$\angle(\text{HCH})$	101.0	103.1	104.8	102.9
	$\angle(\text{CSH})$	97.9	100.2	93.0	97.3
	$\angle(\text{HSH})$	93.6	91.9	96.0	94.0
	E_T		-432.71598	-432.77518	-437.02679
 3	$r(\text{CS})$	2.118	1.807	2.610	2.385
	$r(\text{CH})$	1.113	1.098	1.101	1.097
	$r(\text{SH})$	1.335	1.334	1.353	1.329
	$\angle(\text{SCH})$	93.5	101.4	87.8	91.1
	$\angle(\text{HCH})$	100.5	104.9	104.9	102.5
	$\angle(\text{CSH})$	105.4	108.5	107.9	106.1
	$\angle(\text{HSH})$	93.0	90.2	95.6	93.5
	E_T		-432.70806	-432.76839	-437.02090
 4	$r(\text{CS})$	1.798	1.782	1.886	1.815
	$r(\text{CH}_1)$	1.085	1.088	1.077	1.081
	$r(\text{CH}_{2,3})$	1.087	1.089	1.076	1.081
	$r(\text{SH})$	1.331	1.320	1.356	1.330
	$\angle(\text{SCH}_1)$	108.6	108.2	105.7	106.8
	$\angle(\text{SCH}_{2,3})$	112.2	112.5	110.1	111.3
	$\angle(\text{CSH})$	95.4	95.1	97.8	97.3
	$\omega(\text{H}_1\text{CSH}_{2,3})$	119.0	118.7	118.7	118.5
E_T		-432.89607	-432.92985	-437.18375	-437.25261
 5	$r(\text{CS})$	1.841	1.805	1.944	1.833
	$r(\text{CH}_1)$	1.089	1.091	1.074	1.077
	$r(\text{CH}_{2,3})$	1.089	1.092	1.075	1.079
	$r(\text{SH})$	1.349	1.339	1.353	1.332
	$\angle(\text{SCH}_1)$	109.7	110.7	108.2	110.2
	$\angle(\text{SCH}_{2,3})$	107.0	107.4	104.4	106.3
	$\angle(\text{CSH})$	100.1	98.4	102.4	100.7
	$\omega(\text{H}_1\text{SCH}_{2,3})$	120.8	121.0	121.1	121.3
$\omega(\text{H}_1\text{CSH})$	49.0	47.5	51.0	49.1	
E_T		-433.27243	-433.33228	-437.46857	-437.55983

^a Bond lengths in Å, bond angles in degrees.
^b In hartrees.

systems are collected in Tables 1 and 2, respectively. Results for the simple hydrides are reported in Table 3. The relative energies are summarized in Tables 4 and 5.

A number of points can be made concerning the CSH₄ and CPH₅ surfaces. The experimental energy difference for the equilibrium process of eq. [4] is reasonably well reproduced at both the 4-31G

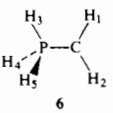
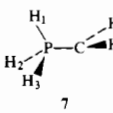
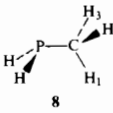
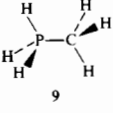


and 4-31G* levels. Thus, addition of *d* AO's to a

split-valence basis set has only a modest effect upon this net proton transfer – dissociation process. An analogous result is obtained at the STO-3G and STO-3G* levels, but the energy is greatly overestimated by these minimal basis sets. The problem is caused by a lack of flexibility within such basis sets, and also by basis set superposition (29).

Since the *tautomerization* energy of CH₂SH₂ is *greater* than that of CH₂PH₃, and, at the same time, the *dissociation* energy of CH₂SH₂ is *less* than that

TABLE 2. Geometries^a and total energies^b of selected CPH₅ systems and CH₃PH₃⁺

Molecule	Parameter	Basis set				
		STO-3G	STO-3G*	4-31G	4-31G*	
 6	$r(\text{CP})$	1.674	1.601	1.701	1.641	
	$r(\text{CH}_1)$	1.058	1.068	1.065	1.070	
	$r(\text{CH}_2)$	1.058	1.069	1.065	1.071	
	$r(\text{PH}_3)$	1.372	1.371	1.405	1.389	
	$r(\text{PH}_{4,5})$	1.393	1.391	1.438	1.414	
	$\angle(\text{PCH}_1)$	117.6	118.8	117.6	118.3	
	$\angle(\text{PCH}_2)$	119.5	122.6	120.6	122.0	
	$\angle(\text{CPH}_3)$	112.3	111.4	110.8	110.9	
	$\angle(\text{CPH}_{4,5})$	120.8	122.0	121.7	122.1	
	$\omega(\text{H}_1\text{CPH}_{4,5})$	119.6	119.1	118.8	119.0	
	E_T	-377.03267	-377.16908	-380.87381	-380.99523	
	 7	$r(\text{CP})$	1.897	1.607	1.721	1.652
		$r(\text{CH})$	1.101	1.071	1.069	1.074
		$r(\text{PH}_1)$	1.387	1.399	1.461	1.428
$r(\text{PH}_{2,3})$		1.373	1.376	1.410	1.394	
$\angle(\text{PCH})$		100.0	119.7	117.2	118.3	
$\angle(\text{CPH}_1)$		132.1	127.4	129.1	128.8	
$\angle(\text{CPH}_{2,3})$		110.9	113.7	112.2	112.8	
$\omega(\text{H}_1\text{PCH})$		52.8	80.2	75.9	75.9	
$\omega(\text{H}_1\text{CPH}_{2,3})$		124.5	120.5	121.4	120.7	
E_T		-377.05050	-377.17013	-380.87503	-380.99680	
 8		$r(\text{CP})$	1.841	1.830	1.915	1.861
		$r(\text{CH}_1)$	1.084	1.085	1.079	1.082
		$r(\text{CH}_{2,3})$	1.083	1.086	1.080	1.084
		$r(\text{PH})$	1.381	1.379	1.435	1.410
	$\angle(\text{PCH}_1)$	113.1	113.4	112.2	113.2	
	$\angle(\text{PCH}_{2,3})$	110.2	110.0	108.6	109.2	
	$\angle(\text{CPH})$	96.1	95.7	97.5	97.5	
	$\omega(\text{H}_1\text{CPH}_{2,3})$	120.8	121.0	121.1	121.3	
	$\omega(\text{H}_1\text{CPH})$	47.2	46.7	47.9	47.4	
	E_T	-377.22385	-377.27661	-381.01277	-381.09103	
	 9	$r(\text{CP})$	1.834	1.795	1.886	1.810
		$r(\text{CH})$	1.086	1.090	1.078	1.082
		$r(\text{PH})$	1.380	1.378	1.401	1.385
		$\angle(\text{PCH})$	109.0	109.3	108.4	109.2
$\angle(\text{CPH})$		111.5	111.5	111.6	111.8	
E_T		-377.63158	-377.69947	-381.33341	-381.43344	

