π Bond Strengths in the Second and Third Periods

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Abstract: All possible π bonds formed between the elements C, N, O, Si, P, and S are considered. The π bond strengths are estimated by the cis-trans rotation barriers (where possible) and by hydrogenation energies. The ability of these elements to form strong π bonds is in the order O > N ≈ C ≫ S > P > Si. In addition, computed bond lengths and vibrational stretching frequencies are reported for both the singly and doubly bound compounds. The structure of the lowest triplet state of each double-bonded compound is given, along with the singlet-triplet splitting.

The field of p_π-p_π bonding involving elements from the third period of the periodic table, and below, became an active research area only in the 1970s, with efforts intensifying sharply in the 1980s. Perhaps one reason for the late development of the field was the so-called "Double Bond Rule", which states that elements with a valence principal quantum number of three or greater will not participate in π bonding. In fact, in the mid 1960s the paucity of compounds containing heavy atom multiple bonds led to the classification of such molecules as "nonexistent compounds".[1]

In 1948, Pitzer[2] noted the relative lack of examples of π-bonded heavy elements. He explained this by the qualitative argument that since heavier elements have longer bond lengths, their p_π-p_π overlap integrals should be smaller than those for corresponding second period elements. Since bond strengths are usually believed to be proportional to overlap integrals (see, for example, extended Hückel theory), the reluctance of heavy elements to π bond was explained in a simple, intuitive manner.

However, in 1950 Mulliken[3] tested this idea by actually computing the values of the overlap integrals, by using a minimal Slater orbital basis and assumed geometries. He found that in fact the overlap integrals did not decrease significantly when heavy atoms replaced their second row congeners. To illustrate his result, we have computed similar overlap integrals by using Hartree-Fock quality atomic orbitals and bond distances typical of —N=N— and —P=P— compounds. The π overlap is actually larger in the phosphorus case, 0.65 vs. 0.62! This discovery led Mulliken to conclude "the differences between second and third period atoms with respect to readiness of formation of multiple bonds...are shown to be attributable to increased strengths of σ bonds in the third period." A number of workers have objected to this on the grounds that, for example, Si-Si σ bonds are weaker than C-C σ bonds. What Mulliken meant, of course, was that the *difference* between σ and π bond strengths is larger in the third and higher periods than in the second.

A preliminary feel for the relative strengths[4-9] of σ vs. π bonding for the second and third period elements may be obtained from Tables I and II. Table I shows that σ bond strengths decrease toward the right of the periodic table. Because this tailing off is larger in the second period, the third period elements actually possess greater σ bond strengths in groups 16 and 17. Table II shows that when π bonds are also formed, as in the homonuclear diatomics, the second period elements always have markedly stronger bonds. In fact, C_2 contains two π bonds, in preference to a σ and π bond!

In a recent landmark paper Kutzelnigg[10] surveyed chemical bonding between main group elements. He explains the weakness of π bonding in the heavier main group elements in terms of lone pair repulsions and isovalent hybridization. The differences between the second period elements and their heavier congeners are attributed to the fact that the former do not have any core p orbitals. Kutzelnigg advances the novel viewpoint that it is the second period elements which are "unusual" in their π bonding and many other properties.

Table I. Homopolar σ Bond Strengths[g]

H_3C-CH_3	88[a]	H_3Si-SiH_3	74[e]
H_2N-NH_2	64[b]	H_2P-PH_2	61[f]
HO-OH	50[c]	HS-SH	66[c]
F-F	37[d]	Cl-Cl	57[d]

[a] Reference 4. [b] Reference 5. [c] Reference 6. [d] Reference 7. [e] Reference 8. [f] Reference 9. [g] kcal/mol.

Table II. Diatomic Bond Strengths

C_2	143	Si_2	74
N_2	225	P_2	116
O_2	118	S_2	101

[a] Reference 7. [b] kcal/mol.

In spite of their significantly lower π bond strengths, it has been possible in recent years to generate and characterize molecules containing many different types of heavy atom π bonds. A number of strategies may be employed to form such compounds.[11] The multiply bonded element may be stabilized by incorporation into a delocalized or aromatic π system, by imparting an overall charge, or by ligating the π bond to a transition metal. As the above methods all produce chemically altered π bonds, the final synthetic stratagem (using bulky substituents to impart kinetic stability to the double bond) produces the most satisfactory examples of multiple bonds. This method has been used to generate solution stable and even isolable compounds containing one and, more recently, two π-bonded heavy elements.

A number of review articles on the subject of heavy element π bonding exist. Jutzi[12] has reviewed multiple bonds between carbon and the elements P, As, Sb, Bi, Ge, and Si. Since then Appel, Knoll, and Rupert[13] have updated the story of the C=P bond. Compounds containing the —P=N— bond have been reviewed by Abel and Mucklejohn.[14] Cowley[15,16] has twice surveyed multiple bonding in group 14 and group 15. Perhaps the most attention in the field of heavy atom π bonding has focused on the element silicon, because of its relationship to carbon. One of the authors[17] has reviewed theoretical calculations on multiply bound silicon. Gusel'nikov and Nametkin[18] surveyed the status

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of silicon multiple bonding up to 1979. This review has recently been brought up to date (late 1985) by Raabe and Michl.[19] Wiberg[20] has reviewed the mixed multiple bonding between the elements Si and Ge and the elements C and N.

That the field continues to be actively pursued is indicated by the recent report of an allene analogue containing a —P=C=P— group.[21] Additional π-bonded compounds between even heavier members of groups 14, 15, and 16, such as the solution stable Ge=P[22] and Sn=P[23] and an Si=Se intermediate,[24] are now known. In fact, it would seem to be safe to stand the "Double Bond Rule" on its head by predicting that eventually compounds representing all possible double bonds between atoms from groups 14–16 will be isolated and characterized.

The purpose of the present theoretical work is to provide information on double bonds that has been slow to emerge from the synthetic studies. Often only NMR and UV–vis spectra are taken for the solution stable species. Bond lengths are not yet known for those compounds for which crystals have not been prepared. IR stretching frequencies are not always available for these bonds. And finally, perhaps the most fundamental question is: What are the strengths of the π bonds? Kutzelnigg[10] has already addressed this latter question but obtained in many instances results that differ strikingly from the present results.

The present paper limits itself to all possible simple (i.e., hydrogen ligated) single- and double-bonded compounds formed from any two of the atoms C, N, O, Si, P, and S. (The peroxide analogues are not considered, as their corresponding doubly-bound compounds are diatomic triplets). The π bond strengths in these compounds are estimated in two ways: from calculated rotation barriers and from heats of hydrogenation. The computed bond lengths for the singly- and doubly-bonded compounds are reported. Finally, the stretching frequencies of the multiple bonds are estimated. In as many instances as possible, the computed properties are tested by comparison to experimental quantities, especially for the experimentally better characterized second period bonds.

The present work is an extension of three of our earlier papers. Our study of the Si=C bond[25] has been repeated with the inclusion of d orbitals, which improve the computed geometries, without changing our estimate of the π bond strength. The rotation about the Si=N bond[26] is reconsidered, with a second saddle point located. Key results of our recent paper[27] on the —N=N—, —P=N—, and —P=P— bonds are included here for completeness.

The paper is organized as follows. After some exposition of the computational approach, general trends in bond lengths and vibrational frequencies are discussed. Then, the rotational barriers and corresponding π bond strengths are considered. Next, hydrogenation energies are used to provide a second means of determining π bond strengths. Finally, we present a set of recommended π bond strengths and discuss the ability of the six atoms C, N, O, Si, P, and S to participate in strong π bonds.

Computational Methods

Reliable structures may be obtained with relatively small basis sets at the restricted SCF level of computation for closed shell molecules. However, even ordinary single bond distances involving third period elements such as phosphorus are normally computed to be too long, unless the basis set contains d orbitals.[27] In addition, split valence basis sets without d orbitals are well known to give in many instances incorrect bond angles around nitrogen atoms. Therefore, as will be detailed below, our computed structures are obtained by using d orbitals located on all second and third period atoms. Once the geometries of the molecules are known, complete force constant matrices and vibrational frequencies are computed at the SCF level.

Although meaningful results for structures and frequencies of closed shell molecules can be obtained at the SCF level with small bases, the accurate computation of energy differences normally requires both larger bases and the inclusion of electron correlation effects. The energy differences for the hydrogenation reactions

$$H_mA{=}BH_n + H_2 \rightarrow H_{m+1}A{-}BH_{n+1}$$

are computed at the full (including triples) fourth order of Møller–Plesset perturbation theory (MP4),[28] by using an extended basis set detailed below.

