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Substituted Silabenzenes

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Ab initio calculations have been carried out on a group of substituted monosilabenzenes. Twelve different substituents are considered (Cl, F, SH, OH, PH_2, NH_2, CH_3, SiH_3, NO_2, CN, OCH_3, COOH), each placed in the four unique positions on the ring. The relative energies and stabilities, aromaticities (as measured by bond separation reactions), electron density distributions, and dipole moments of these compounds are considered and discussed with the aid of density difference plots.

Introduction

A number of experimental[1-8] and theoretical[9-16] papers dealing with aromaticity in silicon-containing ring compounds have recently appeared in the literature. In 1977, Barton and Banasiak were the first to isolate methylsilabenzene.[1a] This was followed in 1978 by the first unambiguous evidence for the existence of silabenzene, reported by Barton and Burns.[1b] Theoretical work on silabenzene was begun in 1978 by Schlegel et al.[9] who predicted the structure of silabenzene using STO-3G[17b] at the self-consistent field (SCF) level and a year later by Blustin[10] who used an adaption of Frost's floating spherical Gaussian orbital (FSGO) model[18] to calculate the geometric structure of this compound.

More recently, 3-21G*[17d] calculations were reported by Chandrasekhar et al.[11] on silabenzene and several of its isomers (Figure 1) to determine relative stabilization and aromaticity. These calculations revealed that the silylene isomers **1c** and **1d** are ca. 20 kcal/mol higher in energy than **1a**, while the Dewar form, **1b**, is less stable by a further 18 kcal/mol. The least stable isomer considered, **1e**, was calculated to have a triplet ground state. Gordon and Boudjouk predicted silabenzene to be more than 80% as aromatic as benzene.[12] They employed bond separation energies at both the STO-2G[17a] and 3-21G[17c] levels as a gauge of aromaticity. We have recently predicted that the ortho, meta, and para isomers of disilabenzene are 38%, 80%, and 62% as aromatic as benzene, respectively,[13] again using bond separation reactions at the SCF/3-21G level as a quantitative measure of aromaticity. Chandrasekhar and Schleyer[15] performed 3-21G*//STO-3G calculations on 1,4-disilabenzene and its valence isomers, again illustrating the reduced aromaticity of silabenzenes and relative weakness of π Si–C over π C–C and σ Si–C bonds. The first findings showing that hexasilaprismane is the most stable of the Si_6H_6 isomers was performed by Nagase et al.[19a] It was determined in this study that hexasilaprismane has a smaller resonance stabilization energy based on the ΔE's for the appropriate homodesmic reactions. These results were later confirmed by Sax and Janoschek[16] using valence-only calculations. More recently, higher level split valence calculations were applied to Si_6H_6 isomers by Clabo and Schaefer[19b] and Nagase et al.[19c]

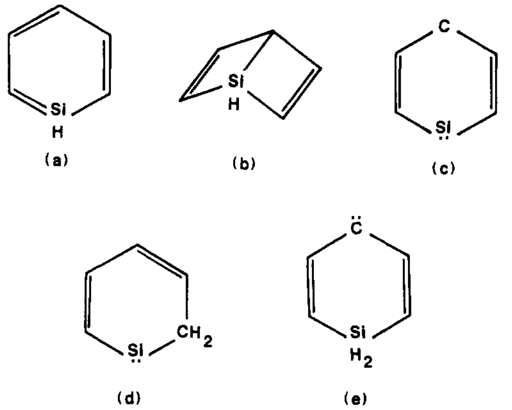

Figure 1. (a) Silabenzene. (b) Dewar silabenzene. (c) 1-Silacyclohexadienylidene. (d) 2-Silacyclohexadienylidene. (e) 4-Silacyclohexadienylidene.

The present paper considers the effects of substituents on monosilabenzene. The 12 substituents considered are F, Cl, OH, SH, OCH_3, NH_2, PH_2, CH_3, SiH_3, CN, NO_2, and COOH. Each of these substituents may be placed in the four unique positions on the ring. Of particular interest

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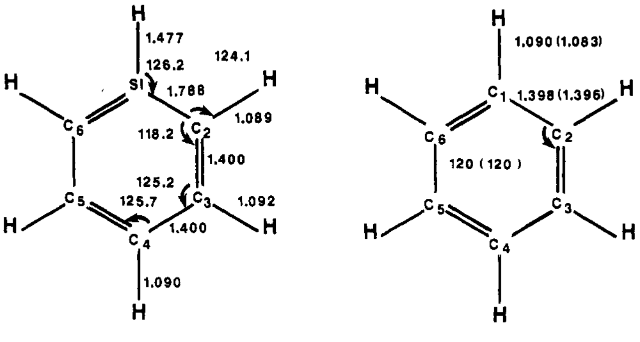
in this paper are relative isomer energies and stabilities, aromaticities, electron density distributions, and dipole moments for each substituted silabenzene. Because we include a broad range of substituents and properties, the analogous substituted benzenes are considered as well. Except for the halogens, lists of ortho-, para- versus meta-directing effects of substituents on the benzene ring are usually limited to second period species;[20] thus, the effect expected for SiH_3, PH_2, and SH is not clear. We have used total density difference plots as an interpretive tool in determining the directing properties of all substituents in both benzene and silabenzene.