^a Bond lengths in Å, bond angles in degrees.
^b In hartrees.

of CH₂PH₃, it follows that the sulfonium ylide is intrinsically the less stable species. This is in accord with experiment (30).

The most important finding is that inclusion of *d* AO's on the second row atoms has a large effect upon the stabilities of the ylides. With the split-valence basis set the stabilization is nearly 27 kcal/mol in both cases. Consequently, deletion of the *d* AO's forces the ylides to lie too close to their dissociation limits. Indeed, as seen in Table 4, the sulfonium ylide 1 is actually calculated to be less stable than the dissociation products, even without correction for basis set superposition.

On the other hand, the energy differences associated with the normal valent species of eq. [4] do not depend greatly upon the presence of *d* AO's, as already noted. This indicates that the concept of hypervalence may be of some value in defining

those species that require *d* AO's for a proper description.

Table 6 compares the proton affinities calculated for the two ylides and their stable tautomers. The experimental proton affinities of methanethiol and methylphosphine are also included for comparison. It is clear that the 4-31G* basis set predicts this experimental quantity quite well (31). The very similar proton affinities of CH₂SH₂ and CH₂PH₃ with the *d*-orbital basis sets are noteworthy. Apparently, PH₃⁺ and SH₂⁺ substituents have almost the same effect upon the protonation of an adjacent carbanionic centre.

Structures of the Ylides

CH₂SH₂

The data of Table 1 reinforce the observations already made concerning the role of *d* AO's spec-

TABLE 3. Geometries^a and total energies^b of CH₂, H₂S, and PH₃ at the 4-31G* basis set level^c

Molecule	Parameter	
¹ A ₁ CH ₂	r(CH)	1.097
	∠(HCH)	102.9
	E _T	-38.83140
¹ Δ CH ₂ ^d	r(CH)	1.054
	∠(HCH)	180.
	E _T	-38.79835
H ₂ S	r(SH)	1.329
	∠(HSH)	93.7
	E _T	-398.25771
PH ₃	r(PH)	1.409
	∠(HPH)	94.1
	E _T	-342.09026

^aBond lengths in Å, bond angles in degrees.

^bIn hartrees.

^cResults for these systems at the STO-3G, STO-3G*, and 4-31G levels may be found in ref. 10a (H₂S, PH₃) and in ref. 10b (CH₂).

^dComplex orbitals were used.

ificantly in the description of the hypervalent species methylenesulfurane (cf. 13b). Thus, the geometries of methanethiol **4** and methylsulfonium cation **5** show only minor dependence on the basis set; the principal trends are longer C—S bond lengths at the split-valence level, and the shortening of this bond upon addition of *d* AO's (10). In contrast, the geometries of the ylides depend greatly upon the choice of basis set.

Computations were performed initially on conformation **1**, in which the carbon centre is con-

strained to planarity and the HCH plane bisects the H₂S plane. These constraints result in somewhat similar structures with the different basis sets, and the C—S bond length varies in the manner already described for **4** and **5**.

Release of all constraints, to allow both pyramidalization at carbon and C—S torsion, illustrates the effect of the *d*AO's. When these functions are present, the carbon centre remains planar and no rotation occurs, so that **1** is the true minimum. In the absence of these functions, the carbon centre becomes strongly pyramidal, the C—S bond lengthens to values greater than 2 Å and the molecule rotates to the anti structure **2**. It is noteworthy that optimization of the *anti* conformation using the *d* AO-containing basis sets also reveals pyramidalization at carbon and C—S bond lengthening; however, **2** then becomes a rotational maximum. The *syn* conformation **3** was also examined. It is a rotational maximum with all basis sets.

Therefore, at the STO-3G* and 4-31G* levels, **1** is the only minimum on the conformational hypersurface. It lies in a deep well with respect to C—S torsion (see below). On the other hand, at the STO-3G and 4-31G levels, **2** is the most stable conformation, and is 5.0 and 3.7 kcal/mol, respectively, more stable than the *syn* conformation **3**, which remains the maximum on the rotational potential. No distinguishable minimum corresponding to a *gauche* conformation (e.g. **10**) exists at 4-31G, although a careful search did reveal an extremely shallow minimum 1.3 kcal/mol above **2** at STO-3G.

TABLE 4. Relative energies^a of selected points on the singlet CSH₄ surface

System	Basis set				Expt. ^b
	STO-3G	STO-3G*	4-31G	4-31G*	
4	0.	0.	0.	0.	0.
1	134.0	82.3	110.2	83.5	
2	113.0	97.1	98.5	94.5	
¹ A ₁ CH ₂ + H ₂ S	133.1	133.7	106.3	103.2	101.1
¹ Δ CH ₂ + H ₂ S	163.6	164.2	119.3	123.3	

^aIn kcal/mol (theoretical values are uncorrected for zero-point vibration).