The most challenging computational problem presented by π-bonded compounds is the treatment of their 90° twisted singlet biradicals. These biradicals represent the rotational barrier for cis–trans isomerization and must be treated at the MCSCF level. We have previously found[25,27] that a satisfactory treatment of these biradicals may be obtained by a four-electron, four-orbital full optimized reaction space (FORS)[29] MCSCF calculation. This wave function contains all electron configurations obtained from distributing the four A=B bonding electrons in the σ, π, π*, and σ* orbitals in all possible ways. This relatively simple MCSCF wave function contains at most 20 configurations. Dynamical correlation effects not included in the MCSCF wave function are incorporated by means of second-order CI calculations (SOCI) wherein all single and double excitations from the MCSCF active orbital space as well as the labile lone pair orbitals on A or B (if any) into the MCSCF virtual orbital space are permitted. These SOCI calculations typically involve 20 000–80 000 configurations.

Three atomic basis sets were employed in this work. The small 3-21G basis[30] supplemented by d functions on all non-hydrogen atoms was used for all geometry optimizations and force field calculations. Single-point calculations at the MCSCF and SOCI level were performed with the 6-31G basis,[31] again supplemented by d functions. These first two bases will be referred to as 3-21G(d) and 6-31G(d) in this paper. Finally, single point MP4 calculations were carried out with an extended basis that will be denoted EXT in this paper. This basis consists of the 6-311G basis[32] for H and second period elements and the McLean–Chandler (12s,9p)/[6s,5p] basis[33] for third period atoms. The EXT basis also includes a set of p functions (exponent 1.0[34]) on hydrogens as well as the d functions on the heavy atoms.[35] The same d polarization exponents are used for all three bases, namely second period:[34] N, 0.75; C, 0.80; O, 0.85; third period:[31a] Si, 0.45; P, 0.55; S, 0.65. The 3s contaminant resulting from the use

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Table III. Bond Lengths[a,r]

bond	exp[s]	SCF	bond	exp	SCF	MCSCF
H_3C-CH_3	1.534[b]	1.534	$H_2C=CH_2$	1.339	1.315	1.353
H_3Si-CH_3	1.869	1.889	$H_2Si=CH_2$	*1.702[l]	1.695	1.743
$H_3Si-SiH_3$	2.327	2.342	$H_2Si=SiH_2$	*2.160[m]	2.116	2.217
H_2N-NH_2	1.447	1.426	HN=NH	1.252	1.216	1.269
H_2P-NH_2	*1.71[c]	1.701	HP=NH	*1.544[n]	1.556	1.619
H_2P-PH_2	2.219	2.205	HP=PH	*2.01[o]	1.994	2.068
H_3C-NH_2	1.471	1.460	$H_2C=NH$	1.273	1.248	1.289
H_3Si-NH_2	*1.725[d]	1.721	$H_2Si=NH$	*1.568[p]	1.572	1.624
H_3C-PH_2	1.863[e]	1.858	$H_2C=PH$	1.671[q]	1.650	1.700
H_3Si-PH_2	2.25[f]	2.256	$H_2Si=PH$		2.050	2.106
H_3C-OH	1.421	1.404	$H_2C=O$	1.208	1.181	
H_3Si-OH	*1.634[g]	1.636	$H_2Si=O$		1.494	
H_3C-SH	1.819	1.815	$H_2C=S$	1.611	1.593	
H_3Si-SH	*2.136[h]	2.139	$H_2Si=S$		1.927	
H_2N-OH	1.453	1.413	HN=O	1.212	1.175	
H_2P-OH	*1.65[i]	1.637	HP=O	1.512	1.459	
H_2N-SH	1.719[j]	1.709	HN=S		1.541	
H_2P-SH	*2.11[k]	2.119	HP=S		1.903	

[a] Experimental bond lengths are from ref 41, unless otherwise noted. Computed bond lengths were obtained with the 3-21G(d) basis. [b] Reference 42. [c] In bis(diphenylphosphino)isopropylamine, ref 43. [d] In disilazane, ref 44. [e] Reference 45. [f] Reference 46. [g] In disiloxane, ref 47. [h] In disilathiane, ref 48. [i] In P_4O_6, ref 49. [j] Reference 50. [k] In P_4S_4, ref 51. [l] In a bulkily substituted compound, ref 52. [m] In tetramesityldisilene, ref 53. [n] In a bulkily substituted compound, ref 54. [o] Average of several bulkily substituted molecules, ref 16. [p] In di(*tert*-butyl), tri(*tert*-butyl)silylsilanimine, ref 55. [q] Reference 56. [r] In Å. [s] An asterisk (*) designates a bond length taken from a substituted compound.

of six Cartesian d functions was retained in all calculations. It is frequently convenient to summarize the computational *ansatz* and basis set together; e.g., MP4/EXT//SCF/3-21G(d), where // means a MP4/EXT single-point energy calculation was performed at a geometry obtained at the SCF/3-21G(d) level.

Two programs were used for these calculations. GAUSSIAN82[37] was used for SCF level geometry optimizations. SCF level force field calculations were also performed with this program, with use of analytical energy second derivatives.[38] This program was also used for the MP4 calculations. All MCSCF and SOCI calculations were done with the North Dakota State University version of the GAMESS program.[39] MCSCF level force fields were computed by finite differencing of analytic energy first derivatives. The geometry optimization and transition state location procedure in both programs is the gradient method of Schlegel.[40]

Structures. The computed 3-21G(d) A—B and A=B bond lengths in the saturated $H_{m+1}A-BH_{n+1}$ compounds and the corresponding doubly bound $H_mA=BH_n$ molecules are shown in Table III. This table also contains experimental bond lengths[41-56] for most of the compounds. In several cases, the bond lengths of the parent (all hydrogen) compounds are not known. In these cases, if the actual ligands are not too strongly perturbing (i.e., fluorine or other very nonelectroneutral substituents are not

Table IV. Stretching Frequencies[a,w]

bond	exp[x]	SCF	bond	exp	SCF
H_3C-CH_3	995	1046	$H_2C=CH_2$	1623	1853
H_3Si-CH_3	700	736	$H_2Si=CH_2$	985[n]	1080
$H_3Si-SiH_3$	432[b]	466	$H_2Si=SiH_2$	*630[o]	653
H_2N-NH_2	1087[c]	1230	HN=NH	1529[p]	1882
H_2P-NH_2		910	HP=NH		1245
H_2P-PH_2	428[d]	480	HP=PH	*610[q]	715
H_3C-NH_2	1044	1133	$H_2C=NH$	1638[r]	1898
H_3Si-NH_2	*671[e]	907	$H_2Si=NH$		1260
H_3C-PH_2	676[f]	747	$H_2C=PH$		1109
H_3Si-PH_2	454[g]	485	$H_2Si=PH$		673
H_3C-OH	1033	1186	$H_2C=O$	1746	2033
H_3Si-OH	859[h]	951	$H_2Si=O$	1202[h]	1394
H_3C-SH	710[i]	778	$H_2C=S$	1059[s]	1196
H_3Si-SH	*501[j]	545	$H_2Si=S$		787
H_2N-OH	895[k]	1147	HN=O	1565[t]	1929
H_2P-OH	797[l]	935	HP=O	1188[u]	1409
H_2N-SH		751	HN=S		1245
H_2P-SH	477[m]	522	HP=S	*716[v]	791

[a] Unless otherwise noted, experimental values are taken from ref 57. Computed values were obtained with the 3-21G(d) basis set. [b] Reference 58. [c] Reference 59. [d] Reference 60. [e] In the pentamethyl derivative, ref 61. [f] Reference 62. [g] Reference 63. [h] Reference 64. [i] Reference 65. [j] Average of the symmetrical (487) and asymmetrical (516) stretches in disilathiane, ref 66. [k] Reference 67. [l] Reference 68. [m] Reference 69. [n] Reference 70. [o] In tetramethyldisilene, ref 71. See also page 436 of ref 19. [p] Reference 72. [q] In bis(tri-*tert*-butylphenyl)-diphosphene, ref 16. [r] Reference 73. [s] Reference 74. [t] Reference 75. [u] Reference 76. [v] In ClP=S, ref 77. [w] In cm^{-1}. [x] An asterisk (*) designates a bond length taken from a substituted compound.

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considered), the experimental value is included but is marked with an asterisk (*). These values are offered for comparison only and are not included in the analysis described in the next two paragraphs.

There are 12 molecules in Table III for which the computed singly bonded compounds may be directly compared to experiment. The error (exp–SCF) in the bond lengths ranges from −0.02 to 0.02 Å, with the SCF bond lengths being (as usual) generally too small. It is interesting to note that those cases for which the SCF bond lengths are too long always involve silicon. The average absolute error is 0.015 Å, about normal for this level of theory.