Theoretical studies have previously been carried out to determine substituent effects on benzene for various substituent groups.[21-28] Hehre, Radom and Pople[21a] (HRP) used STO-3G SCF calculations to investigate conformations, stabilities, and charge distributions of 35 monosubstituted benzenes, employing a standard geometric model proposed by Pople and Gordon.[21b] A more recent study by Mehler and Gerhards[22] (MG) involved substituent effects for eight monosubstituted benzenes. The latter calculations were carried out by using a minimal basis set (MB) constructed to mimic the valence shell description of larger basis sets. Properties considered included total energies, stabilities, dipole moments, ionization potentials, and charge distributions.

Computational Methodologies

All geometries have been optimized with the STO-2G basis set,[17a] using the optimization methods in GAUSSIAN80[29a] and GAUSSIAN82.[29b] Gordon and Boudjouk have previously shown that STO-2G gives reliable structures for molecules such as those considered here.[12] The one exception, as has been previously noted,[23] is the fact that the minimal basis set tends to overestimate N–O bond distances.

In the determination of the geometries of the substituted silabenzenes, the angles and bond lengths defining the ring were fixed at the values optimized for unsubstituted monosilabenzene. The remaining geometrical parameters defining the substituents were fully optimized. To test this approach, a full optimization was carried out on 1-fluorosilabenzene at the STO-2G level. It was found that all ring bond lengths are within 0.015 Å and bond angles are within 1° of the silabenzene values. The corresponding energy differed by less than 2 kcal/mol from that of the constrained structure. This may be taken as justification for not reoptimizing the internal ring structure for each substituent, particularly since we are mainly interested in qualitative trends. Fixing the ring structure is also necessary for examining density differences. Taft and coworkers[30a] have also suggested that full optimization is not generally necessary for demonstrating qualitative trends such as isodesmic reaction energy studies of benzene derivatives. There are very few reported cases of fully optimized monosubstituted benzene structures. Pang et al. have used the 4-31G[17e] basis to optimize toluene[30b] and some fluorinated benzenes.[30c] Vincent and Radom[30d] have reported STO-3G geometries of benzenediazonium ions and related system. Schaefer et al.[30e] and Konschin[30f] have reported the fully optimized STO-3G structures of planar and orthogonal phenol. These, along with experimental evidence,[31] have shown that substituents cause only small structural changes in the phenyl ring from its regular conformation in benzene. These distortions predominantly affect the region near the substituted carbon.



2a **2b**

Figure 2. (a) STO-2G optimized geometry of silabenzene (C_{2v} symmetry assumed). (b) STO-2G optimized geometry of benzene. Experimental values are in parentheses. Bond lengths are in angstroms; angles are in degrees.

In this study, single point calculations were performed with the 3-21G basis set at the partially optimized STO-2G geometries (denoted 3-21G//STO-2G). Density difference plots, used as an aid in the discussion of the results, were drawn from 3-21G wave functions by using the plotting programs PLTORB[32a] and DENDIF.[32b] Selected calculations were also performed with the 3-21G* basis set. For aniline and aminosilabenzene, a set of five d functions were added to nitrogen in this basis.

A quantitative measure of the delocalization stabilization may be estimated by using the appropriate bond separation reaction for each molecule.[33] Such a reaction relates the parent compound to its component isolated single and double bonds by a reaction in which the number and types

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Table I. Bond Lengths (Å) and π-Overlap Values for Conformational Isomers of Substituted Benzenes, Substituted Silabenzenes, Benzenethiol, and Aminosilabenzene

(a) Substituted Benzenes

		C–X π overlap		
substituent	C–X STO-2G	STO-2G	3-21G// STO-2G	3-21G*// STO-2G
OH				
planar	1.395	0.0261	0.0262	
orthogonal	1.416	0.0086	0.0034	
SH				
planar	1.816	0.0072	0.0101	−0.0082
orthogonal	1.827	0.0046	−0.0005	0.0017
OCH_3				
planar	1.399	0.0260	0.0275	
orthogonal	1.420	0.0109	0.0023	
NH_2				
Py1	1.485	0.0037	−0.0076	−0.0125
Py2	1.460	0.0176	0.0124	0.0113
planar	1.414	0.0336	0.0264	0.0865
PH_2				
Py1	1.847	0.0056	0.0078	0.0120
Py2	1.881	0.0052	−0.0054	−0.0021
planar	1.847	0.0108	−0.0242	−0.0003