^bThe heats of formation of CH₃SH and H₂S were taken from ref. 27, and ³B₁ CH₂ from ref. 25. The CH₂ ³B₁ - ¹A₁ separation was taken from ref. 26.

TABLE 5. Relative energies^a of selected points on the singlet CPH₅ surface

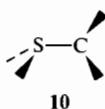
System	Basis set				Expt. ^b
	STO-3G	STO-3G*	4-31G	4-31G*	
8	0.	0.	0.	0.	0.
7	108.8	66.8	86.4	59.1	
6	120.0	67.5	87.2	60.1	
¹ A ₁ CH ₂ + PH ₃	135.0	137.0	111.0	106.3	(108.8)
¹ Δ CH ₂ + PH ₃	165.5	167.5	123.9	127.0	

^aIn kcal/mol (theoretical values are uncorrected for zero-point vibration).

^bThe heat of formation of PH₃ was taken from ref. 27, and that of CH₃PH₂ was taken from ref. 28. See also footnote b of Table 4.

TABLE 6. Proton affinities^{a,b} of CSH₄ and CPH₅ species

System	Basis set				Expt. ^c
	STO-3G	STO-3G*	4-31G	4-31G*	
CH ₃ SH	236.2	252.5	178.7	192.8	188.6
CH ₂ SH ₂	349.2	334.8	277.2	276.3	
CH ₃ PH ₂	255.9	265.3	201.2	214.9	204.8
CH ₂ PH ₃	364.6	332.2	287.6		

^aIn kcal/mol.^bTheoretical values are derived from the most stable conformation with each basis set.^cValues taken from ref. 32.

These results are of some importance in assessing the validity of a model proposed recently for the prediction of the relative acidities of diastereotopic protons in sulfonium salts (33). This model is derived from an examination of the C—S rotational potential of CH₂S(CH₃)₂ at the 4-31G level with the following major assumptions: (i) a pyramidal carbon; (ii) a 1.85 Å C—S bond length; (iii) 105° angles at sulfur; (iv) rigid rotation. With these various assumptions, the computations of Graham and Heathcock lead to a *gauche* minimum. It should be clear that this result is an artifact for two reasons, viz., the neglect of *d* AO's and the choice of geometry.

Figure 1 illustrates further the consequences of the imposition of geometrical constraints and the usefulness of a computational procedure which allows ready optimization of all parameters. The figure shows C—S torsion of **2** at the STO-3G level with rigid rotation of the fully optimized structure ($r_{CS} = 2.06$ Å) and of the structures having $r_{CS} = 1.86$ Å and 1.66 Å. It can be seen that a *gauche* minimum could be made to exist by the artificial choice of an appropriately short C—S bond length and, presumably, other arbitrary constraints.³ There is a parallel between the artificial behaviour achieved in Fig. 1 and the experimental properties of non-hypervalent A₂X₄ systems. In hydrazines ($r_{NN} \sim 1.45$ Å) (34), the *gauche* conformation is adopted, while diphosphines ($r_{PP} \sim 2.20$ Å) and diarsines ($r_{ASAS} > 2.4$ Å) (35) prefer the *anti* conformation.

In view of the large effect of *d* AO's upon the energy of CH₂SH₂ it seems, at first glance, surprising that the geometries computed for **1** under C_s symmetry at STO-3G or 4-31G are close to the fully optimized values obtained at STO-3G* or 4-31G*.

³In fact, holding $r_{CS} = 1.66$ Å and optimizing all other parameters of **2** and **10** at the STO-3G level produces *gauche* minima lying 9.8 and 18.6 kcal/mol, respectively, below the *anti* structure.

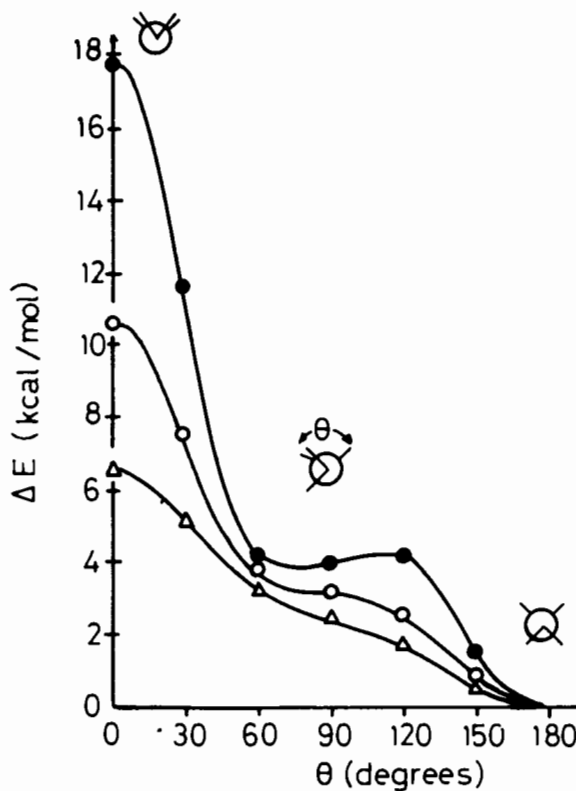


FIG. 1. Effect of geometrical constraint upon the C—S torsional potential of **2** at the STO-3G level. Δ , $r_{CS} = 2.06$ Å (fully optimized); \circ , $r_{CS} = 1.86$ Å; \bullet , $r_{CS} = 1.66$ Å.