In Table III, there are eight cases for which the computed doubly-bonded distances can be compared directly to experiment. Here the error (exp–SCF) varies from 0.02 to 0.05 Å. The average error is 0.03 Å, slightly larger than that for the singly-bound distances. A quick glance at the table shows many of the doubly bound distances are unknown experimentally. A very good estimate of these bond distances can be obtained by subtracting 0.03 from the SCF values.

The MCSCF bond lengths shown for some of the doubly-bonded compounds are all slightly longer than experiment. This is due to the mixing of some antibonding character into the bond description. The remaining SCF and MCSCF structural parameters are available on request.

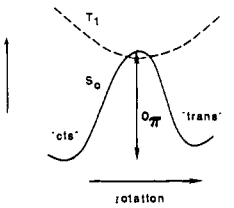
Frequencies. The experimental[57-77] and computed vibrational stretching frequencies are compared in Table IV. Once again, an asterisk (*) marks those frequencies taken from a substituted compound. It should be noted that substituents affect frequencies not only through their electronic differences from hydrogen but also through their masses. For example, the C=O stretch[57] in H_2C=O is 1746, in D_2C=O is 1700, and in F_2C=O is 1928 cm^{-1}. Thus, the values labeled with an asterisk (*) are shown only for rough comparison and are not considered in the discussion in the following paragraphs.

There are 14 singly-bonded compounds in Table IV that afford direct comparison to experiment. Normally SCF frequencies are expected to be too high, by about 10%. The multiplicative factor needed to bring the SCF values for 13 of these molecules into agreement with experiment ranges from 0.85 to 0.95, with an average value of 0.91. The molecule H_2NOH is not included in the above, since the SCF value must be scaled by 0.78 to produce agreement with experiment. The SCF calculations seemingly fail to correctly reproduce the coupling between the NO stretching and NH_2 rocking motions.

A direct comparison with experimental frequencies is possible for nine doubly-bound compounds. Here the multiplicative factor needed to bring SCF frequencies into agreement with experiment ranges from 0.81 to 0.91, with an average of 0.86. The average scale factor is smaller than for the singly-bound compounds, because there are now two bonds whose force constant is being overestimated by the SCF wave functions. A reasonably accurate estimate of those experimental double bond stretching frequencies which are currently unavailable may be obtained by multiplying the SCF values in Table IV by 0.86. The remaining SCF frequencies and force constants are available from the authors.

Torsional Barriers. Perhaps the cleanest definition of a π bond strength is obtained from the cis → trans isomerization activation energy. When a doubly-bonded H_mA=BH_n molecule is rotated by 90° to the biradical transition state for isomerization, the A–B π bond is broken, but the A–B, A–H, and B–H σ bonds remain unbroken. Thus, the rotational barrier on the S_0 ground-state surface can be taken as our definition of D_π.

Rotation away from planarity raises the π and lowers the π^* orbitals in energy. Therefore, rotation by 90° on the ground (π^2) state singlet (S_0) surface requires an input of energy as the π bond breaks. However, rotation by 90° stabilizes the triplet $\pi \rightarrow \pi^*$ state (T_1) (since in a planar geometry the π^* orbital is more antibonding than the π orbital is bonding). Qualitatively, the lowest singlet and triplet rotational potential energy surfaces may be represented schematically as follows



If the molecule has lone pairs at either A or B (e.g., HN=NH or H_2C=NH), the lowest vertical triplet state may actually be better described as $n \rightarrow \pi^*$. However, at their rotational minima, the singly occupied orbitals on atom A or B will consist principally or entirely of a valence p orbital. Thus, the relaxed triplet has a biradical electronic structure identical with that of the twisted singlet, apart from the spin coupling of the unpaired electrons. Therefore, Hund's rule would predict that the triplet will lie below the rotated singlet, as shown above. The only exception we find to this is the C=C bond, which will be discussed below.

As described above, theoretical treatment of the rotated species requires a MCSCF wave function correlating the A=B σ and π bonds with their antibonding counterparts. By using this wave function, we have found the structures of the planar compounds and the 90° rotated singlets and triplets. The A=B bond lengths of the planar compounds were already presented in Table III. The singlet transition state structures and equilibrium triplet structures are shown together in Figure 1. In general, these two structures are nearly identical, as one commonly expects for molecules possessing the same electronic configuration. Nonetheless, we stress that while the 90° twisted triplets are at their equilibrium geometries, the very similar rotated singlets are actually at the transition states for cis–trans isomerization on the ground singlet surface.

There are two directions in which one can rotate a double bond. In some cases, as for the C=C and Si=C bonds, the two directions lead to equivalent transition states. For these, therefore, only one

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Table V

molecule	ZPE MCSCF 3-21G(d)	total energies MCSCF 3-21G(d)	MCSCF 6-31G(d)	SOCI 6-31G(d)
		$H_2C{=}CH_2$		
pl	0.0531	−77.718 42	−78.086 10	−78.120 13
rot.	0.0463	−77.607 18	−77.975 71	−78.009 09
trip.	0.0470	−77.604 90	−77.973 49	−78.008 92
		$H_2Si{=}CH_2$		
pl	0.0419	−327.468 15	−329.087 23	−329.118 14
rot.	0.0397	−327.409 58	−329.028 35	−329.059 13
trip.	0.0405	−327.412 20	−329.030 89	−329.062 28
		$H_2Si{=}SiH_2$		
pl	0.0333	−577.242 90	−580.116 00	−580.146 30
rot.	0.0323	−577.203 25	−580.077 84	−580.105 34
trip.	0.0329	−577.206 79	−580.081 38	−580.109 71
		HN=NH		
trans pl	0.0295	−109.541 25	−110.072 80	−110.211 65
rot.	0.0239	−109.432 41	−109.961 20	−110.110 39
trip.	0.0260	−109.439 67	−109.969 44	
		HP=NH		
trans pl	0.0238	−394.450 50	−396.344 92	
rot.	0.0198	−394.371 18	−396.265 51	
trip.	0.0213	−394.375 77	−396.266 71	
		HP=PH		
trans pl	0.0192	−679.356 64	−682.617 04	−682.718 36
rot.	0.0161	−679.300 16	−682.562 50	−682.661 03
trip.	0.0171	−679.301 35	−682.563 52	−682.664 93
		$H_2C{=}NH$		
pl	0.0417	−93.641 87	−94.092 62	−94.167 39
rot. plow	0.0358	−93.520 28	−93.970 71	−94.060 57
trip. plow	0.0377	−93.523 71	−93.973 40	−94.066 69
rot. tent	0.0355	−93.519 04	−93.969 37	−94.058 35
trip. tent	0.0373	−93.522 09	−93.972 30	−94.064 40
		$H_2Si{=}NH$		
pl	0.0310	−343.408 61	−345.109 05	−345.179 96
rot. plow	0.0286	−343.334 65	−345.034 80	−345.119 39
trip. plow	0.0294	−343.340 57	−345.040 10	−345.123 35
rot. tent	0.0282	−343.334 13	−345.034 09	−345.119 13
trip. tent	0.0291	−343.338 03	−345.037 66	−345.123 48
		$H_2C{=}PH$		
pl	0.0353	−378.528 43	−380.340 98	−380.405 99
rot.	0.0309	−378.452 00	−380.265 44	−380.332 93
trip.	0.0320	−378.452 49	−380.265 82	−380.335 48
		$H_2Si{=}PH$		
pl	0.0261	−628.306 45	−631.372 43	−631.434 53
rot. plow	0.0246	−628.255 00	−631.323 11	−631.387 26
trip. plow	0.0251	−628.257 79	−631.325 81	−631.390 94
rot. tent	0.0244	−628.254 53	−631.322 71	−631.385 43
trip. tent	0.0251	−628.257 05	−631.325 06	−631.388 87

molecule	relative enthalpies MCSCF 3-21G(d)	MCSCF 6-31G(d)	SOCI 6-31G(d)
	$H_2C{=}CH_2$		
pl	0.0	0.0	0.0
rot.	65.5	65.0	65.4
trip.	67.4	66.8	66.0
	$H_2Si{=}CH_2$		
pl	0.0	0.0	0.0
rot.	35.4	35.6	35.6
trip.	34.2	34.5	34.2
	$H_2Si{=}SiH_2$		
pl	0.0	0.0	0.0
rot.	24.3	23.3	25.1
trip.	22.4	21.5	22.7
	HN=NH		
trans pl	0.0	0.0	0.0
rot.	64.8	66.5	60.0
trip.	61.5	62.7	58[b]
	HP=NH		
trans pl	0.0	0.0	0.0
rot.	47.3	47.3	44[b]
trip.	45.3	47.5	42[b]
	HP=PH		
trans pl	0.0	0.0	0.0
rot.	33.5	32.3	34.0
trip.	33.4	32.3	32.2
	$H_2C{=}NH$		
pl	0.0	0.0	0.0
rot. plow	72.6	72.8	63.3
trip. plow	71.6	72.3	60.7
rot. tent	73.2	73.5	64.5
trip. tent	72.4	72.7	61.9
	$H_2Si{=}NH$		
pl	0.0	0.0	0.0
rot. plow	44.9	45.1	36.5
trip. plow	41.7	42.3	34.5
rot. tent	45.0	45.3	36.4
trip. tent	43.1	43.6	34.2
	$H_2C{=}PH$		
pl	0.0	0.0	0.0
rot.	45.2	44.6	43.1
trip.	45.6	45.1	42.2
	$H_2Si{=}PH$		
pl	0.0	0.0	0.0
rot. plow	31.3	30.0	28.7
trip. plow	29.9	28.6	26.7
rot. tent	31.5	30.1	29.7
trip. tent	30.4	29.1	28.0

