Second Row Molecular Orbital Calculations. Geometries, Internal Rotation Barriers, and Dipole Moments of Methylsilane, Disilane, Methyl Mercaptan, and Methylphosphine

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Abstract: The internal rotation barriers of methylsilane, methyl mercaptan, methylphosphine, and disilane are calculated with and without complete geometry optimization in three different CNDO parametrizations. It is found that Santry's recent reparametrization is most reliable for both geometries and barriers and that geminal and bonded interference interactions are more important than those between vicinal atoms for these molecules. None of the parametrizations give reasonable dipole moments.

While a number of alternative parametrizations for all valence electron semiempirical molecular orbital (MO) methods applicable to molecules containing second row atoms have appeared in the literature,[1-5] the extent to which these methods have been applied is small compared with the first row. Because of this, the ability of those parametrizations to reproduce various molecular properties has not been very extensively tested. Recently, the most popular of these methods, the CNDO/2 parametrization developed by Santry and Segal,[1] has been used to predict internal rotation barriers in a number of molecules containing atoms from the second row.[6] Labarre and coworkers[6] have restricted themselves to the SPD approach[1] (same orbital exponents on 3s, 3p, and 3d atomic orbitals), making no attempt to investigate the effect of omitting d orbitals from the basis set, and have generally assumed fixed geometries during internal rotation.

Due to our interest in internal rotation barriers and the effect of optimization of geometry on these barriers, the present study was initiated to determine the relative utility of three parametrizations in predicting this property. In addition to SPD, calculations have been carried out using the Santry–Segal SP method, in which d orbitals are omitted, and the reparametrization developed by Santry (SPD′).[2] Further, as a first step in a more extensive survey testing the applicability of existing methods to the prediction of molecular properties, the equilibrium geometries, charge distributions, and dipole moments using the three methods have also been calculated.

Internal Rotation Barriers and Geometries

Two sets of barrier calculations have been carried out, one (MBLD) in which the molecular geometry was held fixed during the internal rotation and one (OPT) in which all angles and bond lengths were optimized for each rotational configuration. In the latter case Powell's conjugate directions computer program[7] was

used, and the resulting bond lengths and angles are estimated to be within 0.002 Å and 0.05° of the CNDO minimum.

Since a set of standard bond lengths has not been chosen for the second row, the experimental values were used in the MBLD calculations, and these are listed in Table I. All angles were assumed to be tetra-

Table I. Standard Bond Lengths (Å)[a]

	C	P	S	Si
H	1.093	1.414	1.335	1.485[b] 1.480[c]
C		1.863	1.819	1.8668
Si				2.32

[a] See Tables IV–VII for experimental references. [b] CH_3SiH_3. [c] Si_2H_6.

hedral, although this is less reasonable for sulfur and phosphorus than for oxygen and nitrogen. The resulting frozen frame barriers are compared with the experimental results in Table II.

Table II. Internal Rotation Barriers (kcal/mol)

	SP MBLD	SP OPT	SPD MBLD	SPD OPT	SPD′ MBLD	SPD′ OPT	Exptl
CH_3SiH_3	0.86	0.36	2.47	1.92	2.83	1.86	1.70[a]
CH_3PH_2	0.60	0.79	1.95	2.92	1.55	1.78	1.96[b]
CH_3SH	0.32	0.71	0.94	2.40	0.63	1.04	1.27[c]
Si_2H_6	0.34	0.11	5.86	14.35	3.09	2.21	1.10[d]

[a] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957). [b] T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961). [c] T. Kojima, *J. Phys. Soc. Jap.*, **15**, 1284 (1960). [d] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).

When d orbitals are omitted from the basis set (SP calculation), all barriers are underestimated by at least a factor of 2. When d orbitals are added with the same orbital exponent (SPD), reasonable results are obtained for methylphosphine and methyl mercaptan, but the two silane barriers are too high. In the Santry parametrization (SPD′), the agreement is worse, relative to SPD, for all molecules except disilane and this barrier is still a factor of 3 too high. It should be noted that the worst agreement between calculation and experiment occurs

(1) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).
(2) D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968).
(3) G. Hojer and S. Meza, *Acta Chem. Scand.*, **26**, 3723 (1972).
(4) R. D. Brown and K. Roby *Theor. Chim. Acta*, **16**, 194 (1970).
(5) H. G. Benson and A. Hudson, *Theor. Chim. Acta*, **23**, 259 (1971).
(6) M. Corosine, F. Crasnier, M. C. Labarre, J. F. Labarre, and C. Leibovici, *Chem. Phys. Lett.*, **20**, 111 (1973), and references cited therein.
(7) M. J. D. Powell, Quantum Chemistry Program Exchange, Program 60.

for CH_3SiH_3 and Si_2H_6, just those molecules for which the assumption of tetrahedral geometry is most reasonable. None of the MBLD results are in qualitative or quantitative agreement with experiment for the set of molecules.