The reason for this is that, when carbon is planar, dissociation of the ylide along only a C—S stretching coordinate would require the formation of CH₂ in the excited ¹Δ state. This causes the CSH₄ energy surface along this stretching coordinate to rise steeply from **1**; therefore, at the STO-3G and 4-31G levels the ylide exists within the symmetry of **1** because of a large symmetry-enforced barrier to separation of the fragments. Such barriers have been recognized previously by Trinquier and Malrieu in their pseudopotential study of CH₂PH₃ (15f).

Pyramidalization at carbon provides a mechanism for dissociation which avoids the high-energy

ridge of the surface. Nevertheless, complete dissociation does not occur because the C—S bond stretching – carbon pyramidalization surface contains a minimum corresponding to **10**, which transforms to **2** when rotation is permitted to occur. The calculated topology of this surface in the absence of *d* AO's is shown in Fig. 2. In agreement with this assessment, the structures obtained for **2** have long C—S bonds and HSH and HCH planes nearly perpendicular to this bond axis. Therefore, **2** is best regarded as 1A_1 carbene solvated by hydrogen sulfide. Such behaviour is reminiscent of that exhibited by so-called oxonium ylides (15g, 36).

When *d* AO's are added to the basis set, **1** is no longer a saddle point on the conformational hypersurface but, as already seen, the minimum. Dissociation is now entirely endothermic, as can be seen in Fig. 3. The enantiomeric dissociation paths *p* and *p'* are directly comparable to Fig. 2 of ref. 15f.

This analysis also accounts for the very modest effect of *d* AO's upon the P—O bond length of H_3PO observed by Wallmeier and Kutzelnigg in their study of hypervalent oxides (37). As pointed out by these workers, direct dissociation of H_3PO leads to an excited state of atomic oxygen. This corresponds to the effect seen here for the isoelectronic CH_2 . However, in the case of H_3PO , no symmetry-breaking path exists and no dramatic bond lengthening occurs upon deletion of the *d* AO's.

Finally, Table 7 lists the STO-3G* and 4-31G* energies computed for pyramidal inversion at sulfur for $CH_3SH_2^+$ and CH_2SH_2 . Comparison of the 4-31G* data with experimental results shows satisfactory agreement.

CH_2PH_3

The phosphorus analog of **1** is **6** (Table 2), in

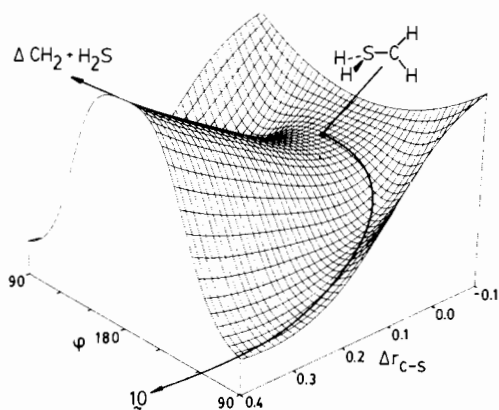


FIG. 2. Dissociation of CH_2SH_2 by a combination of C—S bond stretching and pyramidalization at carbon when *d* AO's are omitted.

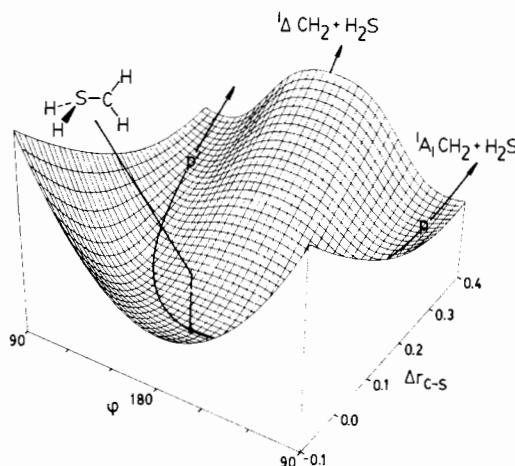


FIG. 3. Effect of *d* AO's upon the C—S bond stretching – carbon pyramidalization surface of CH_2SH_2 .

which a P—H bond formally replaces a sulfur hybrid lone pair. As with the sulfonium ylide, addition of the *d* AO's causes a small decrease in the C—P bond length of **6** and the carbon centre is planar.

With all basis sets, **7** is the rotational minimum. The very nonplanar carbon geometry and C—P bond lengthening obtained at STO-3G is mainly a result of the effects already described for the sulfonium ylide. With all other basis sets, and in general agreement with Lischka (15d), Strich (15e), and Dixon and co-workers (15g), the carbon centre of **7** is nearly planar.

The 4-31G* C—P bond length in **7**, 1.652 Å, is in excellent agreement with previous theoretical (15) and experimental (38) determinations. An interesting feature of the geometries of **6** and **1** is the substantial deviation of the PH_3 moiety from local C_{3v} symmetry. The rotational barrier for CH_2PH_3 (**7** → **6**) is relatively small (0.7 kcal/mol at the STO-3G* level and 1.0 kcal/mol at the 4-31G* level), but larger than calculated previously (15) because the geometry at the PH_3 moiety has been taken into account. The reasons for this unusual geometry are discussed below in some detail.

The bond stretching – carbon inversion energy

TABLE 7. Pyramidal inversion barriers^a at sulfur in methylsulfonium cation and methylenesulfurane

System	Basis set		Expt. ^b
	STO-3G*	4-31G*	
$CH_3SH_2^+$	47.4	29.6	25–29
CH_2SH_2	32.6	15.9	19–23

^aIn kcal/mol.

^bExperimental values taken from refs. 39 and 40.

surface of Fig. 2 is also appropriate for methylene-phosphorane at the STO-3G level although, even without d AO's, the saddle point **6** lies below 1A_1 $\text{CH}_2 + \text{PH}_3$. With all other basis sets, a surface analogous to that shown in Fig. 3 better describes the dissociation of **6**.