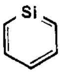
(b) Substituted Silabenzenes

		SI–X overlap		
substituent	SI–X STO-2G	STO-2G	3-21G// STO-2G	3-21G*// STO-2G
OH				
planar	1.756	0.0171	0.0306	
orthogonal	1.748	0.0047	0.0088	
SH				
planar	2.175	0.0070	0.0026	
orthogonal	2.165	0.0016	−0.0027	
OCH_3				
planar	1.752	0.0174	0.0294	
orthogonal	1.745	0.0075	0.0072	
NH_2				
Py1	1.816	0.0004	−0.0002	0.0083
Py2	1.831	0.0113	0.0260	0.0439
planar	1.745	0.0288	0.0452	0.0795
PH_2				
Py1	2.249	0.0023	−0.0002	0.0031
Py2	2.261	0.0021	0.0019	0.0025
planar	2.189	0.0138	0.0124	0.0399

(c) Benzenethiol and Aminosilabenzene

substituent	C–X 3-21G*	Si–X 3-21G*	C–X π overlap	Si–X π overlap
SH				
planar	1.816		−0.0088	
orthogonal	1.787		0.0019	
NH_2				
Py1		1.708		0.0023
Py2				
planar		1.687		0.0865

of formal bonds are conserved. For example, the appropriate bond separation reaction for silabenzene is



$$+ SiH_4 + 5CH_4 \rightarrow 2C_2H_4 + 2C_2H_6 + CH_2SiH_2 + CH_3SiH_3$$

Because the number and types of bonds are conserved in such a reaction, correlation effects are expected to be minimized.

Results and Discussion

Geometries. The predicted geometries of benzene and monosilabenzene are displayed in Figure 2. Force fields for these structures indicate that both are true minima.

Table II. Classical Classification of Benzene Substituents as Ortho, Meta, or Para Directors

ortho–para directors	meta directors
–OH	–CN
$-NH_2$	–COOH
–NHR	–COOR
$-NR_2$	–CHO
–OR	–C(O)R
–NHC(O)R	$-NO_2$
–alkyl	$-NR_3^+$
–aryl	$-SO_3H$
–halogen	$-SO_2R$

The geometries of the substituted compounds, determined as described in the previous section, for the substituted silabenzenes and benzenes are available as supplementary material.

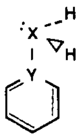
It is interesting to compare the difference in geometries between C_6H_5X and C_5SiH_5X where X = OH or OCH_3 and NH_2 or PH_2. Phenol and methoxybenzene are predicted to be planar as expected since in this conformation one oxygen lone pair is able to conjugate with the π electrons. This is illustrated in Table I where it is shown that the C–O bond lengths increase by 0.01–0.02 Å when the O–H bond is rotated to an orthogonal structure (90° dihedral angle). At the same time, the C–O π overlap decreases.

Although at the STO-2G level of theory benzenethiol is predicted to be planar, higher levels of theory (3-21G//STO-2G and 3-21G*//3-21G*) predict that the orthogonal conformation is lower in energy. At the 3-21G* level, the C–S bond length decreases by 0.03 Å when the S–H bond is rotated to an orthogonal structure (see Table Ic). The C–S π overlap likewise increases.

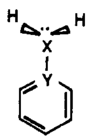
In contrast, the structures for the corresponding substituted OH and OCH_3 silabenzenes are orthogonal rather than planar. Note also (Table Ib) that in the silicon case the Si–O bond lengths *decrease* upon rotation to the orthogonal conformation, again in contrast to the analogous substituted benzenes. Since rotating the hydrogen out of the plane decreases the Si–O π overlap population (as it does in the substituted benzene analogues), the observed effect is apparently due to a combination of weaker π delocalization for the third period atom and a stronger interaction in the σ frame due to the polarization of the Si–C bond. The 2-, 3-, and 4-OH and $-OCH_3$ substituted silabenzenes were assumed to be planar.

In thiolsilabenzene, two third-period elements are bonded together with an even weaker π delocalization. As for benzenethiol, the predicted structure for thiolsilabenzene is the orthogonal conformation. In this conformation, although the Si–S bond length is decreased, the π overlap is much less than in the planar form.

