

assumptions were made concerning bond lengths and bond angles. The only systematic discrepancy occurs in the case of CC single bonds adjacent to fluorine or chlorine. Here the calculated bond lengths seem to be uniformly too small by *ca.* 0.05 Å.

Table III compares calculated and observed dipole moments and first ionization potentials, the latter being estimated by using Koopmans' Theorem.

The agreement between the calculated and observed dipole moments is generally satisfactory, being about as good

as for the compounds previously studied^{1,4} and at least as good as that given by *ab initio* SCF calculations using moderate basis sets. Note in particular the correct prediction of the order of moment in the series CH₃F, CH₂F, CHF₃, and the difference between this series and the corresponding chlorides.

The agreement between the calculated and observed ionization potentials is also quite reasonable though the scatter is greater than it was in the case of hydrocarbons⁴ or compounds containing nitrogen and/or oxygen.⁵ The main trends are nevertheless reproduced in a satisfactory manner, *e.g.*, the *decrease* in ionization potential on successive fluorination of ethylene in contrast to the *increase* in the case of benzene.

Thus MINDO/3 seems to be as applicable to compounds containing fluorine or chlorine as to those of the usual "organic" elements, CHON, and it may be expected to give equally satisfactory interpretations and predictions of chemical behavior.

References and Notes

- (1) Part XXVII: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, preceding paper of the series.
- (2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.
- (3) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, Part XXV of the series
- (4) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, Part XXVI of the series, preceding.
- (5) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262, 1275 (1969).
- (6) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).
- (7) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).
- (8) N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5303 (1972).

Ground States of Molecules. XXIX.¹ MINDO/3 Calculations of Compounds Containing Third Row Elements²

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Abstract: MINDO/3 calculations are reported for a variety of neutral molecules and positive ions containing the third row elements Si, P, or S. The calculated heats of formation, molecular geometries, and ionization potentials are in satisfactory agreement with experiment. Estimates of the π bond energies of multiple bonds involving silicon, and of the resonance energies of silabenzenes, are reported. Proton affinities of analogous compounds of second and third row compounds are compared.

Previous papers of this series^{1,4} have described MINDO/3 calculations for a wide variety of compounds formed by hydrogen, chlorine, and the second row elements C-F. We now report similar calculations for compounds of the third row elements, Si, P, and S.

The calculations were carried out as before, using the parameters listed in part XXV^{4a} and the CDC 6400/6600 computer at The University of Texas Computation Center. Since 3d AOs have not as yet been included in MINDO/3, no attempt was made to extend the calculations to compounds of phosphorus or sulfur in their higher valence states (*e.g.*, phosphates or sulfones). The geometry of each mole-

cule studied was found by minimizing the energy with respect to all geometrical variables, no assumptions of any kind being made. The minimization was carried out by a procedure⁵ based on the Davidon-Fletcher-Powell (DFP) method.

The MINDO/3 method gives heats of atomization (ΔH_a); these were as usual⁴ converted to heats of formation (ΔH_f) using the experimental values for the heats of formation of gaseous atoms previously listed.⁴

Calculations were also carried out for a number of radicals, using the "half-electron" method.⁶ Since the original version of the DFP procedure did not converge satisfactorily

Table I. Calculated and Observed Heats of Formation (ΔH_f) and First Ionization Potentials of Compounds Containing Si, P, or S





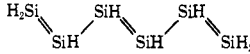




Compd	ΔH_f , kcal/mol (25°)			First ionization potential, eV	
	Calcd	Obsd	Difference	Calcd ^a	Obsd
SiH	83.3	86.3 ^b	-3.0		
SiH ₂	60.3			9.18	
SiH ₃	41.2				
SiH ₄	8.7	8.2 ^b	0.5	12.53	12.82 ^c
Si ₂ H ₆	19.0	19.2 ^b	-0.2	10.53	
Si ₃ H ₈	30.2	28.9 ^b	1.3	9.92	
<i>n</i> -Si ₄ H ₁₀	41.7			9.37	
<i>i</i> -Si ₄ H ₁₀	42.9			9.75	
<i>n</i> -Si ₅ H ₁₂	53.9			9.07	
<i>n</i> -Si ₆ H ₁₄	63.9			8.88	
CH ₃ SiH ₃	-11.8			11.48	
(CH ₃) ₂ SiH ₂	-29.8	-48.0 ^d	18.2	11.03	
(CH ₃) ₃ SiH	-44.5	-42.0 ^e	-2.5	10.74	
(CH ₃) ₄ Si	-55.5	-57.1 ^b	1.6	10.49	10.50 ^f
C ₂ H ₅ SiH ₃	-16.3			10.65	
PhSiH ₃	27.4			9.08	
 SiH ₂	-10.6			9.69	
 Si(CH ₃) ₂	-40.1			9.37	
CH ₃ SiH ₂ SiH ₃	1.57			10.08	
H ₂ Si=SiH ₂	49.2			8.8	
HSi≡SiH	76.6			9.2	
H ₂ Si=CH ₂	17.6			9.6	
(CH ₃) ₂ Si=CH ₂	-19.9			9.0	
HSi≡CH	45.0			10.1	
 SiH	13.7			8.6	
H ₂ C=CHSiH=CH ₂	16.8			8.8	
CH ₃ SiH=SiH ₂	28.6			8.5	
CH ₃ Si=CH	21.9			9.68	
H ₂ C=Si=CH ₂	31.3			9.17	
H ₂ Si=SiHSiH=SiH ₂ , cis	88.4			7.97	
Trans	88.4			7.98	
	143.4			7.50	
	126.8			7.55	
	117.1 ^g			8.17	
	108.7 ^h			8.00	
CH ₂ =CHSiH ₃	8.61			9.90	10.40 ⁱ
P ₂	28.6	34.5 ^b	-5.9	8.63	
P ₄	15.5	14.1 ^b	1.4	8.49	9.54 ^j
PH	82.5	59.2 ^k	23.3	8.13	
PH ₂	29.1	30.1 ^k	-1.0		
PH ₃	2.5	1.3 ^b	1.2	9.83	9.90 ^l
H ₂ PPH ₂	16.0	5.0 ^b	11.0	8.38	
CH ₃ PH ₂	-8.3	-7.0 ^m	-1.3	9.41	
(CH ₃) ₂ PH	-16.6	-15.0 ⁿ	-1.6	8.91	
(CH ₃) ₃ P	-21.9	-23.2 ^o	1.3	8.58	
C ₂ H ₅ PH ₂	-11.7	-12.0 ^m	0.3	9.27	
(C ₂ H ₅) ₂ PH	-23.9	-25.0 ^m	1.1	9.00	
PhPH ₂	30.4			8.36	
HC≡P	3.7			10.69	
H ₂ C=PH	5.2			9.52	
S ₂ ^p	49.0			8.36	
S ₈	20.7	24.4 ^b	3.7	7.78	
HS	31.9	34.1 ^b	-2.2		
H ₂ S	-1.9	-4.9 ^b	3.0	9.99	10.48 ^e
H ₂ S ₂	4.5	2.5 ^b	2.0	9.35	
H ₂ S ₃	8.7	3.6 ^b	5.1	8.55	
H ₂ S ₄	10.8	5.7 ^b	5.1	8.53	
H ₂ S ₅	7.8	8.0 ^b	-0.2	8.41	
CH ₃ SH	-6.1	-5.3 ^b	-0.8	9.53	9.44 ^e
C ₂ H ₅ SH	-21.2	-11.0 ^r	-10.2	9.47	9.21 ^e
<i>n</i> -PrSH	-25.9	-16.2 ^t	-9.7	9.51	9.16 ^u
<i>i</i> -PrSH	-27.6	-18.1 ^v	-9.5	9.41	