The ability of the 4-31G basis set to provide a reasonable description of the geometry of CH_2PH_3 (but not CH_2SH_2) illustrates the importance of obtaining accurate relative energies for the ylides and the dissociation products. The very poor energy for **1** relative to 1A_1 $\text{CH}_2 + \text{H}_2\text{S}$ at the STO-3G and 4-31G levels renders these surfaces very unstable towards dissociation. This process is prevented because of the existence of a dative-bonded complex **2**. Since CH_2PH_3 is intrinsically more stable than CH_2SH_2 , the dissociation limit lies well above the ylide even without d AO's, and much less bond lengthening occurs. Nevertheless, the d AO's are necessary for the description of the relative energetics of the phosphorus system; their absence simply has less of a geometrical consequence than in the sulfur system.

II. PMO Analyses

All of the *ab initio* results are consistent with the view that stabilization of the carbon lone pair of an ylide is a major factor affecting the energy differences between CH_2SH_2 and CH_2PH_3 and their more stable tautomers. This can be seen more clearly from a PMO analysis of the geometrical and basis set factors which influence the interaction of a CH_2 group with an adjacent H_nX system.

Bonding

The PMO analysis of the model ylide CH_2XH_n consists of the fragmentation $\text{H}_2\text{C}\cdots\text{XH}_n$ and evaluation of the energies associated with the allowed interactions between the two sets of group orbitals. Although many valence orbital interactions are present (e.g., twelve in the case of $\text{H}_2\text{C}\cdots\text{SH}_2$), attention will be focused upon only those interactions associated with n_C , the carbon lone pair. This choice follows from the dominant contribution of this orbital to the HOMO's of these ylides, and the dominant contribution of the two-electron and four-electron interactions associated with this lone pair to the total interaction energies (17c). Although the other interaction energies are not zero, they are overwhelmed by the effects of the carbon lone pair.

Figure 4 shows the interaction diagram for conformation **6** of CH_2PH_3 . Interaction *a* is a four-electron destabilizing interaction between the carbon lone pair (n_C) and the bonding π -type orbital of the PH_3 group (π_y). Interaction *b* is a two-electron stabilizing interaction between n_C and the antibond-

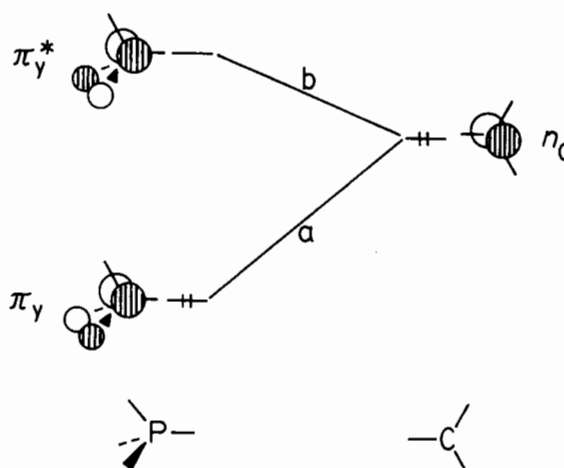


FIG. 4. Frontier orbital interactions in conformation **6** of CH_2PH_3 .

ing PH_3 orbital, π_y^* . This latter interaction is large because n_C is high-lying and π_y^* is low-lying. Figure 5 shows the interaction diagram which results from a 90° rigid rotation of the CH_2 group (i.e., **7**). For a PH_3 group having C_{3v} symmetry, interactions *a* and *b* of Fig. 5 are identical to interactions *a* and *b* of Fig. 4, because the π -type orbitals are doubly degenerate. Therefore, this qualitative argument suggests no conformational preference in CH_2PH_3 . This idealized picture is in accord with the low barrier computed for this ylide, which may be attributed to small variations in the σ -system.

The corresponding interaction diagrams for CH_2SH_2 are shown in Figs. 6 and 7. Figure 6, which refers to **1**, is entirely analogous to Fig. 4 for **6**; however, Fig. 7, which represents a 90° rigid

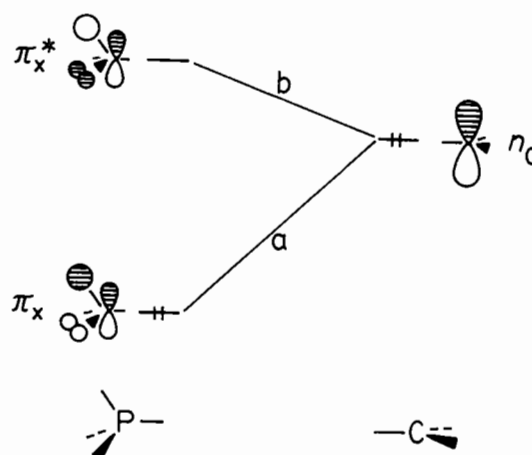


FIG. 5. Frontier orbital interactions in conformation **7** of CH_2PH_3 .

rotation of **1** is very different from Fig. 5. Interaction *a* takes place between n_C and the sulfur lone pair, n_S , while interaction *b* takes place between n_C and the antibonding orbital $\sigma_{SH_2}^*$. The n_C-n_S interaction is more destabilizing than $n_C-\pi_y$ because n_S lies higher in energy than π_y ; the $n_C-\sigma_{SH_2}^*$ interaction is much less stabilizing than $n_C-\pi_y^*$ because the overlap is smaller and $\sigma_{SH_2}^*$ lies higher than π_y^* . The result is a strong preference for conformation **1**.

Rotation of **1** by 90° leads to an increase in the C—S bond length and pyramidalization at carbon since the strong $n_C-\pi_y^*$ interaction is lost and the destabilizing n_C-n_S interaction is reduced by such changes. Conformation **2** is the result.