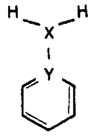
Three structures were considered for the NH_2- and PH_2-substituted benzenes and silabenzenes



Py1



Py2



Planar

As one would expect, the structure of aniline is predicted to be the Py2 conformation at the STO-2G and 3-21G*//STO-2G levels.[34] Although the planar structure would

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[34] Note that planar aniline and 1-aminosilabenzene are predicted to be planar at the 3-21G//STO-2G level. This is due to the tendency of double zeta basis sets to prefer planar nitrogen: see, for example (a) Lehn, J. M.; Munsch, B. *J. Chem. Soc., Chem. Commun.* **1970**, *994*, 6. (b) Gordon, M. S. *Chem. Phys. Lett.* **1986**, *126*, 451.

Table III. Predicted Classification of Ortho-, Meta-, and Para-Directing Tendencies for Substituted Benzenes and Silabenzenes

ortho–para directors		meta directors	
benzene	silabenzene	benzene	silabenzene
$-F$	$-F$	$-PH_2$ Py1	$-PH_2$ Py1
$-Cl$	$-Cl$	$-CN$	
$-OH$ planar	$-OH$ planar	$-NO_2$	$-NO_2$
$-OH$ orthog	$-OH$ orthog	$-COOH$	$-COOH$
$-SH$ planar	$-SH$ planar	$-SiH_3$	$-SiH_3$
$-NH_2$ Py1	$-NH_2$ Py1	$-SH$ orthog	$-SH$ orthog
$-NH_2$ Py2	$-NH_2$ Py2		
$-PH_2$ Py2	$-PH_2$ Py2		
$-CH_3$	$-CH_3$		
$-OCH_3$ planar	$-OCH_3$ planar		
$-OCH_3$ orthog	$-OCH_3$ orthog		

Table IV. C–X (Si–X) Bond Lengths for Halobenzenes (Halosilabenzenes) As Compared to Normal C–X (Si–X) σ Bond Lengths (Å)

Halobenzenes

substituent	R(C–X)	$R(CH_3–X)$
F	1.343	1.370
Cl	1.762	1.780

Halosilabenzenes

substituent	position	R(C–X)	$R(CH_3–X)$	R(Si–X)	$R(SiH_3–X)$
F	1			1.687	1.699
	2	1.342	1.370		
	3	1.347			
	4	1.346			
Cl	1			2.088	2.109
	2	1.765	1.780		
	3	1.773			
	4	1.768			

allow the maximum conjugation of the nitrogen lone pair with the π system of the ring, the nitrogen still prefers to retain its pyramidal structure. The π overlap between nitrogen and the ring carbon to which it is attached increases in the order Py1 ≪ Py2 < planar (Table Ia) with the Py2 conformation also having a much shorter C–N bond than Py1.

The structure of phosphinobenzene, on the other hand, is predicted to be the Py1 conformation. This becomes apparent only after addition of d orbitals to the phosphorus basis set (e.g., 3-21G*//STO-2G). Notice that the C–P distance in the preferred Py1 conformation is shorter than in the Py2 structure and is similar to that of the planar structure where maximum conjugation of the lone pair and ring π system is possible. For the larger basis sets, the overlap population between phosphorus and the ring carbon to which it is attached is much larger in the Py1 conformation than in the Py2 conformation. As noted above for sulfur the overall effect for phosphorus is smaller than that for nitrogen due to the decreased ability of third period atoms to form π bonds.[35] The bond length trends are clearly dictated by more than just π overlap considerations.

In contrast to aniline, for which the Py2 conformation is the predicted structure at the 3-21G*//STO-2G level, the preferred structure for aminosilabenzene is planar at this same level of theory. A 3-21G*//3-21G* calculation was performed to confirm this, and, in addition, it was found that the Py2 conformation actually optimizes to the planar structure. The π overlap between nitrogen and silicon is much greater in the planar conformation, and the Si–N bond length is significantly shorter.

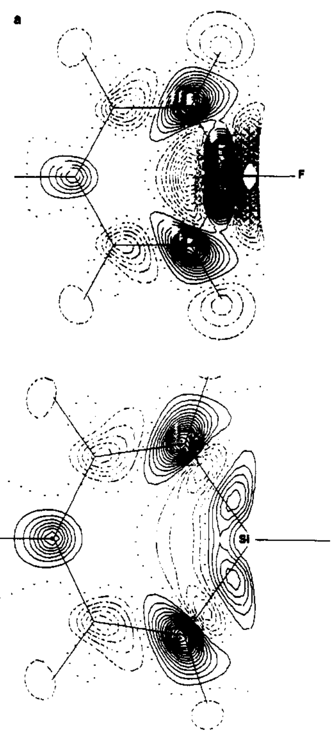

Figure 3. 3-21G//STO-2G density difference plots taken in a plane 0.7 B above the plane of the ring. Value in parentheses refers to the increment between consecutive contours, in electrons/bohr^3: (a) fluorobenzene minus benzene (0.0005); (b) fluorosilabenzene minus silabenzene (0.0005).