Table I (Continued)

Compd	ΔH_f , kcal/mol (25°)			First ionization potential, eV	
	Calcd	Obsd	Difference	Calcd ^a	Obsd
<i>n</i> -BuSH	-32.1	-21.1 ^f	-10.0	9.51	
<i>n</i> -C ₃ H ₁₁ SH	-38.9	-25.9 ^f	-13.0	9.50	
PhSH	22.8	26.9 ^w	-4.1	8.48	
CH ₃ SCH ₃	-8.3	-8.9 ^w	0.6	9.15	8.67 ^a
CH ₃ SCH ₂ CH ₃	-23.4	-14.3 ^f	-9.1	9.15	
CH ₃ SSCH ₃	-6.3	-5.6 ^b	-0.7	8.85	8.97 ^a
CH ₃ SSSCH ₃	-0.1	0.0 ^z	-0.1	8.16	
Thiophene	34.4	27.6 ^w	6.8	8.90	8.87 ^y
2-Methylthiophene	18.7	19.9 ^z	-1.2	8.66	
	-27.4	-8.1 ^{aa}	-19.3	9.12	
CS ₂	27.2	28.0 ^b	-0.8	9.68	10.08 ^{bb}
CH ₂ =CHSH	13.2			8.96	
CH ₃ CH=S	12.0			9.10	
H ₂ C=C=S	38.6			8.78	
H ₂ C=S	30.8			9.34	
(CH ₃) ₂ C=S	-0.7			8.88	
	-14.4			8.72	
CH ₃ CSSH	-0.4			8.78	

^a From Koopmans' theorem. ^b D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U.S.) Tech. Note*, No. 270-3 (1968). ^c A. W. Potts and W. C. Price, *Proc Roy. Soc., Ser. A*, **326**, 165 (1972). ^d S. Kaye and G. F. Lewenz, *J. Amer. Chem. Soc.*, **75**, 3753 (1953). ^e G. G. Hesse, F. W. Lampe, and L. H. Sommer, *ibid.*, **87**, 5327 (1965). ^f C. G. Pitt and H. Bock, *Chem. Commun.*, 28 (1972). ^g Nonequilibrium geometry with alternating SiSi and Si=Si bonds. ^h Equilibrium geometry with equal SiSi bond lengths. ⁱ U. Weidner and A. Schweig, *J. Organometal. Chem.*, **39**, 261 (1972). ^j S. Evans, P. J. Joachim, A. F. Orchard, and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 41 (1972). ^k JANAF Thermochemical Tables, The Dow Chemical Co., 1965, 1966, 1967. ^l D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970. ^m Y. Wada and R. W. Kiser, *J. Phys. Chem.*, **68**, 2290 (1964). ⁿ Y. Wada, Ph.D. Thesis, Kansas State University, 1964. ^o L. H. Long and J. F. Sackman, *Trans. Faraday Soc.*, **53**, 1606 (1957). ^p For ¹Δ state. ^q H. Bock and G. Wagner, *Angew. Chem., Int. Ed. Engl.*, **11**, 150 (1972). ^r J. P. McCullough, W. N. Hubbard, F. R. Frow, I. A. Hossenlopp, and G. Waddington, *J. Amer. Chem. Soc.*, **79**, 561 (1957). ^s I. Omura, K. Higasi, and H. Baba, *Bull. Chem. Soc. Jap.*, **29**, 504 (1956). ^t R. E. Pennington, D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, I. A. Hossenlopp, and G. Waddington, *J. Amer. Chem. Soc.*, **78**, 3266 (1956). ^u L. D. Isaacs, W. C. Price, and R. G. Ridley, "The Threshold of Space," M. Zelikoff, Ed., Pergamon Press, London, 1957, pp 143-151. ^v J. P. McCullough, H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, R. E. Pennington, and G. Waddington, *J. Amer. Chem. Soc.*, **76**, 4796 (1954). ^w J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970. ^x B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **67**, 1283 (1963). ^y P. J. Derrick, L. Asbrink, O. Edqvist, B. O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 177 (1971). ^z J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, M. E. Gross, R. E. Pennington, J. F. Messerly, W. D. Good, and G. Waddington, *J. Amer. Chem. Soc.*, **75**, 5075 (1953). ^{aa} S. Sunner, *Acta Chem. Scand.*, **9**, 847 (1955). ^{bb} A. D. Walsh, *Trans. Faraday Soc.*, **41**, 35 (1945).

for open shell systems,⁷ the geometries were calculated by the earlier SIMPLEX method.⁸

Table I shows the heats of formation (ΔH_f) calculated in this way for a number of compounds containing Si, P, or S, together with first ionization potentials estimated from Koopmans' theorem and experimental values where available. The agreement with experiment is very satisfactory, being in general rather better than for the compounds previously studied.^{1,4} Large deviations (~ 20 kcal/mol) occur only in three cases and two of these are probably spurious.