[a] Harmonic zero-point energy and total energies in hartrees. Relative enthalpies are in kcal/mol. All energies are calculated at MCSCF/3-21G(d) geometries. [b] Estimated as described in ref 27.

transition structure is shown in Figure 1. However, factors such as the customary pyramidalization of silyl radicals (the SiH_3 radical is bent) or the introduction of asymmetry into the normally flat CH_3 group (see Figure 1G) can cause the occurrence of two different transition states. Both such structures are given in Figure 1. The energies of the "plow" or s-trans forms are usually within about 1 kcal/mol of the "tent" or s-cis transition states. These energies are sufficiently close so that both transition states will be important in cis–trans isomerization kinetics.

Because the cis and trans structures may have different energies and because there may be two rotational transition states, we must be more specific about our definition of D_π. We choose as our definition the activation energy required to rotate from the more stable of the cis and trans isomers through the lower energy saddle point.

The total energies and harmonic zero-point energies of the planar singlets, twisted singlets, and twisted triplets are given in Table V. The vibrational analyses show the triplet structures given in Figure 1 are energy minima (all frequencies are real), while the twisted singlet structures are all transition states. The unique imaginary frequencies associated with torsional reversion to the planar singlets are included in Figure 1. The rotational barriers and singlet–triplet splittings as a function of both basis set and calculational method are also shown in Table V. These adiabatic energy differences ($\Delta H°(0\ K)$) are obtained from the total energies after correction for zero-point motion. In general, inclusion of the zero-point energy reduces the classical rotation barriers by 1–2 kcal/mol.

The computed barriers to rotation shown in Table V are remarkably constant with respect to improvements in the basis set and in the sophistication of the electron correlation treatment. For example, the rotation barrier for the C=C bond is 65.5 kcal/mol at the MCSCF/3-21G(d) level, 65.0 at MCSCF/6-31G(d), and 65.4 in the best calculation, SOCI/6-31G(d). Except

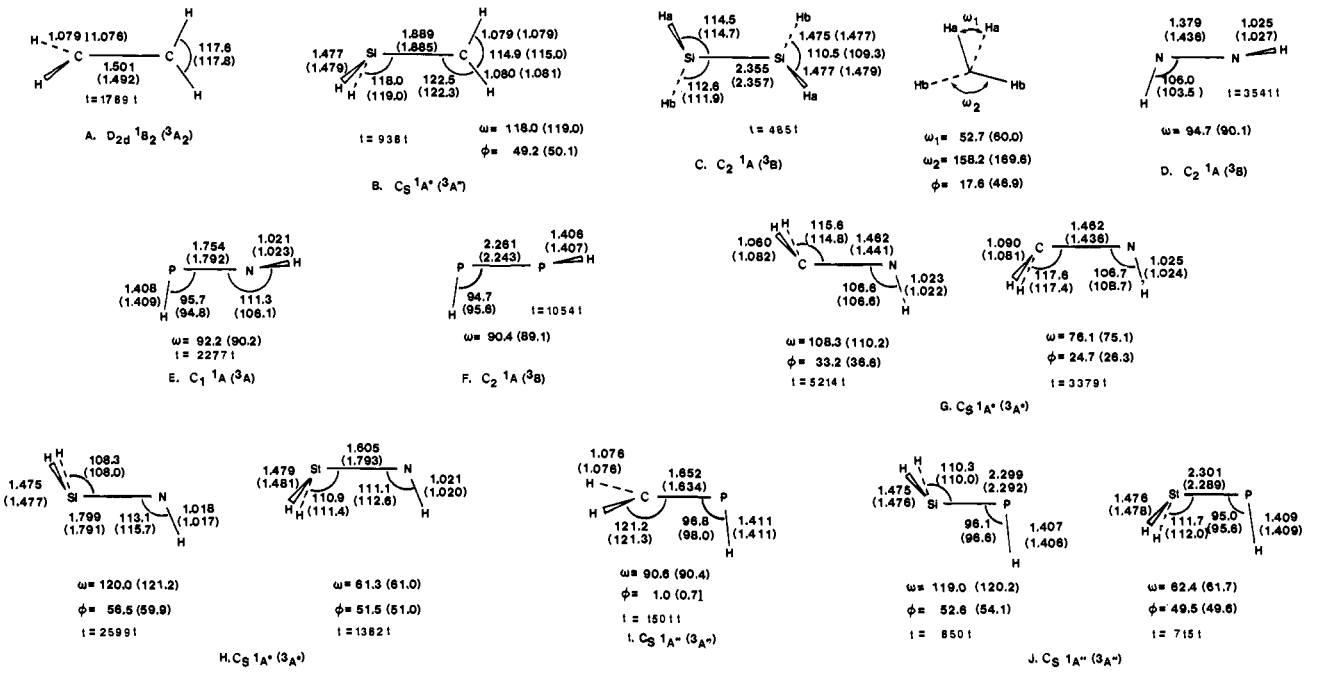

Figure 1. MCSCF/3-21G(d) transition states for π bond rotation, with triplet equilibrium structures in parentheses. Bond distances in Å, angles in deg. ω is the dihedral angle HABH, and ϕ is the flap angle between bond AB and plane BH_2 at pyramidal atom B. The imaginary frequency for rotation of the singlet structures toward planarity is given by i, in cm^{-1}. Point group symmetry and electronic states are also shown.

for the molecules containing nitrogen lone pairs, all the computed rotational barriers display much the same insensitivity to improvements in the calculational procedure. (SOCI calculations for nitrogenous molecules which do not allow N lone pair excitations to occur are also very little changed from the corresponding MCSCF result,[27] thus these nitrogen lone pairs clearly play an important role). For this reason, only the highest level results from SOCI/6-31G(d) calculations will be discussed below.

In the following paragraphs we discuss π bond rotation for the specific molecules. The references given cannot be inclusive and so focus on more recent work, especially those papers concerned primarily with some aspect of the π bonding.

C=C. The best characterized π bond, both experimentally and theoretically, is unquestionably that in ethene. The effect of torsional motion on the ground and excited states of this molecule have been considered by Walsh[78] and Merer and Mulliken.[79] The latter paper reviews experimental data as of 1969 and in a figure shows the triplet T state lying below the rotational maximum in the singlet ground state (which is customarily called the N state). The latter is done in accord with Hund's rules but is unsupported by experimental evidence. The 0-0 transition to the T state is too weak to appear in this state's weak absorption spectrum. To the authors' present knowledge, the correct order of these states is experimentally unknown.

In the last 10 years, a number of theoretical papers have indicated that the T and rotated N states represent a violation of Hund's rules, in that the singlet lies below the triplet. A detailed discussion of this point has appeared recently, in terms of "antiferromagnetic coupling".[80] This apparent violation was first discussed in the literature in terms of "dynamic spin polarization".[81] Fortunately, a simple explanation is possible. Calculations in which only the two π electrons are correlated (two configuration SCF) predict the triplet to lie below the singlet.[82] Thus the two unpaired π electrons behave in accordance with Hund's rule. The reverse state order, that is the violation of Hund's rule, is predicted by almost any calculation that correlates the motion of the CC σ bonding electrons. Thus single excitation CI,[81] more extensive multireference CI,[83] singlet UHF,[84] four electrons in four orbitals MCSCF,[85] and GVB treatments[80] all predict the least energy rotation path on the singlet N state potential energy surface to lie entirely below the T surface. The derivation of Hund's rule assumes that the doubly-occupied orbitals common to both states have the same energy. This is not true for the CC σ bond.