The predicted 3-21G*//STO-2G structure for phosphinosilabenzene, similar to the benzene analogue, is the Py1 conformation. While the Si–P bond length is less than in the Py2 structure, the π overlap is similar in both. Unlike the benzene analogue, the planar conformation has the largest π overlap and a significantly shorter Si–P bond length.

To summarize, the π overlap trends are similar, although somewhat attenuated, for the third period relative to the second period atoms. For the third period atoms these π interactions become less effective, leading to preferred structures which minimize H–H steric interactions and which allow stronger σ bonding.

Density Difference Plots. Because the π-electron network in substituted benzenes and silabenzenes can serve as a source of electrons for electrophilic reagents, electrophilic substitution reactions are a characteristic of this type of molecule. For benzene some substituents are thought to direct ring π electrons toward the positions which are ortho and para relative to the point of substitution, while others are regarded as meta directors. Since this polarization of the ring π density can have an effect on the reactivity of the ring toward further substitution, it is of interest to investigate the possibility of classifying the various silabenzene substituents as ortho, meta, and/or para directors, with respect to silabenzene, in a manner analogous to that for benzene. Table II gives the commonly quoted directing tendencies for substituents attached to benzene.[36]

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(35) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* 1987, *109*, 5217–5227.

(36) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon: Boston, MA, 1966.