In the first, dimethylsilane, it is almost certainly the experimental ΔH_f that is in error. One would expect the ΔH_f of silane to change linearly with successive replacements of hydrogen by methyl; this relation is followed by the values for silane and its trimethyl and tetramethyl derivatives, all of which are based on recent thermochemical studies. Interpolation gives an estimated ΔH_f for dimethylsilane of -28 kcal/mol, in good agreement with the MINDO/3 value but 20 kcal/mol greater than the experimental one which more-over rests on an older measurement.

The calculated value for PH came from a standard MINDO/3 closed shell calculation and therefore refers to the lowest singlet state. However, PH has a triplet ground state and the difference between the calculated and observed ΔH_f in Table I (~ 1 eV) is about that expected for the singlet-triplet separation, judging by calculations⁹ for NH and NH₂⁺.

The only unquestionable error occurs in the case of tetrahydrothiophene. This presumably reflects the tendency of MINDO/3 to overestimate the stability of five-membered rings,¹⁰ due no doubt largely to the underestimate of eclipsing interactions.⁴

The results for the series of sulfides H₂S_x are interesting. MINDO/3 tends⁴ to give ΔH_f that are too negative for compounds such as hydrazines or peroxides in which adjacent second row atoms have lone pairs of electrons. This error is due to the neglect of electron repulsion integrals that represent electrostatic effects produced by the dipole moments of lone pair electrons in hybrid AOs ("hybridization moments"). Simple valence theory attributes the failure of third row elements to act as good hydrogen bond donors to lack of hybridization,¹¹ this also being reflected by bond angles close to 90° (e.g., H₂S, 92.2°; H₃P, 93.7°; Table II). Here the lone pair electrons effectively occupy 3s or 3p AOs and so do not give rise to polarity. The failings of MINDO/3 therefore do not apply in this case and the ΔH_f of compounds with adjacent sulfur atoms are consequently well reproduced.

Table II shows geometries calculated by MINDO/3 together with experimental ones where available. Here again the agreement is generally satisfactory. The lengths of CS and CP single bonds seem to be systematically underestimated by ca. 0.06 Å; on the other hand, the differences between the lengths of single and multiple bonds seem to be well reproduced in the comparisons S₂-S₈ and (RSH or R₂S)-CS₂.

The results for thiophene are interesting. It will be seen (Tables I and II) that MINDO/3 reproduces its heat of formation, its ionization potential, and its molecular geometry in a satisfactory manner even though 3d AOs have not as