The present work also finds that the N surface lies entirely below the T surface. However, in the most refined calculation (SOCI/6-31G(d)) the separation between these states is very small, only 0.6 kcal/mol. *The C=C bond is the only case found in the present work in which Hund's rule is violated.* More typically, the triplet structures lie 1-3 kcal/mol below the rotational maxima on the singlet surface.

The experimental activation energy for cis-trans isomerization in ethene is 65 kcal/mol.[86] The isomerization of 2-butene also requires 65 kcal/mol.[87] Our best computed result is 65.4 kcal/mol. Thus, the computed barrier agrees very well with experiment.

Si=C. The parent silene $H_2Si{=}CH_2$ was the subject of our recent paper,[25] so the present results will be only briefly discussed here. Our previous paper presented the entire reaction path for rotational isomerization, illustrating the pyramidalization which occurs at silicon. The present results differ mainly in that the use of d functions on the Si and C atoms results in shorter, more reasonable SiC bond lengths. The present result for the adiabatic rotational barrier, 35.6 kcal/mol, is nearly unchanged from our previous result of 35.4.

Dobbs and Hehre[88] have recently considered the π bond strengths in the ethene analogues, $H_2C{=}XH_2$, and have obtained the following theoretical π bond strengths: for X equal to C, 64-68; Si, 35-36; Ge, 31; Sn, 19 kcal/mol.

Si=Si. Disilenes have been the subject of much interest since their isolation in 1981. Unlike the planar silenes, disilenes may

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be planar or puckered at Si, according to the substituents.[19] Perhaps the most comprehensive calculations on disilene (with comparison to silene and ethene) have been performed by Kohler and Lishka.[89] These workers find that the parent compound is slightly nonplanar. However, this conclusion depends on the basis set and level of electron correlation.[19] In the present work, SCF/3-21G(d) calculations predict a planar disilene but with an out-of-plane bending frequency (b_{2g}) of just 84 cm^{-1}. When some π^* antibonding is mixed in, as in the present MCSCF/3-21G(d) calculations, the molecule distorts into a trans bent configuration. The MCSCF/3-21G(d) flap angle between the H_2Si planes and the Si=Si bond is 34.7°. However, the energy required to planarize the molecule at this level of calculation is only 1.7 kcal/mol. Disilenes are simply quite floppy molecules with respect to this bending away from planarity.

One calculation of the Si=Si π bond strength has been carried out. In that work[90] the triplet equilibrium structure[89] was used as an approximation to the singlet rotational transition state. As shown in Figure 1C, the geometry of rotated disilene actually differs markedly from that of the triplet. In fact, this is the only case in Figure 1 where there is a significant geometric difference between the rotated transition states and the equilibrium triplet structures. The primary difference is that the Si atom is less pyramidal in the singlet state, which engenders changes in dihedral angles as well. In fact, the rotated singlet has a smaller flap angle than in the π-bonded "planar" form! However, there is very little change in energy associated with this change in pyramidalization. The energy of the singlet state at the triplet structure is only 0.3 kcal/mol less than at the exact transition state.

There should exist a second transition state for rotation, with one of the SiH_2 groups pyramidalized in the opposite direction. We have not attempted to locate this low symmetry, alternate saddle point.

The SOCI/6-31G(d) barrier to rotation is found to be 22.7 kcal/mol. This result is similar to the previous multireference CI calculations[90] described above, which predicted a barrier to twisting of 22 ± 2 kcal/mol. The same paper[90] contains a 26 ± 5 kcal/mol estimate of the experimental cis–trans isomerization barrier in a substituted disilene.

N=N, P=N, and P=P. The rotation about these group 15 double bonds was the subject of our recent paper,[27] which also considered nonclassical structures such as H_2P=P. The results are unchanged from that work, except that vibrational contributions to the enthalpies are now included. The results are reproduced here for the sake of completeness. The SOCI/6-31G(d) rotational barriers for HN=NH, HP=NH, and HP=PH are 60, 44, and 34 kcal/mol.

C=N. The cis–trans isomerization in methanimine H_2C=NH can proceed by the low-energy route of inversion at N or rotation about the double bond. The higher energy rotational route is the one considered here, because of its connection to π bond energies. Bonačič-Koutecký and Michl (BM)[91] have recently presented detailed potential energy surface (PES) maps for both types of motion on the S_0, S_1, and T_1 surfaces. The calculations employ multireference CI wave functions based on triplet state orbitals by using principally the 4-31G basis. Perhaps the most surprising result obtained by BM is that the PES maps show no transition state for rotation about the double bond. Instead, such rotated structures are found to be unstable with respect to linearization at nitrogen. That is, rotated structures collapse through a conical surface intersection toward the inversion transition state (see Figure 4 of BM).

The present results differ qualitatively. Two MCSCF/3-21G(d) transition states for rotation were located quite easily, at just the geometries one would expect (see Figure 1G). These structures are minimum energy structures under the constraint of C_s symmetry. The CN distances in these transition states are about 1.46 Å, quite typical of single CN bonds (see Table III). The HNC angles are also quite ordinary. Because the NH group disturbs the ordinarily planar carbon radical center, both "plow"- and "tent"-shaped transition states are found. These have very similar energies, with the SOCI/6-31G(d) barrier to rotation through the "plow" form being 63.3 kcal/mol and with rotation through the "tent" form requiring just 1.2 kcal/mol more.

Our "plow" $^1A''$ biradical transition structure lies below the $^1A'$ zwitterionic state (C positive, N negative), at the $^1A''$ geometry. MCSCF/6-31G(d) optimization of the closed shell state leaves it 0.70 eV above the open shell transition state. This means that the minimum of the $^1A''$ state occurs before the conical intersection, rather than after it as in Figure 4 of BM. (We have not located this intersection point in our work, but it unquestionably exists. This intersection divides the biradical rotation barrier from the closed shell inversion barrier. Similar surface intersections must also exist in all the group 15 containing molecules, such as HN=NH.) The PES maps in BM were obtained by using a CN distance of 1.37, apparently a compromise between single and double bond distances (1.27 Å in the present work). BM also did not allow for pyramidalization at the carbon. Thus the difference between the present results and those of BM is due to the complete optimization of the rotational transition state geometry in the present work. The geometric compromises made by BM were necessary to permit their consideration of the global topology of the S_0, S_1, and T_1 surfaces. The present results focus on only a single portion of the molecular PES and complement, rather than detract from, the pioneering work of BM on the full PES maps.

Comparison with experiment is apparently not possible. The thermal cis–trans isomerization is believed to proceed by inversion at N rather than rotation, and the photochemical $n \rightarrow \pi^*$ cis–trans isomerization studies extant have not yet yielded any energetic estimates.[92]

Si=N. The parent silanimine H_2Si=NH was the study of a recent paper from this group.[26] This paper considered rotation and inversion in silanimine as well as the more stable aminosilylene isomer. The present investigation of rotation about the π bond differs in adopting the uniform d exponent used here, in locating the slightly higher energy "plow" transition state, and in including vibrational contributions to the enthalpy differences. The present SOCI/6-31G(d) rotation barrier through the "plow" structure shown in Figure 1H is 36.5 kcal/mol. Rotation through the "tent" transition state requires 0.1 kcal/mol less. Both transition structures are quite pyramidal at silicon.

Unfortunately, while silanimines have been known since 1974, they are not yet well characterized experimentally.[19] Stable silanimines were isolated in 1986,[55,93] and the Si=N bond length was determined.[55] No stretching frequency or π bond strength is available for comparison to our results,

By analogy to H_2C=NH, one would expect inversion at nitrogen in H_2Si=NH to be a lower energy alternative for cis–trans isomerization than rotation about the double bond. This is in fact true, as two studies[26,94] have shown the barrier to inversion through a linear nitrogen is 6 kcal/mol. Note that standard 3-21G* calculations which employ d orbitals only at silicon erroneously predict a linear geometry at nitrogen for silanimine.[95] The 6-31G* basis employing d orbitals at both heavy atoms gives a structure with a bent geometry at N.[94] This corresponds closely to our present SCF/3-21G(d) result, which has a HNSi angle of 127.3°.

That d orbitals are a *sine qua non* for correct prediction of geometries around N is one of the primary reasons the 3-21G(d) basis used here for structure determinations includes d orbitals on second period atoms. For example, they have been shown to

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be vital in predicting a nonplanar nitrogen in the singly bound H_3Si-NH_2.[96,97]

C=P. The rotation about the double bond in the parent methylenephosphine ($H_2C=PH$) differs from that in its analogue methanimine in that there is only one rotational transition state. As shown in Figure 1I, the carbon atom puckers by only 1°. This is presumably due to the much longer CP bond having removed the distorting influence of the PH bond. Our SOCI/6-31G(d) rotational barrier is 43.1 kcal/mol. No comparison of this value with experiment is possible.