The qualitative PMO analysis just presented has focused on the net effects of an XH_n fragment upon one common orbital, n_C , of an adjacent CH_2 moiety. If this treatment is reasonable, the relative magnitudes of the stabilization (or destabilization) by SH_2 and PH_3 should be related to the intrinsic stabilities of the two ylides, i.e., the tautomerization and dissociation energies. Table 8 reports the results of a quantitative PMO analysis on **1** and **6** with the different basis sets. This indicates that **6** is more stabilized than **1** in all cases. The same trend was seen in the tautomerization energies.

The function of the *d* AO's is to polarize or rehybridize the π -type antibonding acceptor orbitals of XH_n into the C—X region. As can be seen by comparison of the magnitudes of interaction *b* for **1** and **6** from Table 8, the *d* orbital polarization of the π^* orbitals increases the overlap with n_C and greatly strengthens the stabilization.

That such a polarization exists can be demonstrated by examination of electron density plots.

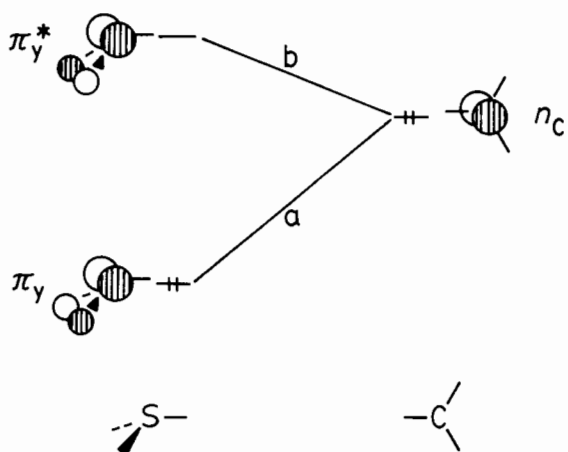


FIG. 6. Frontier orbital interactions in conformation **1** of CH_2SH_2 .

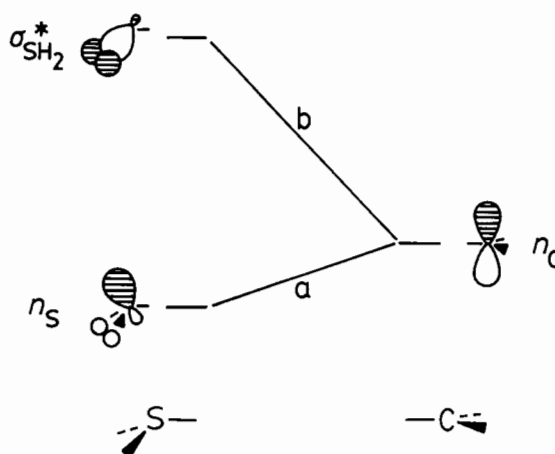


FIG. 7. Frontier orbital interactions in CH_2SH_2 following a 90° rotation of conformation **1**.

Figures 8 and 9 show the electron density in the HOMO (taken in the yz plane) of the sulfonium ylide **1** at the 4-31G and 4-31G* levels, respectively. Clearly the *d* AO's have not altered the nodal characteristics of this predominantly *p*-type lone pair on carbon. Their effect only becomes evident in the density difference plot. Figure 10 shows the electron density difference in the HOMO for **1** at the 4-31G* - 4-31G level; an identical result is observed for **6**. This figure now demonstrates that the effect of the *d* AO's is to concentrate charge into the C—S or C—P π -bonding region.

The form of this figure is dominated by the *d* AO's on sulfur; thus, in the 4-31G* HOMO of **1** the coefficients of the two contributing carbon *d* AO's are 0.002 and 0.023, while those of the corresponding sulfur *d* AO's are 0.060 and -0.136. In addition, deletion of the *d* AO's from carbon has no significant effect upon the sulfur *d* and carbon *p* coefficients computed at 4-31G*. The effect of the analysis presented here is to cast the role of *d* AO participation in a somewhat different language than is customary in the concept of $p_\pi-d_\pi$ bonding, with its implication of conjugation with "free standing" *d* orbitals.

Geometric Consequences

The orbital interactions considered in Figs. 4–7 also provide insight into the origins of the geometric distortions in the XH_n fragments of these ylides. Each of these interactions will lead to distortion of XH_n to permit minimization of the four-electron destabilization or maximization of the two-electron stabilization. Such effects have been discussed recently for methyl groups by Radom and co-workers (41).

Figure 11 shows interactions *a* and *b* of **1**.

TABLE 8. Quantitative PMO analyses of CH₂SH₂ and CH₂PH₃

Basis set	Molecule	Interaction energy ^a			Difference ^c
		Interaction <i>a</i>	Interaction <i>b</i>	Total	
STO-3G ^b	1	31.7	-57.0	-25.3	-8.8
	6	26.7	-60.8	-34.1	
STO-3G*	1	28.2	-107.5	-79.3	-18.6
	6	18.7	-116.6	-97.9	
4-31G ^b	1	47.6	-31.9	15.7	-9.5
	6	39.3	-33.1	6.2	
4-31G*	1	44.0	-45.1	-1.1	-12.2
	6	31.6	-44.9	-13.3	