Table II. Calculated and Observed Geometries of Compounds Containing Si, P, or S

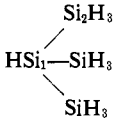
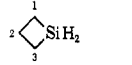
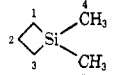
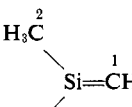
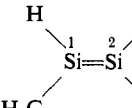
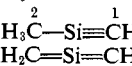
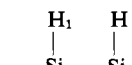
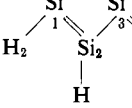
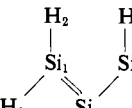
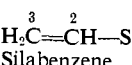
Compd	Ref	Calcd (obsd) bond lengths (ab, A), bond angles (abc), and dihedral angles (abcd)
SiH	<i>a</i>	1.505 (1.520)
SiH ₂	<i>b</i>	SiH, 1.507 (1.516); HSiH, 96.5° (92.1°)
SiH ₃		SiH, 1.469; HSiH, 112.9°
SiH ₄	<i>c</i>	SiH, 1.470 (1.480)
Si ₂ H ₆	<i>d, e</i>	SiH, 1.476 (1.470); SiSi, 2.290 (2.320); HSiSi, 112.7° (109.5° assumed)
Si ₃ H ₈	<i>d</i>	Si ₁ H, 1.479; Si ₂ H, 1.491; SiSi, 2.307; SiSiSi, 118.4°; HSi ₁ Si ₂ , 112.7°; HSi ₂ Si ₁ , 108.8°
<i>n</i> -Si ₄ H ₁₀	<i>d</i>	Si ₁ H, 1.475; Si ₂ H, 1.489; Si ₁ Si ₂ , 2.318; Si ₂ Si ₃ , 2.342; SiSiSi, 115.6°; HSi ₁ Si ₂ , 113.0°; HSi ₂ Si ₁ , 109.1°
	<i>d</i>	Si ₁ H, 1.502; Si ₂ H, 1.479; SiSi, 2.326; HSi ₁ Si ₂ , 104.5°; HSi ₂ Si ₁ , 112.9°
<i>n</i> -Si ₃ H ₁₂	<i>d</i>	Si ₁ H, 1.479; Si ₂ H, 1.485; Si ₃ H, 1.481; Si ₁ Si ₂ , 2.321; Si ₂ Si ₃ , 2.329; Si ₁ Si ₂ Si ₃ , 116.9°; Si ₂ Si ₃ Si ₁ , 115.4°; HSi ₁ Si ₂ , 112.9°
<i>n</i> -Si ₆ H ₁₄	<i>d</i>	Si ₁ H, 1.482; Si ₂ H, 1.488; Si ₃ H, 1.488; Si ₁ Si ₂ , 2.308; Si ₂ Si ₃ , 2.332; Si ₃ Si ₄ , 2.236; Si ₁ Si ₂ Si ₃ , 117.2°; Si ₂ Si ₃ Si ₄ , 117.2°; HSi ₁ Si ₂ , 113.4°
H ₃ CSiH ₃	<i>d, e</i>	SiH, 1.480 (1.480); CH, 1.116 (1.09); CSi, 1.837 (1.857); HSiH, 108.4° (107.6°; 112.0°); HCH, 102.2° (109.5°)
CH ₃ SiH ₂ CH ₃	<i>d-f</i>	SiH, 1.492 (1.480); CH, 1.116; CSi, 1.854 (1.860; 1.871); CSiC, 117.8° (110.0°; 111.0°); HSiH, 104.6°; HCSi, 116.0 (109.5°)
HSi(CH ₃) ₃	<i>d, e</i>	SiH, 1.504 (1.480); SiC, 1.870 (1.873); CH, 1.114 (1.090); HSiC, 113.0° (110.0°); HCSi, 116.1° (109.0°)
Si(CH ₃) ₄	<i>d, g, h</i>	CH, 1.119; CSi, 1.886 (1.930; 1.888); HCSi, 115.5
CH ₃ CH ₂ SiH ₃	<i>d</i>	SiH, 1.475; CSi, 1.869; HSiC, 112.1°; SiCC, 117.4°; HCSi, 112.9°
C ₆ H ₅ SiH ₃	<i>i</i>	SiH, 1.488; CSi, 1.878 (1.843); HSiC, 112.1°
CH ₃ SiH ₂ SiH ₃	<i>d</i>	Si ₁ H, 1.485; Si ₂ H, 1.479; SiSi, 2.317; CSi, 1.861; CH, 1.116; SiSiC, 116.4°; HSi ₁ Si ₂ , 109.6°; HSi ₂ Si ₁ , 112.4°
	<i>j</i>	SiH, 1.482 (1.480); CSi, 1.891 (1.900); CC, 1.533 (1.590); C ₁ H, 1.119 (1.130); C ₂ H, 1.122 (1.130); CCC, 107.0° (109.0°); CSiC, 78.5° (80.0°); HSiH, 102.7° (100.0°)
	<i>d</i>	SiC ₁ , 1.890; SiC ₄ , 1.871; C ₁ C ₂ , 1.532; C ₄ SiC ₃ , 112.2°; C ₁ C ₂ C ₃ , 102.6°
H ₂ Si=SiH ₂		SiH, 1.466; SiSi, 2.023; HSiSi, 124.5°
(H ₃ C) ₂ Si=Si(CH ₃) ₂		CH, 1.116; CSi, 1.857; SiSi, 2.102; CSiSi, 123.0°; HCSi, 115.9°
HSi≡SiH		SiH, 1.440; SiSi, 1.829
H ₂ C=SiH ₂		CH, 1.112; SiH, 1.468; CSi, 1.630; HSiC, 122.1°; HCSi, 128.3°
		C ₁ H, 1.108; C ₂ H, 1.117; C ₁ Si, 1.671; C ₂ Si, 1.859; HC ₁ Si, 128.0°; HC ₂ Si, 115.5°; C ₁ SiC ₂ , 121.°
		Si ₁ H, 1.472; Si ₂ H, 1.467; SiSi, 2.049; CSi, 1.832; CH, 1.119; CSiSi, 129.0°; HSi ₁ Si ₂ , 118.5°; HSi ₂ Si ₁ , 124.3°
		C ₁ Si, 1.503; C ₂ Si, 1.796; C ₁ H, 1.095; C ₂ H, 1.121
		SiC, 1.632; CH, 1.111; HCSi, 127.7°
		H ₁ Si, 1.463; H ₂ Si, 1.473; Si ₂ H, 1.479; Si ₁ Si ₂ , 2.041; Si ₂ Si ₃ , 2.249; SiSiSi, 127.8°; H ₁ SiSi ₁ , 125.9°; H ₂ SiSi ₁ , 125.3°; HSi ₂ Si ₁ , 117.9°
		H ₁ Si, 1.470; H ₂ Si, 1.469; Si ₂ H, 1.482; Si ₃ H, 1.483; Si ₁ Si ₂ , 2.046; Si ₂ Si ₃ , 2.237; Si ₃ Si ₄ , 2.066; Si ₁ Si ₂ Si ₃ , 129.6°; Si ₂ Si ₃ Si ₄ , 129.2°; H ₁ SiSi ₁ , 124.2°; H ₂ SiSi ₁ , 125.9°; HSi ₂ Si ₁ , 114.4°; HSi ₃ Si ₁ , 113.3°
Hexasilabenzene (Si ₆ H ₆)		SiSi, 2.148; SiH, 1.480
		C ₁ H, 1.108; C ₂ H, 1.118; C ₃ H, 1.103; SiH, 1.471; C ₁ Si, 1.660; C ₂ Si, 1.818; CC, 1.330; CSiC, 127.8°; SiCC, 134.6°
Silabenzene (C ₇ SiH ₈)		CSi, 1.753; C ₂ C ₃ , 1.405; C ₃ C ₄ , 1.409; SiH, 1.461; C ₂ H, 1.112; C ₃ H, 1.111; C ₄ H, 1.080

Table II (Continued)