Si=P. The final double bond for which rotational motion can be explored is silaphosphene ($H_2Si=PH$). These compounds have been detected in solution, but very little is known about them.[19] As a result, most of what is known is based on a theoretical study in our group of single, double, and triple SiP bonding.[98] That study, however, did not include an examination of rotation in silaphosphene. As shown in Figure 1J, we have found two transition states for rotation, with strongly pyramidalized silicon. The SOCI/6-31G(d) rotation through the "plow" intermediate requires 28.7 kcal/mol, with an additional 1.0 kcal/mol required to isomerize via the "tent" transition state.

Since the inversion barrier at phosphorus in HP=PH is 72 kcal/mol,[27] it is unlikely that inversion is an energetically favorable alternative to rotation in either $H_2C=PH$ or $H_2Si=PH$.

Hydrogenation Reactions. There are two possible objections to the use of the rotation barrier about the $H_mA=BH_n$ σ bond as the definition of the π bond strength. First, the A–B σ bond does lengthen during the isomerization. There may also be some pyramidalization of the hydrogens in the AH_m or BH_n moieties, with accompanying rehybridization in the σ bonds. Thus, the isomerization energetics involve more than simply D_π. Secondly, and perhaps more importantly, the definition does not apply to the bonds involving =O or =S, as without attached hydrogens, these molecules have no "handles" to "turn".

An alternative method is the use of hydrogenation thermochemical cycles. The energy required to dehydrogenate a singly-bound compound to produce a double bond can be used to estimate the strength of that double bond, by the following thermochemical cycle:

$$H_{m+1}A\text{-}BH_{n+1} \rightarrow H_mA\text{-}BH_{n+1} + H \qquad D(A\text{-}H)$$

$$H_mA\text{-}BH_{n+1} \rightarrow H_mA\text{-}BH_n + H \qquad D(B\text{-}H)$$

$$H_mA\text{-}BH_n \rightarrow H_mA=BH_n \qquad -D_\pi$$

$$2H \rightarrow H_2 \qquad -D(H\text{-}H)$$

$$H_{m+1}A\text{-}BH_{n+1} \rightarrow H_mA=BH_n + H_2 \qquad \Delta H°\ (0\ K)$$

Provided that the overall heat of the dehydrogenation reaction and the other bond dissociation enthalpies are known, the π bond strength is obtained as

$$D_\pi = D(A\text{-}H) + D(B\text{-}H) - \Delta H°\ (0\ K) - D(H\text{-}H) \quad (1)$$

D(H–H) is 103.3 kcal/mol.[7] It is impossible to measure the energy change for the second sequential removal of a hydrogen atom from the single bond to produce the fictitious A–B biradical. Therefore, we choose for both D(A–H) and D(B–H) the energy required to remove this hydrogen from the original singly-bound compound, to produce either an A- or B-centered radical. Ideally, we would prefer to learn D(A–H) and D(B–H) from the compound in question, as these values change slightly from molecule to molecule. Unfortunately, only some of these energies are known, so that in other molecules one is forced to estimate them. The origin of the D(A–H) values used here is described in the Appendix.

If experimental values for $\Delta H°$ (0 K) are available, D_π can be obtained entirely from experimental bond energies. However, the difficulty in isolating many of the parent doubly-bound compounds means that no thermochemical information is available for them. However, computed values for $\Delta H°$ can be employed in this cycle, combined with experimental values for D(A–H) and D(B–H). This is the approach taken here.

Calculations at the MP4/EXT level on the monohydrides AH_m show that even this rather accurate level of calculation has sizeable errors in the bond dissociation energetics of saturated hydrides

$$AH_m \rightarrow \dot{A}H_{m-1} + H$$

The MP4/EXT errors ϵ(A–H) (defined as the experimental minus theoretical enthalpy change for the above reaction) found[99] for these AH bond strengths for various A's are H, 4; second period, C, 3; N, 6; O, 8; F, 9.5; third period, Si, 3; P, 5; S, 5; and Cl, 6 kcal/mol. Because these errors are fairly sizeable, we prefer to use experimental rather than theoretical D(A–H) and D(B–H) values for $H_{m+1}A\text{-}BH_{n+1}$ compounds in the above thermochemical cycle.

Since experimental values for $\Delta H°$ (0 K) are available for only five of the π bonds, theoretical values must be employed. At first glance, one expects theory to do much better at the computation of $\Delta H°$ (0 K) than D(A–H), since the number of electron pairs is unchanged in this reaction. Unfortunately, the MP4/EXT values are still subject to appreciable error in some of the five cases. These errors may be directly attributed to the computed errors in the homolytic bond cleavages just discussed. The MP4/EXT error can be written as the sum of the errors in the above thermochemical cycle

$$\epsilon(\Delta H°\ (0\ K)) = \epsilon(A\text{-}H) + \epsilon(B\text{-}H) - \epsilon(H\text{-}H) - \epsilon(\pi) \quad (2)$$

where ϵ is always the enthalpy error (experimental minus theoretical value) for the bond-*breaking* reaction. If the error in breaking any electron pair were a constant, the right hand side of (2) would vanish, and the computed theoretical values for $\Delta H°$ (0 K) would be exactly right. However, as the values given in the preceding paragraph show, these errors do not precisely cancel, and so we correct our raw computed $\Delta H°$ (0 K) values according to eq 2. By using the five molecules where $\Delta H°$ (0 K) is known experimentally, a value of $\epsilon(\pi)$ = 3 kcal/mol produces the best agreement between theory and experiment.

The SCF and MP4 total energies of all molecules, along with zero-point vibrational energies are given in Table VI. The energetics of molecular dehydrogenation are given in the first three columns of Table VII. The experimental heats of reaction are taken from the recent NBS compilation,[101] supplemented by the heats of formation for methanimine,[102] diimide,[5] and thioformaldehyde.[6] In some instances, the experimental enthalpies of formation have been corrected to 0 K by the present authors, by using the experimental vibrational frequencies. The raw theoretical values of $\Delta H°$ (0 K) are obtained by combining the MP4/EXT ΔE's with the SCF/3-21G(d) changes in zero-point energy, multiplied by 0.90 to account for the SCF overestimate of vibrational frequencies. The corrected theoretical values are then obtained from these raw values by using eq 2. For the five cases where comparison with experiment is possible, the results are good, except for methanimine. It may be seen that the corrections introduced by eq 2 are often substantial, varying from almost 0 to 8 kcal/mol.

The next two columns in Table VII give the bond dissociation energies we combine according to eq 1 with the corrected MP4/EXT enthalpies to produce the final column, the D_π values from hydrogenation energies. A few completely experimental

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Table VI. Hydrogenation Energetics[a]