The OPT barriers are also listed in Table II, while the corresponding geometries are compared with experiment in Tables III-VI. The effect of geometry optimization on the SP barriers is mixed, the methyl- and di-

Table III. Calculated Geometries of Methylsilane[a,b]

| | SP | | SPD | | SPD' | | |
	S	E	S	E	S	E	Exptl[c]
C-Si	2.069	2.070	1.883	1.886	1.936	1.940	1.8668
C-H	1.115	1.115	1.120	1.119	1.118	1.118	1.093
Si-H	1.618	1.618	1.602	1.602	1.591	1.591	1.485
HCSi	110.33	110.43	108.65	109.04	110.44	110.78	
HCH	108.60	108.51	110.28	109.90	108.49	108.14	107.67
CSiH	110.91	111.09	112.56	113.30	113.83	114.20	
HSiH	108.00	108.51	106.20	105.39	104.78	104.36	108.25

[a] Bond lengths in ångströms, angles in degrees. [b] S, staggered; E, eclipsed. [c] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).

Table IV. Calculated Geometries of Disilane[a,b]

| | SP | | SPD | | SPD' | | |
	S	E	S	E	S	E	Exptl[c]
Si-Si	2.424	2.424	2.197	2.309	2.409	2.424	2.32
Si-H	1.619	1.620	1.604	1.599	1.588	1.588	1.480
SiSiH	112.79	112.89	96.65	104.42	109.78	110.47	109.47
HSiH	105.97	105.86	118.71	114.01	109.15	108.47	109.47

[a] Bond lengths in ångströms, angles in degrees. [b] S, staggered; E, eclipsed. [c] G. W. Bethke and E. B. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957).

Table V. Calculated Geometry of Methylphosphine[a,b]

| | SP | | SPD | | SPD' | | |
	S	E	S	E	S	E	Exptl[c]
C-P	1.957	1.959	1.806	1.814	1.852	1.855	1.863
C-H$_a$[d]	1.114	1.115	1.112	1.121	1.116	1.118	1.093
C-H$_b$	1.115	1.114	1.121	1.115	1.117	1.116	
P-H	1.537	1.536	1.519	1.519	1.507	1.507	1.414
PCH$_a$	110.80	108.71	120.39	101.63	112.66	109.53	
PCH$_b$	109.20	110.53	101.96	112.42	109.21	111.25	
H$_a$CH$_b$	109.23	108.94	111.22	109.62	108.64	108.11	109.75
CPH	96.26	96.95	101.14	101.42	102.93	103.52	97.50
HPH	97.08	96.40	90.09	88.79	95.30	94.60	93.41

[a] Bond lengths in ångströms, angles in degrees. [b] S, staggered; E, eclipsed. [c] T. Kojima, E. L. Breig, and C. C. Lin, *J. Chem Phys.*, **35**, 2139 (1961). [d] H$_a$ is the methyl hydrogen in the molecular symmetry plane.

Table VI. Calculated Geometries of Methyl Mercaptan[a,b]

| | SP | | SPD | | SPD' | | |
	S	E	S	E	S	E	Exptl[c]
C-S	1.856	1.858	1.740	1.745	1.779	1.781	1.819
C-H$_a$[d]	1.114	1.113	1.119	1.114	1.117	1.116	1.093
C-H$_b$	1.114	1.114	1.114	1.116	1.116	1.117	
S-H	1.451	1.451	1.436	1.435	1.433	1.432	1.335
SCH$_a$	107.84	110.05	101.08	110.61	108.14	110.76	
SCH$_b$	109.70	108.79	111.41	107.51	111.14	110.08	
H$_a$CH$_b$	109.83	109.78	110.62	110.65	108.80	108.72	109.75
CSH	94.65	95.86	100.67	100.67	102.82	103.75	96.50

[a] Bond lengths in ångströms, angles in degrees. [b] S, staggered; E, eclipsed. [c] T. Kojima, *J. Phys. Soc. Jap.*, **15**, 1284 (1960). [d] H$_a$ is the methyl hydrogen in the molecular symmetry plane.

silane results being worse, while the methylphosphine and methyl mercaptan barriers are somewhat improved. This is undoubtedly a reflection of the geometries. Both the C-Si (Table III) and Si-Si bond lengths are rather overestimated, pushing the two ends of the molecule too far apart, and the Si-H bond length is too big in both molecules. While the C-P and P-H bond lengths are also overestimated (Table V), the calculated CPH angle is 13° less than tetrahedral (in good agreement with experiment) and the barrier is slightly increased over the MBLD result. The same is true for methyl mercaptan (Table VI).