Compd	Ref	Calcd (obsd) bond lengths (ab, Å), bond angles (abc), and dihedral angles (abcd)
		SiH, 1.457; SiSi, 2.283
P ₂	<i>k</i>	1.713 (1.893)
P ₄	<i>l</i>	2.081 (2.210)
PH	<i>a</i>	1.427 (1.432)
PH ₂	<i>m</i>	PH, 1.423 (1.429); HPH, 98.2° (91.7°)
PH ₃	<i>n</i>	PH, 1.419 (1.419); HPH, 100.3° (93.7°)
H ₂ PPH ₂ , trans		PH, 1.432; PP, 2.096; HPP, 104.5°
CH ₃ PH ₂	<i>o, p</i>	CH, 1.120 (1.094; 1.093); PH, 1.422 (1.423; 1.414); CP, 1.796 (1.858; 1.863); HPH, 98.4° (93.4°); HCH, 101.5° (109.8°)
(H ₃ C) ₂ PH	<i>o</i>	CH, 1.120 (1.097); PH, 1.423 (1.445); CP, 1.798 (1.853); CPC, 111.9° (99.2°); HCP, 115.8° (109.8°)
(CH ₃) ₃ P	<i>q, r</i>	CH, 1.122 (1.091); CP, 1.812 (1.846; 1.841); CPC, 110.4° (98.6°; 99.1°); HCP, 116.1° (110.7°)
CH ₃ CH ₂ PH ₂		PH, 1.418; CP, 1.826; CC, 1.505; PCC, 121.7°; HPC, 105.4°
(CH ₃ CH ₂) ₂ PH		PH, 1.449; CP, 1.830; CC, 1.500; CPC, 110.4°
C ₆ H ₅ PH ₂		PH, 1.428; CP, 1.811; HPC, 105.9°
HC≡P	<i>s</i>	CH, 1.109 (1.067); CP, 1.473 (1.542)
H ₂ C=PH		PH, 1.428; CP, 1.606; HPC, 108.5°
PH ₃ ⁺	<i>t</i>	1.416 (1.420)
CH ₃ PH ₃ ⁺		PH, 1.420; CP, 1.788; HPC, 113.0°
(H ₃ C) ₄ P ⁺		PC, 1.842
S ₂	<i>u, v</i>	1.859 (1.887)
S ₈	<i>w</i>	2.047 (2.070)
HS		1.347
H ₂ S	<i>x</i>	HS, 1.351 (1.328); HSH, 97.0° (92.2°)
H ₂ S ₂	<i>y</i>	HS, 1.358; SS, 2.073 (2.050); HSS, 102.9°
H ₂ S ₃		HS, 1.367; SS, 2.098; SSS, 70.8°; HSS, 106.4°
H ₂ S ₄		HS, 1.358; S ₁ S ₂ , 2.097; S ₂ S ₃ , 2.077; SSS, 74.2°; HSS, 109.4°
H ₂ S ₅		HS, 1.356; S ₁ S ₂ , 2.099; S ₂ S ₃ , 2.107; HSS, 108.9°; S ₁ S ₂ S ₃ , 65.3°; S ₂ S ₃ S ₄ , 123.3°
CH ₃ SH	<i>z</i>	HS, 1.345 (1.329); CS, 1.742 (1.818); CH, 1.109 (1.104); HSC, 104.2° (100.3°), HCS, 111.9° (108.5°)
	<i>d, aa</i>	CS, 1.749 (1.810); HS, 1.352; HSC, 105.1°
	<i>d</i>	SH, 1.352; CS, 1.772; HSC, 105.2°
	<i>d</i>	SH, 1.363; CS, 1.793; HSC, 96.4°
	<i>d</i>	SH, 1.357; CS, 1.754; HSC, 102.2°
	<i>d</i>	SH, 1.356; CS, 1.779; HSC, 101.6°
H ₃ CSCCH ₃	<i>d, bb</i>	SH, 1.368; CS, 1.733; HSC, 102.3°
	<i>d, bb</i>	CH, 1.104 (1.06, assumed); CS, 1.750 (1.820); CSC, 115.4° (ca 105°); HCS, 111.2° (109.5° assumed)
	<i>d</i>	C ₁ S, 1.755; C ₂ S, 1.783; CSC, 115.6°; CCS, 106.6°
	<i>cc</i>	CS, 1.742 (1.780); SS, 2.087 (2.040); CSS, 110.7°; HCS, 111.3°
CS ₂	<i>dd</i>	1.539 (1.553)
	<i>ee</i>	CS, 1.766 (1.718); C ₂ C ₃ , 1.343 (1.352); C ₃ C ₄ , 1.460 (1.455); C ₂ H, 1.091 (1.085); C ₃ H, 1.093 (1.073); CSC, 92.2° (91.3°); HCS, 121.1° (119.2°); HC ₂ C ₃ , 125.0° (124.7°)
		CS, 1.789; C ₂ C ₃ , 1.502; CSC, 97.2°; SCC, 108.5°
		CS, 1.756; C ₂ C ₃ , 1.352; C ₂ C ₆ , 1.470; CSC, 92.7°; C ₃ C ₂ S, 109.8°; C ₆ C ₂ S, 118.7°
		CS, 1.602; CC, 1.477; CH, 1.109
		HS, 1.353; CS, 1.728; CC, 1.314; HSC, 103.1°; SCC, 124.7°
		CS, 1.572; CC, 1.460; SCC, 127.4°
		CS, 1.542; CC, 1.300; HC, 1.098
	<i>ff</i>	CS, 1.749 (1.810); CSC, 115.1° (106.5°); SCS, 117.3° (106.5°)
H ₂ C=S		CS, 1.553; HCS, 127.7°
		S ₁ C, 1.589; S ₂ C, 1.713; HS, 1.346; CC, 1.464; SCS, 129.8°; HSC, 113.4°; S ₂ CC, 102.2°

Table II (Continued)

Compd	Ref	Calcd (obsd) bond lengths (ab, Å), bond angles (abc), and dihedral angles (abcd)
H ₃ S ⁺		HS, 1.371; HSH, 100.9
(H ₃ C) ₃ S ⁺		CS, 1.811; CSC, 114.4
H ₂ S ⁺	gg	HS, 1.368 (1.358); HSH, 97.6 (93.0)