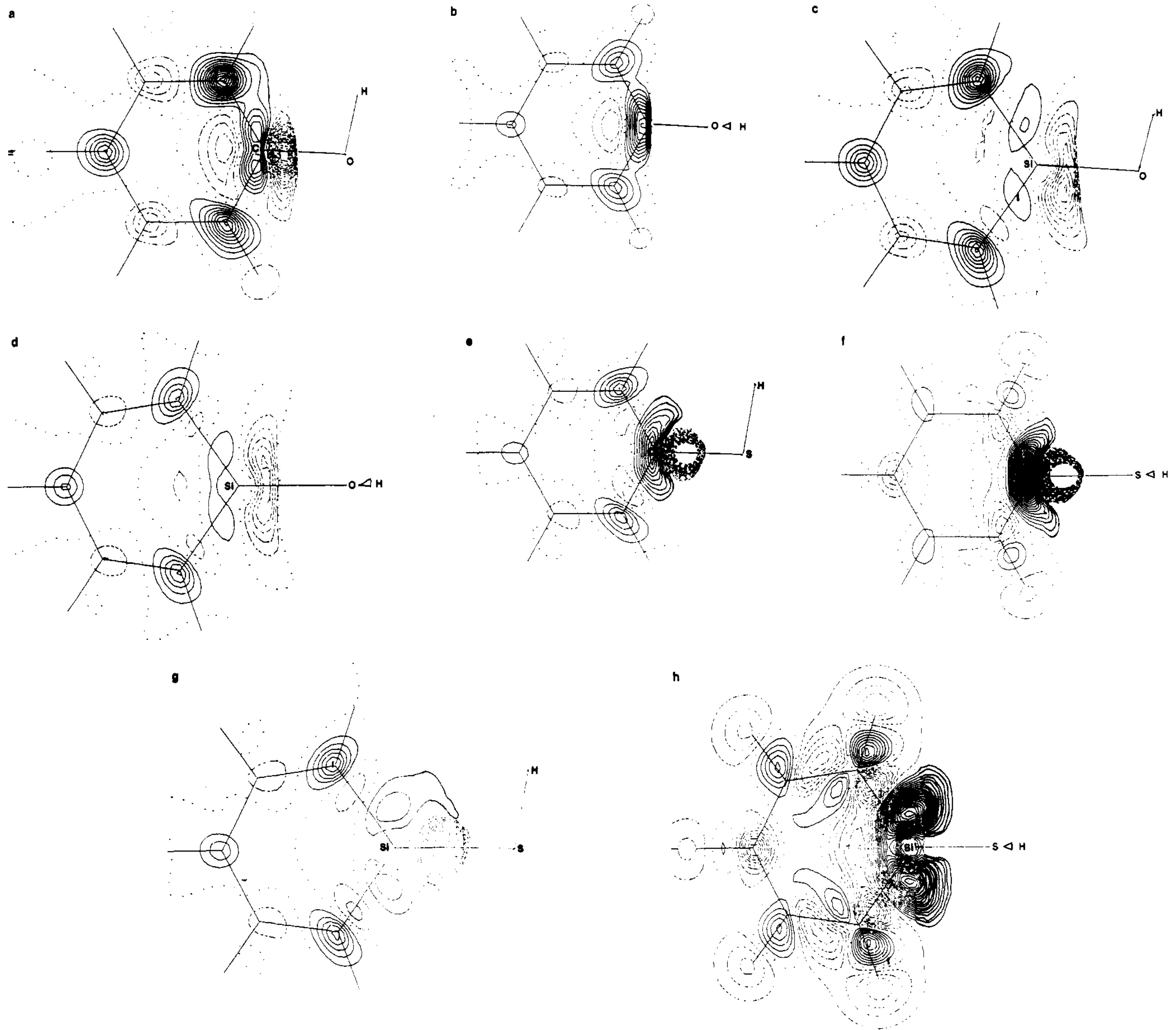

Figure 4. 3-21G//STO-2G density difference plots taken in a plane 0.7 B above the plane of the ring. Value in parentheses refers to the increment between consecutive contours, in electrons/bohr^3: (a) phenol (planar) minus benzene (0.001); (b) phenol (orthogonal) minus benzene (0.001); (c) hydroxysilabenzene (planar) minus silabenzene (0.001); (d) hydroxysilabenzene (orthogonal) minus silabenzene (0.001); (e) benzenethiol (planar) minus benzene (0.001); (f) benzenethiol (orthogonal) minus benzene (0.0005); (g) thiolsilabenzene (planar) minus silabenzene (0.001); (h) thiolsilabenzene (orthogonal) minus silabenzene (0.0001).

One approach to understanding directing tendencies of substituents in aromatic rings is to examine density difference plots. We have constructed such plots for each molecule in a plane parallel to and 0.7 bohr above the plane of the aromatic ring. Although this plane includes some σ density, the contours primarily represent π-electron density of the molecule.[37] The density difference map is constructed by subtracting the density of silabenzene ρ_{SiB} from that of the particular substituted silabenzene $\rho_{\mathrm{SiB-X}}$. Contours plotted of the resulting density difference, $\Delta\rho = \rho_{\mathrm{SiB-X}} - \rho_{\mathrm{SiB}}$, reveal the effect that the substituent has upon the π density of the ring. Only the effect of the substituent on the ring is of interest, so the very large density difference for the substituent minus hydrogen is removed from the plot. The results of the plots are shown in Figures 3–8. The analogous plots for benzene are shown for comparative purposes.

The distance between contours is in general taken to be 0.001 (e/bohr^3), except where otherwise noted in the figure captions. A contour with positive $\Delta\rho$ (indicated in the diagram by the solid lines) corresponds to a buildup in π-electron density relative to that of silabenzene. A contour with negative $\Delta\rho$ (indicated by the dashed line) corresponds to a depletion of π-electron density relative to that of silabenzene. According to this convention, we can categorize ortho–para or meta directors as those substituents which cause a buildup of electron density in the positions ortho and para or meta to the substituent. By analyzing these plots, we categorize the 12 substituents as indicated in Table III. Note that for benzene the conclusions in Tables II and III are in complete agreement.

In all figures, notice the lack of any negative charge buildup on silicon, whether or not the particular substituent is ortho–para or meta directing: For all the molecules considered, silicon is the least electronegative atom and therefore prefers to remain positive.

The following discussion of individual substituent directing tendencies for substituted silabenzenes is limited

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[37] Note that this is truly π density only for completely planar molecules. However, for consistency we consider both planar and nonplanar substituted molecules at 0.7 Å above the ring plane.