molecule	SCF/3-21G(d)	ZPE[b]	SCF/EXT	MP4/EXT
H_2	−1.122 96	0.010 62	−1.132 49	−1.167 70
$H_3C—CH_3$	−78.858 02	0.079 44	−79.253 74	−79.616 72
$H_2C=CH_2$	−77.664 96	0.054 59	−78.056 70	−78.384 97
$H_3Si—CH_3$	−328.650 49	0.065 22	−330.310 57	−330.620 54
$H_2Si=CH_2$	−327.418 10	0.043 12	−329.074 45	−329.363 44
$H_3Si—SiH_3$	−578.427 52	0.052 95	−581.354 77	−581.612 48
$H_2Si=SiH_2$	−577.203 62	0.033 61	−580.122 70	−580.361 47
$H_2N—NH_2$	−110.631 81	0.057 07	−111.211 07	−111.618 31
HN=NH	−109.463 31	0.030 67	−110.027 40	−110.406 73
$H_2P—NH_2$	−395.584 63	0.047 28	−397.531 28	−397.879 23
HP=NH	−394.385 02	0.024 39	−396.321 39	−396.654 06
$H_2P—PH_2$	−680.489 19	0.038 97	−683.805 63	−684.095 70
HP=PH	−679.309 86	0.019 62	−682.616 03	−682.889 82
$H_3C—NH_2$	−94.755 01	0.068 30	−95.243 22	−95.627 05
$H_2C=NH$	−93.578 58	0.042 84	−94.057 48	−94.409 96
$H_3Si—NH_2$	−344.581 12	0.053 92	−346.332 41	−346.662 59
$H_2Si=NH$	−343.349 44	0.031 88	−345.094 71	−345.410 25
$H_3C—PH_2$	−379.671 14	0.058 59	−381.526 11	−381.853 86
$H_2C=PH$	−378.475 48	0.036 30	−380.323 78	−380.629 38
$H_3Si—PH_2$	−629.465 45	0.045 94	−632.586 49	−632.860 17
$H_2Si=PH$	−628.267 48	0.026 90	−631.380 48	−631.635 70
$H_3C—OH$	−114.469 60	0.054 77	−115.076 55	−115.466 86
$H_2C=O$	−113.307 45	0.028 88	−113.900 13	−114.259 82
$H_2Si—OH$	−364.320 32	0.041 52	−366.186 00	−366.523 45
$H_2Si=O$	−363.104 86	0.020 65	−364.961 79	−365.287 60
$H_3C—SH$	−435.670 96	0.049 41	−437.742 30	−438.077 32
$H_2C=S$	−434.482 25	0.026 72	−436.542 24	−436.853 15
$H_2Si—SH$	−685.487 90	0.036 99	−688.824 97	−689.104 10
$H_2Si=S$	−684.309 33	0.018 68	−687.634 97	−687.890 11
$H_2N—OH$	−130.332 36	0.043 21	−131.027 76	−131.445 05
HN=O	−129.147 83	0.015 49	−129.823 88	−130.214 48
$H_2P—OH$	−415.308 10	0.034 23	−417.370 18	−417.726 07
HP=O	−414.120 87	0.011 26	−416.171 61	−416.513 16
$H_2N—SH$	−451.564 22	0.038 13	−453.725 32	−454.083 72
HN=S	−450.353 20	0.014 00	−452.499 95	−452.843 05
$H_2P—SH$	−736.496 30	0.029 66	−740.029 82	−740.326 70
HP=S	−735.316 29	0.009 83	−738.836 39	−739.114 70

[a] Total energies, in hartrees. 1 hartree = 627.51 kcal/mol. [b] Zero-point vibrational energy, in hartrees, computed at the SCF/3-21G(d) level.

Table VII. Thermochemical Determination of D_π

atoms		raw[a] MP4/ EXT ($\Delta H°$)	corr[a] MP4/ EXT ($\Delta H°$)	exp[b] ($\Delta H°$)	D(A–H)[c]	D(B–H)[c]	D_π
A	B						
C	C	32.2	31	30.9	98.0	98.0	62
Si	C	49.6	49		89.6	99.2	37
Si	Si	47.4	46		86.3	86.3	23
N	N	18.6	24	26 ± 2	98	98	69
P	N	29.1	33		80	98	42
P	P	19.0	22		80	80	35
C	N	22.6	25	30 ± 3	94.6	98.4	65
Si	N	46.7	49		90	98	36
C	P	29.0	30		98	80	45
Si	P	30.9	32		86	80	35
C	O	16.1	20	20.4	95.9	104.1	77
Si	O	37.0	41		90	104	50
C	S	28.6	30	28.1	96.6	89.0	53
Si	S	24.7	26		88	89	50
N	O	29.8	37		98	104	62
P	O	21.4	27		80	104	53
N	S	38.2	42		98	89	42
P	S	22.6	26		80	89	40

[a] Units are kcal/mol. MP4/EXT energy differences are combined with zero-point energies and corrected for systematic errors by the procedure described in the text. [b] Reference 101, see also the text. [c] See the appendix for sources. Values with decimal places are experimental; other values are deduced as described in the Appendix.

Table VIII. A=B π Bond Strengths[a]

atoms			rot.	hydrogntn		recmnded
A	B	K[b]	this work	this work	exp[c]	this work
C	C	70	65.4	62	59, 65	65
Si	C	33	35.6	37	38, 39	38
Si	Si	28	22.7	23	26	25
N	N	94	60.0	69	55, 64	60
P	N		44	42		44
P	P	34	34.0	35		34
C	N	65	63.3	65		63
Si	N		36.4	36		36
C	P	48	43.1	45		43
Si	P		28.7	35		29
C	O	90		77		77
Si	O	40		50		50
C	S	63		53	52	52
Si	S			50		50
N	O	88		62		62
P	O	36		53		53
N	S			42		42
P	S			40		40

[a] Units are kcal/mol. [b] Kutzelnigg, ref 10. [c] References may be found in the text.

thermochemical values are available for comparison. The π bond strength for C=C is estimated as 59 kcal/mol[6] and for C=S as 52 ± 3 kcal/mol.[103] There are two experimental thermochemical estimates of the π bond strength for Si=C: 39 ± 5[8] and 38 kcal/mol.[104] The experimental values we[27] deduced from the literature for HN=NH, 64 ± 11 and 55 ± 6 kcal/mol are subject to great uncertainties in the heats of formation. There is also a recent estimate[105] of 59.3 kcal/mol for the second π bond in N_2.

Discussion

Both types of π bond energies mentioned in this paper are gathered in Table VIII. This table also includes a few experimental values and the values given by Kutzelnigg.[10] The final column of this table is a set of recommended values for D_π. The recommended values are obtained by choosing experimental values, where available. For other cases, the present theoretical results are selected, with precedence given to the more straightforwardly obtained rotational barriers, where these are possible. In all cases but N=N and Si=P, the two methods used give the same result, to within 3 kcal/mol. Agreement between our calculated results and the few available experimental values is also good. We therefore feel that a realistic assessment of the accuracy of our recommended D_π values is about ±5 kcal/mol. The accuracy of D_π for those cases where only hydrogenation energetics can be used to define the π bond strengths is perhaps less. Not only is there only one theoretical determination of the D_π value, there is more "guesswork" in the values used for D(A–H) in these compounds.

The present values differ considerably from those given by Kutzelnigg[10] in several cases. Kutzelnigg draws his values mainly from diatomic data. This involves more complicated assumptions about bond energy additivities than the present definitions. We refer the reader to Kutzelnigg's Appendix 2 for a discussion of his values. However, we note that at least in the case of N=N, the internal agreement between the two methods used in this work is 9 kcal/mol, whereas Kutzelnigg's value differs by 30 kcal/mol. This gives us some confidence in the values presented here. The values of Kutzelnigg for N=N, C=O, and N=O are meant to reproduce total bond energies for bond orders greater than 2, which may account for the discrepancies for these molecules.

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Table IX. Atomic π Bond Energies[a]

atom	E_π	atom	E_π
C	32.5	Si	12.5
N	30	P	17
O	37.5	S	23

[a] In kcal/mol. See text for the definition.

Next, we discuss the chemical consequences of the recommended D_π values in Table VIII. When the π bond is formed from two second period atoms, it has a high strength. The C=C, C=N, N=N, and N=O π bonds are about equally strong, 60–65 kcal/mol, with C=O being about 15 kcal/mol stronger. The latter is consistent with the fact that triply-bound CO possesses the strongest chemical bond known, with a total bond strength more than 1.0 eV stronger than the isoelectronic N_2.

In general, when a single third period atom is substituted, the π bond strength decreases and falls even further when a second third period atom is involved. However, this is not uniform; Si=S possesses about the same π bond strength as Si=O!

Of the six elements considered, silicon forms the weakest π bonds. This may be seen in Table VIII by comparing the isoelectronic pairs Si=N to C=P or, less conclusively, Si=O to C=S. When a silicon atom participates in a p_π–p_π bond, it is forced to assume sp^2 hybridization. Because the valence s and p orbitals in second period atoms have similar sizes (for example, carbon has $\langle r_{2s}\rangle = 1.59$ and $\langle r_{2p}\rangle = 1.69$ Å) hybridization is easily accomplished. However, third period atoms have much larger valence p orbitals (e.g., silicon has $\langle r_{3s}\rangle = 2.22$ and $\langle r_{3p}\rangle = 2.75$ Å), and so hybridization is more difficult (in an energy sense). Because of this so-called "inert pair effect"[106] the tendency of third period atoms to form planar structures with strong π bonds is reduced. This is especially true for Si compared to P or S. The latter two elements can participate in π bonding without having to rehybridize, since their lone pair orbitals are free to retain mostly s character.[107] The latter fact is shown by the approximately 95° angles around doubly-bound phosphorus.[27] As a consequence, the Si=Si π bond is the weakest one in the table.

We can attempt to order the elements' ability to form strong π bonds in the following qualitative manner. Let $E_\pi(A)$ represent the π bonding energy attributable to atom A. Then, in the spirit of Pauling and Mulliken, one may simply define

$$E_\pi(A) = \frac{1}{2}D_\pi(H_mA{=}AH_m)$$

The values so obtained are listed in Table IX. For atom A equal to O or S, since we have not included the diatomic triplet molecules O_2 and S_2 in our survey, we define

$$E_\pi(A) = D_\pi(A{=}BH_n) - E_\pi(B)$$

averaging over the four possible choices for atom B.