^a G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 1, 2nd ed. Van Nostrand, New York, N.Y., 1950; A. E. Douglas, *Can. J. Phys.*, **35**, 71 (1957). ^b I. Dubois, *Can. J. Phys.*, **46**, 2485 (1968). ^c S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **22**, 1559 (1954); D. R. J. Boyd, *ibid.*, **23**, 922 (1955). ^d Calculated geometry had staggered conformations and expected symmetry; observed: L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.*, **60**, 1836 (1938). ^e A. C. Bond and L. O. Brockway, *ibid.*, **76**, 3312 (1954). ^f L. Pierce, *J. Chem. Phys.*, **31**, 547 (1959). ^g L. O. Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, **58**, 2036 (1936). ^h W. F. Sheehan, Jr., and V. Schomaker, *ibid.*, **74**, 3956 (1952). ⁱ F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956). ^j L. V. Vilkov, V. S. Mastryukov, Y. V. Baurova, V. M. Volovin, and P. L. Grinberg, *Dokl. Akad. Nauk SSSR*, **177**, 1084 (1967). ^k A. E. Douglas and K. S. Rao, *Can. J. Phys.*, **36**, 565 (1958). ^l L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Phys.*, **3**, 699 (1935). ^m R. N. Dixon, G. Duxbury, and D. A. Ramsay, *Proc. Roy. Soc., Ser. A*, **296**, 137 (1967). ⁿ L. S. Bartell and R. C. Hirst, *J. Chem. Phys.*, **31**, 449 (1959). ^o L. S. Bartell, *ibid.*, **32**, 832 (1960). ^p T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961). ^q L. S. Bartell and L. O. Brockway, *ibid.*, **32**, 512 (1960). ^r D. R. Lide, Jr., and D. E. Mann, *ibid.*, **29**, 914 (1958). ^s J. K. Tyler, *ibid.*, **40**, 1170 (1964). ^t L. Pratt and R. E. Richards, *Trans. Faraday Soc.*, **50**, 670 (1954). ^u Experimental value for ³Σ calculated for ¹Δ. ^v K. Ikonone, *J. Phys. Soc. Jap.*, **8**, 646 (1953). ^w C.-S. Lu and J. Donohue, *J. Amer. Chem. Soc.*, **66**, 818 (1944). ^x H. C. Allen and E. K. Plyler, *J. Chem. Phys.*, **25**, 1132 (1956). ^y D. P. Stevenson and J. Y. Beach, *J. Amer. Chem. Soc.*, **60**, 2872 (1938). ^z R. W. Kilb, *J. Chem. Phys.*, **23**, 1736 (1955). ^{aa} L. E. Sutton, *Chem. Soc. Spec. Publ.*, No. 11 (1958); No. 18 (1965). ^{bb} L. O. Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, **58**, 2036 (1936). ^{cc} D. P. Stevenson and J. Y. Beach, *ibid.*, **60**, 2872 (1938). ^{dd} B. P. Stoicheff, *Can. J. Phys.*, **36**, 218 (1958). ^{ee} B. Bak, D. Christensen, J. Rastrup-Andersen, and E. Tannenbaum, *J. Chem. Phys.*, **25**, 892 (1956). ^{ff} O. Hassell and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947). ^{gg} G. Herzberg, personal communication.

Table III. Calculated and Observed Heats of Formation (ΔH_f) of Cations

Ion	ΔH_f , kcal/mol (25°)	
	Calcd	Obsd ^a
HSi ⁺	254.4	
H ₂ Si ⁺	263.7	265–287
H ₃ Si ⁺	236.0	264
(CH ₃) ₂ SiH ⁺	165.2	179, 195, 199
(CH ₃) ₃ Si ⁺	139.2	140, 155
(CH ₃) ₄ Si ⁺	176.8	171
Si ₂ H ₆ ⁺	247.6	264
PH ₃ ⁺	219.0	231
PH ₄ ⁺	180.8	174
CH ₃ PH ₃ ⁺	165.3	
(CH ₃) ₂ PH ₂ ⁺	154.2	
(CH ₃) ₃ PH ⁺	146.6	
(CH ₃) ₄ P ⁺	142.4	
H ₂ S ⁺	226.6	235
CH ₃ SH ⁺	206.5	212
(CH ₃) ₂ S ⁺	191.7	191
H ₃ S ⁺	190.0	191
CH ₃ SH ₂ ⁺	176.9	174 ^b
(CH ₃) ₂ SH ⁺	168.2	160 ^b
CS ₂ ⁺	247.6	261
Thiophene ⁺	225.4	229
(HSSH) ⁺	214.8	239
(CH ₃ SSCH ₃) ⁺	189.4	201 ^c
(CH ₃) ₃ S ⁺	163.6	
PhS ⁺	236.5	250

^a J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," U.S. Government Printing Office, Washington, D.C. 20402 (1969). ^b Calculated from the proton affinities of CH₃SH and (CH₃)₂S (Table IV). ^c Calculated from the heat of formation and ionization potential of CH₃SSCH₃ (Table I).

yet been included in the treatment. This seems to provide further support for the growing body of evidence that the stability and apparent aromaticity of thiophene do not arise from contributions by 3d AOs of sulfur.¹²

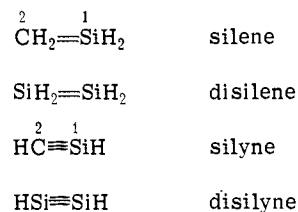
Table III shows the calculated ΔH_f for a number of positive ions and positive radical ions together with experimental values. The agreement with experiment is about as good as for neutral molecules and radicals (Table I), given that nearly all the larger deviations refer to ΔH_f derived from earlier electron impact values for ionization potentials which are now known to be too high by 0.5–1.0 eV. As expected the experimental values are correspondingly greater

than those calculated. These results therefore suggest once more that MINDO/3 can be applied to ions as well as to neutral molecules. Note incidentally that ionization potentials found by difference between the ΔH_f for neutral molecules (Table I) and the corresponding radical cations (Table III) are uniformly smaller by a few tenths of an eV than the values from Koopmans' theorem in Table I (e.g., PH₃, 9.39, 9.83; H₂S, 9.91, 9.99; CH₃SH, 9.22, 9.53; (CH₃)₂S, 8.67, 9.15; thiophene, 8.28, 8.90 eV). This of course would be expected since the two sets of values correspond to adiabatic and vertical ionization, respectively.

In view of the apparent success of this extension of MINDO/3 to the third row elements, we have used it to study several problems of topical interest.

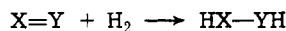
1. π Bond Strengths of Multiple Bonds Containing Silicon. While no compound containing a multiple CSi or SiSi bond has as yet been isolated, and while no reliable calculations for such species have as yet been reported, a number of them have been claimed as intermediates in reactions. The results in Tables I and II are of obvious interest in this connection.