Geometry optimization increases all of the SPD barriers except for methylsilane for similar reasons. The C-Si bond length is reasonably[4] well-reproduced by SPD, although the SiH bond length is again too large and the HCH angle is incorrectly predicted to be greater than tetrahedral. On the other hand, the axial bond lengths in the other three molecules are underestimated, and probably because of this the barriers are too big. This is most obvious for disilane, for which the SPD OPT barrier is an order of magnitude too high. The angles predicted by SPD are also in poorer agreement with experiment than the SP angles.

These first two sets of results emphasize the need for a proper treatment of the role of d orbitals in calculations on second row molecules. Without d orbitals the barriers are always too small and the bond lengths involving second row atoms too big. Simply adding d orbitals with the same exponent and introducing a factor smaller than unity into the interference term[1] is insufficient. This merely overestimates the effect of d orbitals, and both properties are overshot in the opposite direction.

The SPD' results, in which separate resonance parameters are introduced for d orbitals, are intermediate between the former two methods and in fact yield the best overall agreement with both barriers and geometries. Only the Si_2H_6 barrier is overestimated by this method. While an error of 100% is clearly inadequate, both SP and SPD are off by an order of magnitude in their prediction of this barrier. Except for disilane, the agreement of the OPT SPD' barriers with experiment is comparable to that for the analogous first row molecules.[8] The SPD' axial bond lengths are also intermediate between SP and SPD, and the XH (X = Si, P, S) bond lengths are in closest agreement with experiment; however, the SP method is somewhat better at predicting angles.

Analysis of the Barriers

Previous papers on internal rotation in first row molecules using the related INDO method[9] have made use of a localized molecular orbital[10] (LMO) energy analysis to interpret the calculated barriers.[11] In all of the molecules studied, it has been found that the barrier, ΔE, may be interpreted in terms of a vicinal interference barrier, ΔI, where ΔI arises from the change in vicinal interference energy[11] within those LMO's adjacent to the axial bond. These vicinal interference barriers

(8) M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

(9) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2926 (1967).

(10) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 347 (1963).

(11) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **93**, 4649 (1971).

are listed for the optimized geometry SP and SPD′ calculations in Table VII. There are two striking as-

Table VII. Vicinal Interference Barriers (kcal/mol)

	SP	SPD′
CH_3SiH_3	0.44	0.50
CH_3PH_2	0.65	0.81
CH_3SH	0.50	0.57
Si_2H_6	0.27	0.20

pects to this table. First, ΔI is nearly the same for both parametrizations in all four molecules, and second, while for SP $\Delta I \approx \Delta E$, for SPD′ the vicinal interference barriers are much smaller than the calculated barriers. Thus, since the SP OPT barriers are all too small, we are in agreement with Labarre[6] who has concluded that vicinal interactions are less important when a second row atom is at one or both ends of the axial bond.

The question naturally arises as to whether or not such internal rotation barriers can be interpreted in terms of interference barriers at all. According to the localized orbital energy analysis,[11] the total molecular energy may be written as

$$E = R + U + \beta = Q + \beta \tag{1}$$

where R, the quasiclassical electrostatic energy, contains the electronic and nuclear repulsion plus the two-center quasiclassical attraction; U is the one-center, one-electron quasiclassical energy; and β is the two-center, one-electron interference energy. Thus energy changes due to internal rotation may be viewed as a balance between quasiclassical terms (ΔQ) and interference or wave mechanical terms ($\Delta \beta$). For the molecules considered in this paper, the latter contribution to the barriers may be broken into vicinal, geminal, and bonded interference terms.

$$\Delta \beta = \Delta \beta_v + \Delta \beta_g + \Delta \beta_b \tag{2}$$

The SPD′ OPT barriers are broken down according to equations 1 and 2 in Table VIII. In all four molecules,

Table VIII. Breakdown of SPD′ (OPT) Barriers (kcal/mol)