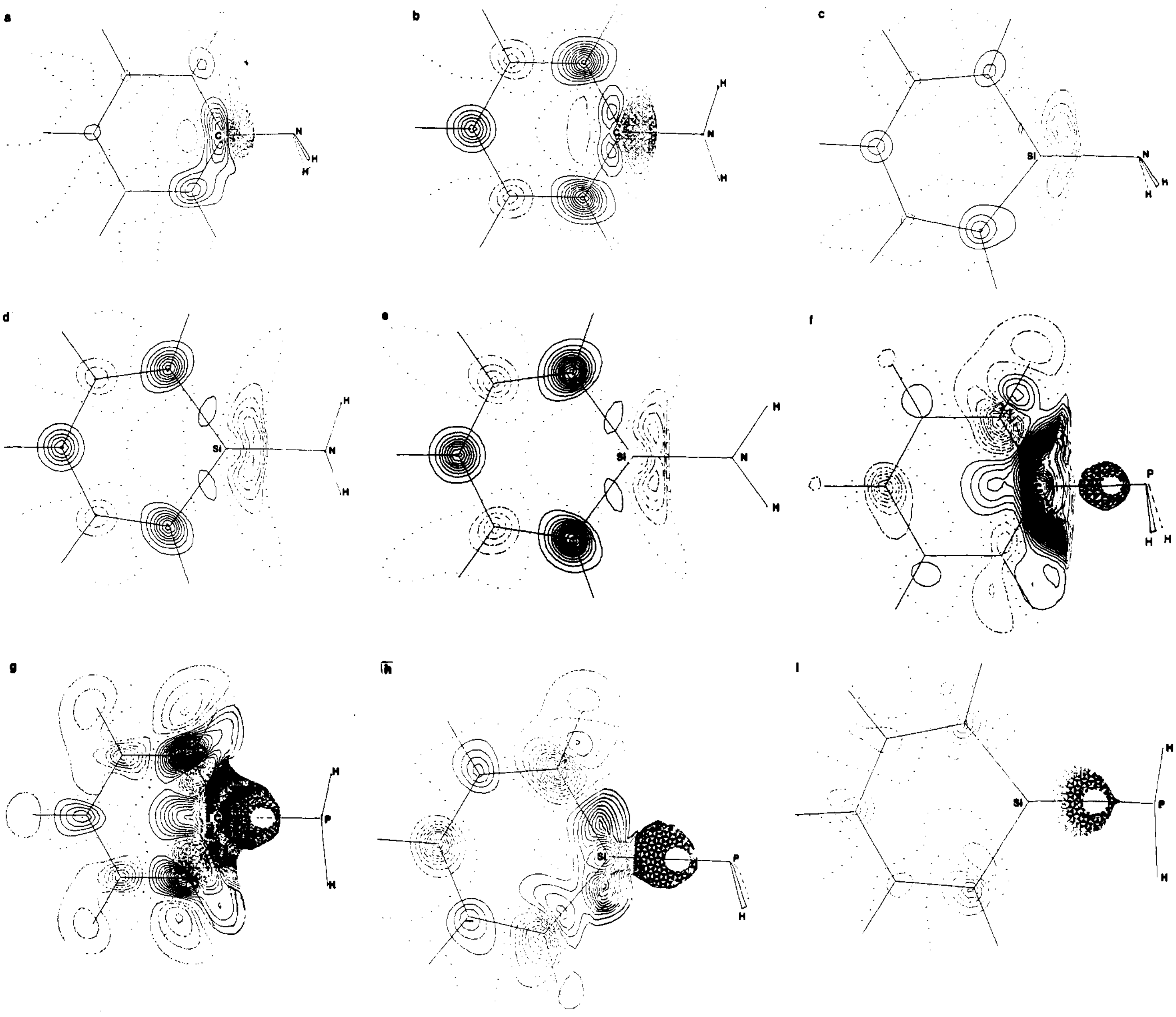


Figure 5. 3-21G//STO-2G density difference plots taken in a plane 0.7 B above the plane of the ring. Value in parentheses refers to the increment between consecutive contours, in electrons/bohr^3: (a) aniline (Py1) minus benzene (0.001); (b) aniline (Py2) minus benzene (0.001); (c) aminosilabenzene (Py1) minus silabenzene (0.001); (d) aminosilabenzene (Py2) minus silabenzene (0.001); (e) aminosilabenzene (planar) minus silabenzene (0.001); (f) phosphinobenzene (Py1) minus benzene (0.0003); (g) phosphinobenzene (Py2) minus benzene (0.0001); (h) Phosphinosilabenzene (Py1) minus silabenzene (0.0001); (i) phosphinosilabenzene (Py2) minus silabenzene (0.0005).

to substituents directly attached to silicon (the ipso position).

Halogens. Fluorine (Figure 3a) and chlorine (not shown) are both predicted to be ortho–para directing when substituted on benzene. The more electronegative fluorine has a greater tendency to direct π electrons to the ortho and para positions. These substituents are likewise ortho–para directors in silabenzene (Figure 3b). The inductive effects, due to the electronegativity difference between the substituent and the ring element to which it is attached, are slightly larger in the silabenzenes. This results in a greater polarization of charge to the ortho and especially the para positions. Notice also in the silabenzenes that, due to the electropositive nature of silicon, negative charge is polarized around the silicon and not directly on the atom.

In addition to the inductive effects, resonance effects due to the donation of the halogen lone pairs into the π system of the ring are illustrated by the lengths of the C–X and Si–X bonds (X = F, Cl). Table IV compares the C–X and Si–X bond lengths in the substituted rings with those of isolated C–X and Si–X σ bonds. For both F and Cl substitution the C–X and Si–X bond lengths are shorter than the isolated C–X and Si–X σ bonds.