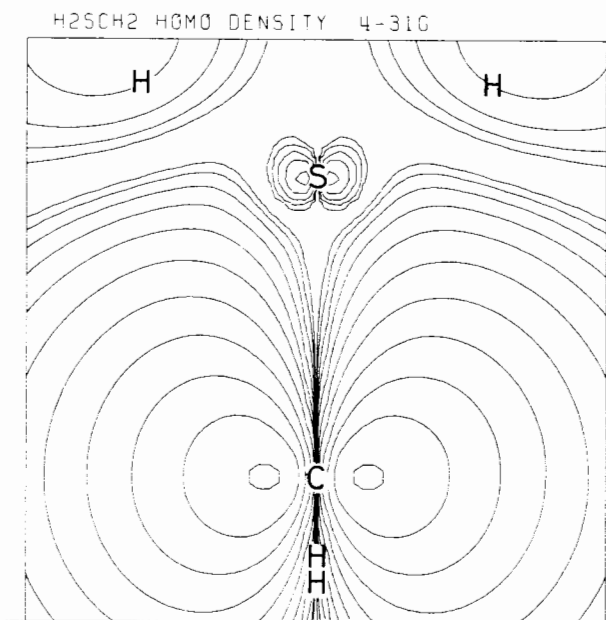
^aIn kcal/mol.^bCalculated at the geometry optimized using *d* AO's.^c $\Delta E_{\text{PMO}}(6-1)$.

FIG. 8. Total electron density plot of the 4-31G HOMO of CH₂SH₂ in the plane perpendicular to the HCH plane with the C—S bond along the *z*-axis. Contour levels are at 0.0001, 0.00022, 0.00047, 0.001, 0.0022, 0.0047, 0.01, 0.022, 0.047, 0.1, 0.22e.

Secondary overlap is depicted by double-headed arrows. In *a* this secondary overlap will cause the HSH plane to tilt away from carbon, so as to decrease the unfavourable overlap associated with the destabilizing interaction. The tilt is in the same direction in *b*, so as to *increase* the overlap associated with the *stabilizing* interaction. The angular distortion resulting from these reinforcing effects leads to CSH angles in **1** which range from 109.2°–113.2° for the four basis sets. The corresponding angle in **4** is 95.1°–97.8° and in **5** it is 98.4°–102.4°.

An additional consequence of interaction *b* is

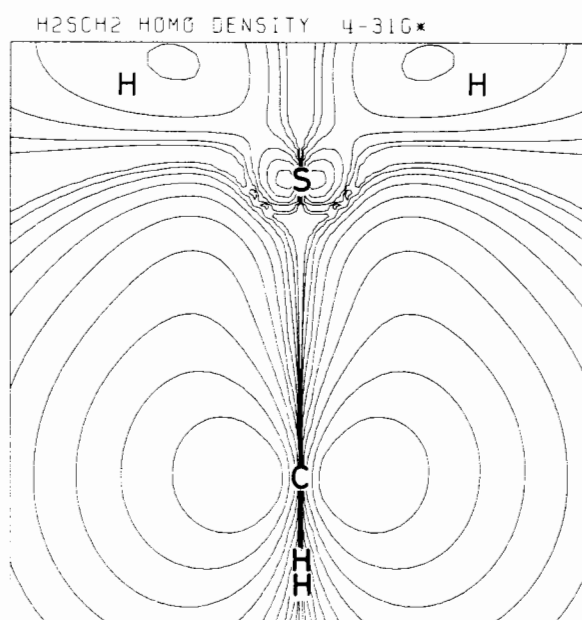


FIG. 9. As for Fig. 8 but at the 4-31G* level.

lengthening of the S—H bonds of **1**, because charge is delocalized into an S—H antibonding region. Inspection of Table 1 reveals that this effect amounts to ca. 0.03 Å, the S—H bond of **1** being longer than those of **2–5**.

Figure 11 also describes interactions *a* and *b* of **6**. In this case, the distortion of PH₃ is greater than that of SH₂. Thus $\angle\text{CPH}_{4,5}$ of **6** ranges from 120.8°–122.1°, compared to a $\angle\text{CPH}$ range in **8** of 95.7°–97.5°. This suggests that a PH₃ group is more readily deformed than an SH₂ group,⁴ but interaction *b* is also stronger in **6** than in **1**. The disparity between the two different $\angle\text{CPH}$ angles of **6**

⁴The calculated diagonal force constant for this rocking mode is $k_{\text{rock}} = 1.05$ mdyne Å/rad² for **6** and $k_{\text{rock}} = 1.24$ mdyne Å/rad² for **1**.

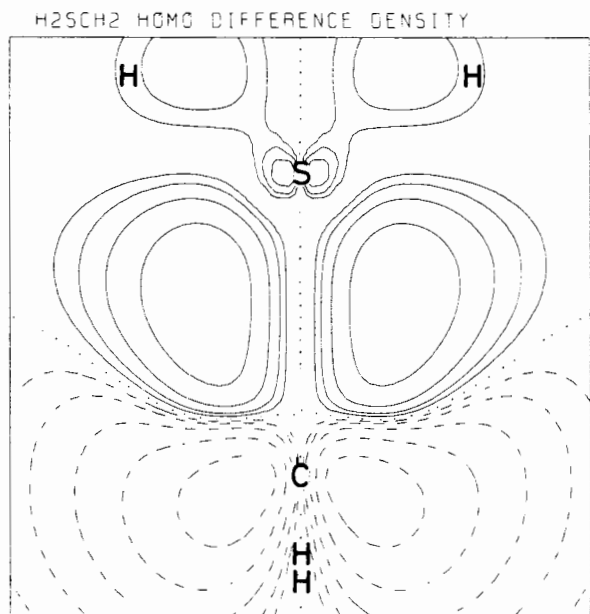


FIG. 10. Electron density difference plot ($4\text{-}31\text{G}^* - 4\text{-}31\text{G}$) for the HOMO of CH_2SH_2 in the plane perpendicular to the HCH plane with the C—S bond along the z -axis. Solid contours refer to regions which gain electron density upon addition of d -orbitals; dashed contours represent regions which lose electron density. Dotted lines represent nodes. Contour levels are at ± 0.001 , ± 0.0022 , ± 0.0047 , ± 0.01 , $\pm 0.022e$.

corresponds to a tilt angle (the angle between the nominal C_3 axis of the PH_3 group and the C—P bond⁵) of $+7.6^\circ$ at the $4\text{-}31\text{G}^*$ level. Interaction 6 also leads to selective weakening of the P— $\text{H}_{4,5}$ bonds compared to P— H_3 , as can be seen in the $0.02\text{ \AA} - 0.03\text{ \AA}$ difference recorded in Table 2 (cf. 24b).