As a gauge of the usefulness of this definition of E_π, one can estimate D_π for the mixed A=B bonds from

$$D_\pi^{esl}(H_mA{=}BH_n) = E_\pi(A) + E_\pi(B)$$

These values are listed in Table X, together with our recommended values from Table VIII. The following points are noteworthy: (a) D_π^{esl} generally provides a good estimate of D_π^{rec}, except for Si=S and N=S. For example, C=N, Si=O, P=O, and P=S are estimated nearly exactly. (b) The root mean square agreement between these estimates and the recommended values is 6 kcal/mol. This level of agreement means not too much significance should be placed on the numerical values given for E_π. Nonetheless, the agreement is good enough to establish a trend. (c) Upon the basis of the E_π values given in Table IX, we conclude that the efficacy of π bonding by the six elements considered here is in the order O > N ≈ C ≫ S > P > Si.

Table X. Comparison of Estimated π Bond Energies

bond	D_π^{rec}	D_π^{est}	error
Si=C	38	45	7
P=N	44	47	3
C=N	63	62.5	-0.5
Si=N	36	42.5	6.5
C=P	43	49.5	6.5
Si=P	29	29.5	0.5
C=O	77	70	-7
Si=O	50	50	0
C=S	52	55.5	3.5
Si=S	50	35.5	-14.5
N=O	62	67.5	5.5
P=O	53	54.5	1.5
N=S	42	53	11
P=S	40	40	0

Finally we mention some specific, interesting facts gleaned from the recommended D_π values in Table VIII. Several π bonds involving Si which are very poorly characterized experimentally[19] such as Si=N, Si=O, Si=P, and Si=S are actually stronger than the better characterized Si=Si bond. This paucity of information must result either from a lack of experimental attention or from the kinetic instability due to the polarity of these bonds, rather than the inherent thermodynamic stability of these molecules. A complicating factor is that compounds such as Si=O lack sites at one end for steric protection by bulky groups. A surprising fact is that the Si=S π bond appears to be about as strong as Si=O. (Note that the SiO σ bond would be expected to be stronger than the SiS σ bond).

The P=O π bond is 10 kcal/mol more stable than the N=S π bond, which in turn is just barely stronger than the P=S bond involving two third period atoms. This result is supported by some experimental observations. Both HN=O and HP=O are well known species. The molecule Cl—P=S was reported only in 1983.[77,108] Molecules containing —N=S linkages are as yet unisolated, with NSF and NSCl containing sulfur–halogen rather than nitrogen–halogen bonds.[109] There are, however, two theoretical calculations[110,111] predicting HN=S to be more stable than the NSH isomer.

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Appendix

Only some of the necessary D(A–H) experimental bond dissociation energies (BDE) are available. The BDE is defined as the enthalpy change for the bond-breaking reaction, at 0 K. In general, the readily available BDE's for the simple AH_m hydrides are larger than in a molecule of type $H_{m+1}A$–BH_{n+1}. Data for the simple hydrides are taken from ref 100, except as noted. The reasoning behind the choices of BDE's used in Table VII is as follows (all units are kcal/mol).

CH. The BDE in methane is 103.2. The influence of substituents on this bond is fairly well known. The BDE is 98.0 in H_3C–CH_3,[112] 94.6 ± 2.0 in H_2N–CH_3,[113] 95.9 ± 1.5 in HO–C-

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H_3,[114] 99.2 in Me_3Si-CH_3,[8] and 96.6 in $MeS-CH_3$.[103] The value of 98 used for H_2P-CH_3 is an average of the latter two compounds.

NH. The BDE in ammonia is 105.8. The value in H_3C-NH_2[112] is 98.4. We have assumed a value of 98 for all other NH bonds.

OH. The BDE in water is 118.0. The BDE in H_3C-OH[112] is 104.1, and we have assumed a value of 104 for all other OH bonds.

SiH. The BDE in silane is 90.3 ± 1.2.[115] This BDE is 89.6 in CH_3-SiH_3[8] and 86.3 in $H_3Si-SiH_3$.[8] We have used a value of 90 for all other substituents, since their electronegativity is closer to methyl than silyl.

PH. The BDE in phosphine is 82 ± 2. This value is obtained from the experimental heat of formation of PH_2,[9] corrected to 0° with scaled theoretical frequencies.[100] This value differs from the value of 84 given by the original workers.[9] Since substituents usually lower the BDE, we adopt a value of 80 for all other PH bonds.

SH. The BDE in hydrogen sulfide is 90.0. The BDE in H_3C-SH[103] is 89.0 ± 1.0. This value is used for all other SH bonds.

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Dimanganese Complexes of a Septadentate Ligand. Functional Analogues of the Manganese Pseudocatalase

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Abstract: Two new dimanganese(II) complexes have been prepared and characterized as the first functional analogues of the manganese pseudocatalase enzyme of *L. plantarum* (Beyer, W. F.; Fridovich, I. *Biochemistry* **1986**, *24*, 6420). These have the formulas $Mn_2(L)Cl_3$ (**1**) and $Mn_2(L)(OH)Br_2$ (**2**) in which Cl^- and OH^-, respectively, serve as one of two bridging ligands, the other coming from the alkoxide group of the binucleating ligand *N,N,N',N'*-tetrakis(2-methylenebenzimidazolyl)-1,3-diaminopropan-2-ol (HL). The solution structure of these complexes has been characterized by EPR spectroscopy at both 34 and 9 GHz. This reveals the presence of two equivalent high-spin Mn(II) ions electronically coupled by a weak electron spin exchange interaction. Analysis of the axial zero-field splitting ($D = -0.072$ cm^{-1}) of this spin $S = 5$ complex in terms of the magnetic dipole interaction between the two Mn ions yields a lower limit to their separation of 3.2 Å. Cyclic voltammetry reveals that three separable oxidation processes occur for **2** at $E_p = 0.60$ V (A), 0.80 V (B), and 1.03 V (C), while **1** exhibits only two oxidations: a reversible one-electron process at 0.57 V (A) analogous to **2** and a second oxidation at 1.18 V corresponding to B + C. The hydroxide bridge in **2** thus appears to stabilize the Mn(III) oxidation state relative to Mn(II) in comparison with the chloride bridge in **1**. The binuclear complexes **1** and **2** decompose H_2O_2 catalytically with an initial rate for **1** proportional to $[H_2O_2]^2[Mn_2(L)Cl_3]^1$, while mononuclear Mn(II) is ineffective. The mechanism proceeds through the initial formation of the μ-oxo-containing Mn^{III} intermediate, $[Mn_2^{III}(L)(O)]Cl_2$, which is reduced by a second H_2O_2 to release O_2. A similar mechanism could be operating in the manganese pseudocatalase enzyme of *L. plantarum*, which is known to contain two Mn(III) per subunit and thus may have a binuclear Mn site.

Multinuclear manganese sites that are involved in the catalysis of reactions vital to biological systems are being steadily recognized and studied. Besides the photosynthetic water-oxidizing complex, which is known to utilize 4 Mn ions for the oxidation of water to molecular oxygen,[1] evidence has accumulated that the Mn site of the pseudo-catalase from *Lactobacillus planatrum* is comprised of two Mn ions per protein subunit.[2] This enzyme catalyzes the disproportionation of H_2O_2. Manganese has also been used as an effective probe of the structure of divalent ion sites, owing to its readily detected hyperfine structure seen by EPR. Chien et al. have used this feature to identify a binuclear metal ion site in the enzyme enolase.[3]

Thus there is compelling interest in the characterization of multinuclear manganese complexes in various oxidation states in order to unravel the more complex behavior of the biological sites by serving as models of the structural, spectral, or functional properties. Because of the lack of high-resolution structural data on the Mn sites in these enzymes, most efforts have focused on the characterization of spectral analogues.[4,5]

In the present study we have utilized a septadentate macrocyclic ligand, based on the benzimidazole group, which is capable of binding two metal ions via an alkoxide bridge. Earlier work has established the suitability of this ligand for binuclear copper complexes as models for hemocyanin.[6] The ligand *N,N,N',N'*-tetrakis(α-methylenebenzimidazolato)-1,3-diaminopropane-2-ol is a good chemical analogue for the imidazole residue of histidine, which is found as a ligand to manganese in the protein superoxide dismutase[7] and is believed to be found in the manganese pseudocatalase from *L. plantarum* (Beyer and Fridovich, private

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