	ΔR	ΔU	ΔQ	$\Delta \beta$	ΔE	$\Delta \beta_v{}^a$	$\Delta \beta_g{}^b$	$\Delta \beta_b{}^c$
CH_3SiH_3	−3.32	0.22	−3.10	4.96	1.86	0.50	2.48	1.98
CH_3PH_2	−2.29	−0.45	−2.74	4.54	1.78	0.81	1.72	2.01
CH_3SH	0.23	−0.48	−0.25	1.27	1.04	0.57	0.76	−0.06
Si_2H_6	−8.67	2.29	−6.38	8.56	2.21	0.20	2.74	5.62

[a] Sum of all vicinal interference changes. [b] Sum of all geminal interference changes. [c] Sum of all bonded interference changes.

the quasiclassical barrier opposes the total barrier, while $\Delta \beta$ is the same sign as and larger than ΔE. Thus, the second row molecules are similar to those of the first row to the extent that the barriers may be explained in terms of changes in interference interactions. However, comparison of the last four columns of this table indicates that, as noted above, vicinal interference changes are smaller than ΔE, both the geminal and bonded contributions being more important in general.

Dipole Moments and Charge Distributions

The dipole moments of these molecules are known experimentally, and since one of the purposes of Santry's reparametrization of CNDO[2] was to improve

Table IX. Comparison of Calculated and Experimental Dipole Moments of Small Molecules (D)

Molecule	Santry[a]	Present work (SPD′)[b]	Exptl[a]
CS	2.0	2.56	1.97
COS	1.2	1.00	0.72
SO_2	1.7	1.54	1.59
H_2S	1.4	1.47	1.02
PH_3	0.7	1.09	0.578
PF_3	0.6	0.81	1.025
POF_3	2.3	2.35	1.77
PSF_3	1.3	1.50	0.633
SF_4	0.6	0.07	0.632

[a] Reference 2 of text. [b] Geometries are those quoted in Table VII, ref 2 of text.

Table X. Dipole Moments (D)

	SP		SPD		SPD′		
	MBLD	OPT	MBLD	OPT	MBLD	OPT	Exptl
CH_3SiH_3	0.46	0.50	1.96	2.65	1.61	2.30	0.73[a]
CH_3PH_2	2.85	2.36	3.04	2.36	2.89	2.33	1.10[b]
CH_3SH	2.53	2.44	1.81	1.83	2.29	2.12	1.28[c]

[a] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).
[b] T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961).
[c] T. H. Shaw and J. J. Windle, *ibid.*, **19**, 1063 (1961).

agreement with experimental dipole moments, it is of interest to discuss the effect of parametrization, basis set, and geometry on this agreement. Moreover, Santry and coworkers have pointed out[12] that their original expression[2] for the off-diagonal one-center Fock matrix elements connecting orbitals on second row atoms rendered the method no longer invariant to local axis transformations. The correction for this is simple;[12] however, since the correction was pointed out after parametrization of the method and presentation of calculated dipole moments, it is of interest to investigate the effect of this correction on the latter. Finally, in the course of carrying out the dipole moment calculations, a sign error was discovered in the Y component of the pd polarization contribution. This error has apparently been carried along in a number of papers,[1,2,13] as well as the original CNDINDO program.[14] Correct expressions for the pd polarization terms have recently been published[15] and will not be repeated here.

Table IX compares the dipole moments quoted by Santry with those including the two corrections discussed above. The differences between the two sets of calculations range from negligible (H_2S, POF_3) to one order of magnitude (SF_4). In general, the greater the disparity the worse the agreement of the *corrected* results with experiment. It should be noted that published dipole moments for nonplanar molecules which have been calculated using the uncorrected pd (Y) formula in either parametrization[1,2] should be recalculated.

The dipole moments of methylsilane, methyl mercaptan, and methylphosphine are compared with the experimental values in Table X. Except for the SP

(12) J. R. Sabin, D. P. Santry and K. Weiss *J. Amer. Chem. Soc.*, **94**, 6651 (1972).
(13) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.
(14) P. A. Dobosh, Quantum Chemistry Program Exchange, Program 141. This error has since been corrected by Professor Dobosh.
(15) M. Rajzmann and G. Pouzard, *Theor. Chim. Acta*, **32**, 135 (1973).

calculation on methylsilane, the agreement with experiment is generally rather poor. Qualitatively, all calculations do predict the silicon to be at the negative end of the methylsilane moment, in agreement with recent experimental results[15] even though we find negative (positive) point charges on the carbon (silicon). In fact, all CNDO calculations also predict negative (positive) charges on carbon (phosphorus) in methylphosphine.