First, a question of nomenclature. To avoid the use of the cumbersome terms silaethylene, silacetylene, etc., we suggest the following trivial names for the basic species



Thus 2-silabutadiene (CH₂=CHSiH=CH₂) could equally be termed 1-vinylsilene. It is true that the species SiH₂ has sometimes been referred to as silene; however, analogy with CH₂ (methylene) suggests that a better term would be silylene. Compounds of the type SiR₂ would then be described as silylenes; e.g. Si(CH₃)₂ ≡ dimethylsilylene.

The ability of an unsaturated compound to undergo addition at a double bond X=Y will depend on the π strength of that bond (E_{XY^π}). This can be estimated from the corresponding heat of hydrogenation (ΔE_{XY^h}), which in turn can be found from the heats of formation of X=Y and its dihydro derivative, as follows.



$$\Delta H = \Delta H_{XY}^h = \Delta H_f(HX-YH) - \Delta H_f(X=Y) \quad (1)$$

$$\Delta H_{XY}^h = E_{XY}^r + E_{HH} - E_{HX} - E_{HY} \quad (2)$$

Here E_{HH} , E_{HX} , and E_{HY} are the bond energies of HH, HX, and HY bonds, respectively, while $\Delta H_f(R)$ is the heat of formation of R. The strength of the first π component ($E_{X=Y}^r$) of an $X=Y$ triple bond can be estimated in the same way from the heat of partial hydrogenation of the triple bond to a double bond. Since we wish to compare multiple bonds containing carbon and silicon, we need the bond energies for CH and SiH. The conventional values for these, and H_2 , are

$$E_{HH}, 104.2; E_{CH}, 98.6; E_{SiH}, 77.3 \text{ kcal/mol} \quad (3)$$

The heats of formation of ethane, ethylene, and acetylene are known from experiment (-20.24, -12.45, and 54.34 kcal/mol, respectively⁵). For the corresponding silicon species we use the MINDO/3 ΔH_f in Table I. In this way we arrive at the following values for π bond strengths (kcal/mol)

$$\begin{aligned} C=C, 60.3; C=Si, 42.3; Si=Si, 20.2 \\ C\equiv C, 51.1; C\equiv Si, 44.3; Si\equiv Si, 23.0 \end{aligned} \quad (4)$$

The values for triple bonds are admittedly too high because they should be estimated using CH and SiH bond energies ($E_{CH'}$, $E_{SiH'}$) corresponding to carbon and silicon with sp^2 hybridization.¹³

The difference between $E_{SiH'}$ and E_{SiH} is probably about the same as that (~ 4 kcal/mol)¹⁴ between $E_{CH'}$ and E_{CH} ; if so the triple bond π strengths in eq 4 should all be reduced by *ca.* 8 kcal/mol. Note that the estimated π bond strength of the C=C bond in ethylene (60.2 kcal/mol) is close to the observed barrier to rotation (65 kcal/mol¹⁵).

CSi and SiSi π bonds are therefore predicted to be quite strong, a conclusion supported by the calculated bond lengths and ionization potentials. Thus the percentage contraction in CSi bond length on passing from methylsilane to silene (11%) or the SiSi bond length on passing from disilane to disilene (12%) is close to that in the CC bond length on passing from ethane to ethylene (13%), and similar relations hold for the triple bonds. Likewise silyne and disilyne are predicted to have higher ionization potentials than silene or disilene, respectively, just as the ionization potential of acetylene (11.4 eV) is greater than that of ethylene (10.5 eV). These increases in ionization potential on passing from double to triple bonds reflect the increase in binding energy of a π MO with decreasing bond length.

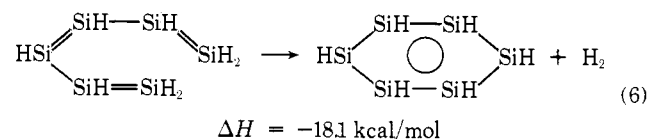
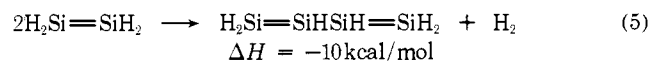
Silenes should therefore be reasonably stable species showing high conformational stability, the barrier to rotation about the C=Si bond being *ca.* 40 kcal/mol. A number of silenes have been reported as stable but highly reactive.¹⁶ Disilenes should also be stable though even more reactive than silenes; rotation about the Si=Si bond should also be facile at room temperature, the barrier to rotation being only *ca.* 20 kcal/mol. Here again several such compounds have been reported as stable but extremely reactive species.¹⁷ Even silynes and disilynes should be capable of existence although no examples seem as yet to have been prepared.

2. Conjugated Polysilaenes and Silabenzenes. Since the bonds in classical polyenes are localized,¹⁸ one would expect the same to be true for the corresponding silylated species. The results in Table I are consistent with this prediction. Thus the increments in ΔH_f in the series $H_2Si=SiH_2$, $H_2Si=SiHSiH=SiH_2$, and $H_2Si=SiHSiH=SiHSiH=SiH_2$, are almost identical,^{14,19} being 39.2 and 38.4 kcal/mol, respectively.

A further interesting point is that the calculated ΔH_f for *cis*- and *trans*-tetrasilabutadienes are the same. In the carbon series the *trans* isomer is the more stable by ≥ 2.1 kcal/mol.²⁰ There is reason to believe that the destabilization of *cis*-1,3-butadiene may be due to nonbonded interactions between the terminal hydrogen atoms. Such repulsions would be absent in the silicon analog, due to the greater length of SiSi bonds.

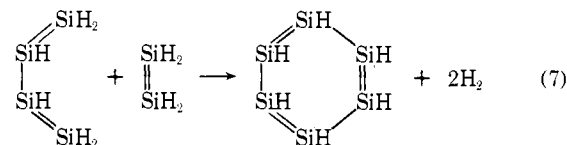
We can therefore estimate¹⁹ the heat of formation for a classical cyclohexatriene, or any silylated derivative of it, by assuming additivity of bond energies. Any extra stabilization ("aromatic energy") will appear as a difference between this value and the actual ΔH_f of the cyclic species. Consider for example hexasilabenzene, Si_6H_6 .