As depicted in Fig. 12, a tilt of the PH_3 group is also expected in 7, but in the opposite sense to that of 6. In this case, an approximately 16° difference between $\angle\text{CPH}_3$ and $\angle\text{CPH}_{4,5}$ is found, corresponding to a tilt angle of -10.4° . These results indicate that the assumption of local C_{3v} symmetry for the PH_3 group about the P—C axis is a much greater approximation than was previously supposed and would have significant effects upon calculated rotational barriers (15a, d, f, g) and the experimental structure refinement of $\text{CH}_2\text{P}(\text{Me})_3$ (30). An additional feature of interaction b in 7 is the prediction that P— H_3 should be longer than P— $\text{H}_{4,5}$ (cf. 24b); this effect is seen in the data of Table 2.

Summary and Conclusions

The first *ab initio* molecular orbital calculations on sulfur-containing carbanions were reported in

⁵Calculated using $3 \cos(\alpha_1 + 2\alpha) = 4 \cos \alpha_2 - \cos \alpha_1$ where α = tilt angle, $\alpha_1 = \angle\text{CPH}_3$, and $\alpha_2 = \angle\text{CPH}_{4,5}$. See ref. 41.

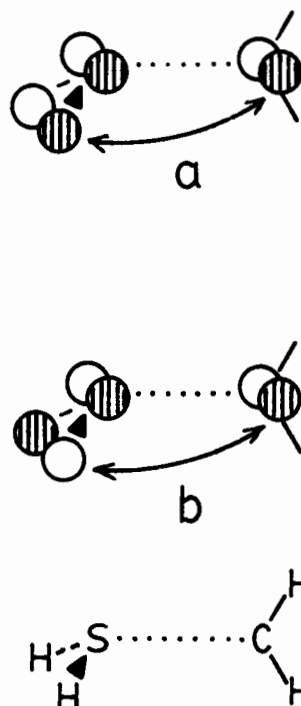


FIG. 11. Secondary frontier orbital interactions in conformation 1 of CH_2SH_2 or conformation 6 of CH_2PH_3 , showing the origin of the tilt of the XH_n group.

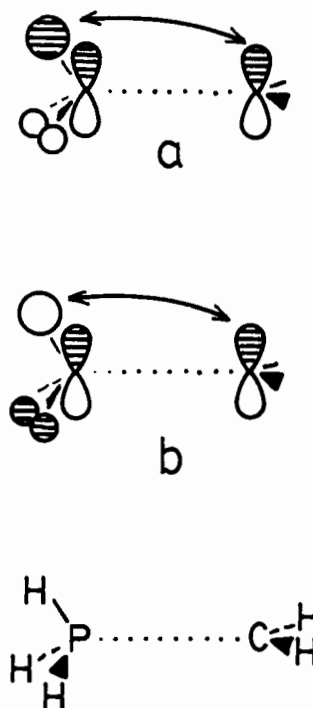


FIG. 12. Secondary frontier orbital interactions in conformation 7 of CH_2PH_3 , showing a tilt of PH_3 in the opposite direction from that in 6.

1969 (42, 43). At that time it was necessary to employ minimal level basis sets and experimental or idealized bond lengths and bond angles. As a result of that work on alpha-sulfinyl and alpha-sulfonyl systems and subsequent, more detailed computations on alpha-thio and alpha-oxycarbanions (44), it was concluded that "the asymmetry of alpha-sulfinyl and alpha-sulfonylcarbanions need not be related to a possible existence of 3d-orbital conjugation" (43), but that "small basis set calculations were ... necessary forerunners to the more extensive and elaborate calculations that now have to be done" (42).

The present work provides some indication of the type of study that will be needed and is now feasible. The experimental properties (geometries, relative stabilities, proton affinities, rotation-inversion behaviour) of sulfonium and phosphonium ylides are reproduced well by the model calculations with the 4-31G* basis set, which contains *d*-type functions on carbon, sulfur, and phosphorus. All other basis sets are deficient, in different ways, and for different reasons. The necessity of *d* AO's to stabilize these hypervalent molecules, and the mechanism of this stabilization, have become clear. At the same time, it has been found that a proper manifestation of the *d*-orbital effects upon the stereochemical properties of these systems depends upon the initial choice of geometry. If the C—X bond length is incorrect, incorrect carbon valence angles or torsional angles about the C—X bond are predicted, whether *d* AO's are present or not. On the other hand, the assumption of planarity at carbon leads to very similar bond lengths and torsional angles with and without *d* AO's, although only in the latter case does such a geometry at carbon correspond to the true energy minimum. In the absence of *d* AO's, this assumption leads to an acceptable C—X bond length because of a symmetry-enforced barrier to dissociation. The existence of such a barrier then obscures the effects of the *d* AO's.

Consequently, a reinvestigation of the geometrical properties of alpha-sulfinyl and alpha-sulfonylcarbanions, and the effects of *d* AO's upon these properties, will require full geometry optimization of all structures at several basis set levels. Depending on the adequacy of the earlier geometrical assumptions (42, 43), the 1969 rotation-inversion behaviour may yet prove to be reliable. However, the conclusions concerning the role of the *d* AO's will probably have to be revised.

Acknowledgements

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