With the limited number of molecules treated in this paper, little can be concluded concerning the general effect of including d orbitals on CNDO calculated dipole moments. For this reason we are presently carrying out an extensive survey of the ability of these and other CNDO approaches to predict such properties as dipole moments, geometries, and rotation and inversion barriers.

The Gauche Effect. "Isolation" of Lone Pair-Lone Pair Interactions[1]

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Abstract: Repulsive potentials (two-electron interactions) among lone pairs situated on adjacent atoms in sp^3 hybrid orbitals have been calculated as a function of the dihedral angle. Systems containing two, three, and four lone pairs arranged 1-1, 1-2, and 2-2, respectively, on adjacent centers have been studied. A minimum-overlap criterion has been employed to (1) ascertain the preferred dihedral angle based on direct, one-electron interactions and (2) the optimal angle for stabilizing interaction with an adjacent bond (back-donation). The results permit a simple interpretation of the equilibrium conformations of systems containing adjacent lone pairs and also may be extended to systems containing lone pairs adjacent to polar bonds, in particular, the case where fluorine is the polar group. The model is felt to be inapplicable for the situation where there are adjacent polar bonds.

In studies of molecular structure, an important point of focus has been those molecules in which there are unshared electron pairs and/or polar bonds associated with adjacent central atoms. The unusual feature of such species is the difficulty in rationalizing their equilibrium conformations in terms of valence-shell electron-pair repulsion theory (VSEPR),[2] a highly successful approach in predicting central atom geometries. As a consequence, *ab initio* SCF-MO studies of such systems (*e.g.*, N_2H_4, H_2O_2, NH_2OH, and CH_2-FOH) have been carried out in several groups.[3-9] The essence of these results is that, given an adequate basis set (at least double ζ in quality), *ab initio* calculations will reproduce the principal features of the rotational profiles for these molecules, including the rather troublesome trans barrier in H_2O_2.[4a,5b,5c,7]

The *ab initio* results, in one sense, have disposed of the problem as they obviously "contain the required information"[8b] regarding rotational profiles. On the other hand, it is not uncommon to encounter rationalizations of the equilibrium conformations of such species as those minimizing lone pair–lone pair repulsions.[10] Wolfe, *et al.*, however, have stated that such interactions "behave as though they are invariant with dihedral angle."[8] Intuitively we would expect such interactions to be important (if not dominant) in determining the equilibrium conformation, but satisfactory decomposition of total energy profiles in terms of such simple chemical ideas has not yet been accomplished. Two decomposition procedures are currently in use and merit some comment. The first examines each component of the total energy, *i.e.*, kinetic energy (T), electron-nuclear attraction (V_{ne}), electron-electron repulsion (V_{ee}), and nuclear-nuclear repulsion (V_{nn}), as a function of dihedral angle. A second approach, introduced by Allen,[11] focuses on the changes in overall attractive ($E_{att} = V_{ne}$) and repulsive ($E_{rep} = T + V_{ee} + V_{nn}$) contributions to the total energy as the dihedral angle is varied. While both approaches are generally useful from an MO point of view, neither will permit a clear view of the role of lone pair–lone pair interactions (if

(1) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., August 26-31, 1973, Abstract No. ORGN 38.

(2) (a) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970); (b) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 389 (1957); (c) this theory was developed to deal with the arrangement of ligands about a central atom; it does *not* address itself to the situation of adjacent lone pairs and bonding pairs.

(3) L. Pedersen and K. Morokuma, *J. Chem. Phys.*, **46**, 3941 (1967).

(4) (a) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967); (b) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2276 (1967).

(5) (a) A. Veillard, *Theor. Chim. Acta*, **5**, 413 (1969); (b) A. Veillard, *Chem. Phys. Lett.*, **4**, 51 (1969); (c) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(6) E. L. Wagner, *Theor. Chim. Acta*, **23**, 115 (1971).

(7) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 2371 (1972).

(8) (a) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972); (b) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971); (c) S. Wolfe, L. M. Tel, J. H. Liang and I. G. Csizmadia *J. Amer. Chem. Soc.*, **94**, 1361 (1972).

(9) See ref 8a for a compilation of the experimental data.

(10) For example, D. B. Boyd, *Theor. Chim. Acta*, **30**, 137 (1973).

(11) (a) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968); (b) for a criticism of this type of analysis, see I. R. Epstein and W. M. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 6094 (1970).