A. Using results in Table I, we find



If the bonds in hexasilabenzene were localized, ΔH would be the same in both cases. Thus the aromatic energy of hexasilabenzene is $(18.1 - 10.0) = 8.1$ kcal/mol.

B. If the bonds in hexasilabenzene were localized, the heat of reaction for the process



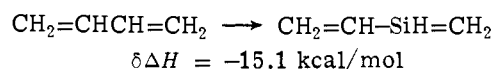
would be just double that for eq 5, *i.e.* -20 kcal/mol. The calculated heats of formation in Table I lead, however, to a value of -28.9 kcal/mol for this process. Thus the aromatic energy of hexasilabenzene is $(28.9 - 20.0) = 8.9$ kcal/mol.

The two estimates agree closely. We may take their mean (8.5 kcal/mol).

The aromatic energy of benzene can be estimated by procedure B, using the data in part XXVI.^{4b} We can use either experimental heats of formation for ethylene, butadiene, and benzene, or MINDO/3 ones. Since the difference in ΔH_f between *cis*- and *trans*-butadiene is probably due to irrelevant nonbonded repulsions, the value for the *trans* isomer should be used in this calculation. The two estimates of the aromatic energy (kcal/mol) are

$$\text{experimental } \Delta H_f, 21.2; \text{ MINDO/3 } \Delta H_f, 9.2 \quad (8)$$

The discrepancy is due to the fact that MINDO/3 seems to underestimate resonance energies in general and aromatic energies in particular (*cf.* ref. 4). Since the same is likely to be the case for hexasilabenzene as well, it seems very likely that it and benzene have in fact comparable aromatic energies. This conclusion is supported by an analogous calculation for monosilabenzene. The effect of monosilylation in a conjugated system can be deduced from the calculated ΔH_f for butadiene and 2-silabutadiene.



Using the MINDO/3 value of ΔH_f for benzene (28.8 kcal/mol), we arrive at an estimate for ΔH_f of silabenzene of 13.7 kcal/mol. This is identical with the calculated value in Table I, implying that the aromatic energies of benzene and silabenzene must be similar.

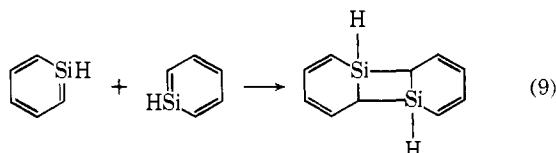
These arguments suggest that silabenzene should be a

Table IV. Comparison of MINDO/3 Proton Affinities for Compounds of Phosphorus and Sulfur with Experiment and with Values for Corresponding Amines and Oxides

Compd	Proton affinity ^a		Proton affinity ^a	
	MINDO/3	Obsd	Compd	Obsd
PH ₃	187.7	185 ^b	NH ₃	207 ^b
CH ₃ PH ₂	192.4		CH ₃ NH ₂	218, ^c 216 ^d
(CH ₃) ₂ PH	195.2		(CH ₃) ₂ NH	225, ^c 222 ^d
(CH ₃) ₃ P	197.5		(CH ₃) ₃ N	229, ^c 227 ^d
SH ₂	174.1	170 ^b	OH ₂	164 ^b
CH ₃ SH	183.0	186 ^b	CH ₃ OH	180 ^b
(CH ₃) ₂ S	189.5	197 ^b	(CH ₃) ₂ O	186 ^b

^a In kcal/mol. ^b Reference 21. ^c Reference 22. ^d Reference 23.

stable species. The heat of dimerization



should be no greater than that for an olefine; the difference in π bond strength between $\text{C}=\text{C}$ and $\text{C}=\text{Si}$ bonds should be just counterbalanced by the loss of aromatic energy (~ 40 kcal/mol) during the reaction.

3. Proton Affinities. Recent work using ion cyclotron resonance spectrometry²¹⁻²³ has shown that the relative basicities of compounds in the gas phase are commonly very different from those in solution. It is therefore interesting to compare the MINDO/3 gas phase proton affinities calculated from the data in Tables I and III with experimental values for them and for analogous compounds of nitrogen and oxygen. Table IV shows this comparison. It will be seen that whereas phosphine is correctly predicted to have a lower proton affinity than ammonia, H₂S, CH₃SH, and CH₃SCH₃ are predicted, again correctly, to have higher proton affinities than the corresponding oxygen compounds. Introduction of successive methyl groups into phosphine is also predicted to successively increase the proton affinity, as has been observed to be the case for ammonia. However, the calculated difference in proton affinity between PH₃ and P(CH₃)₃ seems too small.²⁴

References and Notes

- (1) Part XXVIII: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, preceding paper of this series.
- (2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.
- (3) Robert A. Welch Postdoctoral Fellow.
- (4) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, preceding papers of this series: (a) Part XXV; (b) Part XXVI; (c) Part XXVII.
- (5) M. J. S. Dewar, H. W. Kollmar, H. Metiu, P. J. Student, and P. Weiner, to be published.
- (6) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90**, 1953 (1968).
- (7) The latest version of the DFP procedure can be used for "half-electron" calculations of radicals and triplet states. While convergence is slower than for closed shell systems, it is still much faster than methods (SIMPLEX, Brent) that do not use derivatives of the energy with respect to the geometrical variables.
- (8) See M. J. S. Dewar, *Fortschr. Chem. Forsch.*, **23**, 1 (1971).
- (9) M. J. S. Dewar, R. C. Haddon, W.-K. Li, and P. K. Weiner, *J. Amer. Chem. Soc.*, in press.
- (10) Thus the calculated⁴ ΔH_f for cyclopentene is too negative by nearly 10 kcal/mol.
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- (13) See M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).
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- (18) For a detailed discussion of the meaning of bond localization and references see Dewar,¹¹ p 140.
- (19) Cf. M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 692 (1965).
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- (24) The difference in $\text{p}K_a$ between PH₃ and P(CH₃)₃ is ca. 20 pK units, corresponding to a difference in free energy of protonation of ca. 25 kcal/mol. This is more than double the difference between their calculated proton affinities. Analogy with ammonia and the amines suggests that solvation effects should if anything reduce the difference in basicity between PH₃ and P(CH₃)₃.