OH, SH, OCH$_3$. The density difference plot for the OH substituent is shown in Figure 4 (that for OCH$_3$ is similar). When attached to benzene, OH directs electron density to the ortho and para positions more strongy when the OH is in the (more stable) planar conformation. Similarly, even though the lower energy conformation of silabenzene is the orthogonal form, the ortho–para effect is greater in the planar conformation. As for the halobenzenes, the effect of OH on silabenzene is slightly more pronounced than on benzene when similar conformations are compared. This is probably the result of the fact that the electronegativity difference between oxygen and silicon is greater than that between oxygen and carbon. Both anisole and methoxysilabenzene also appear to be strong ortho–para directors.

The third period substituent, –SH, likewise shows similar directing tendencies for both substituted benzene and silabenzene (Figure 4e–h). For this substituent, however, the particular conformation appears to determine whether

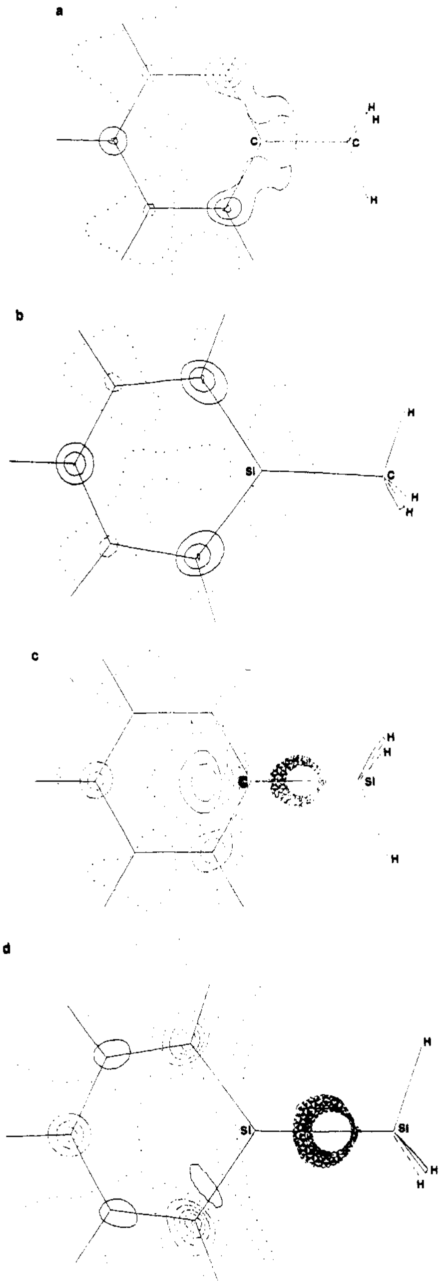


Figure 6. 3-21G//STO-2G density difference plots taken in a plane 0.7 B above the plane of the ring. Value in parentheses refers to the increment between consecutive contours, in electrons/bohr^3: (a) toluene minus benzene (0.001); (b) methylsilabenzene minus silabenzene (0.001); (c) silylbenzene minus benzene (0.0005); (d) silylsilabenzene minus silabenzene (0.0005).

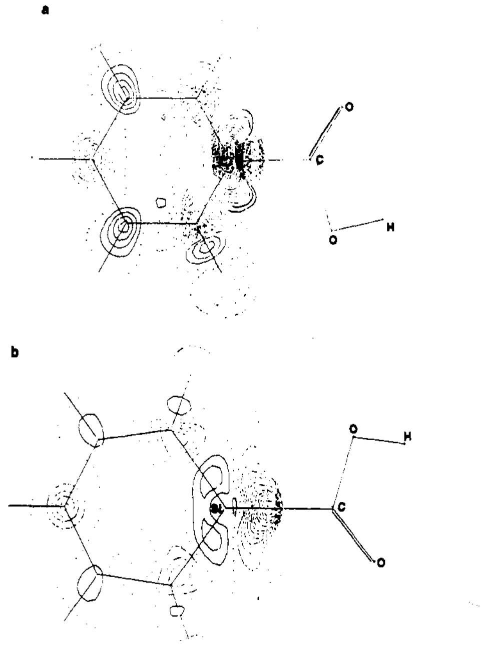


Figure 7. 3-21G//STO-2G density difference plots taken in a plane 0.7 B above the plane of the ring. Value in parentheses refers to the increment between consecutive contours, in electrons/bohr^3: (a) benzoic acid minus benzene (0.0005); (b) carboxysilabenzene minus silabenzene (0.0005).

–SH directs electron density ortho–para or meta. In the planar conformation, for both benzenethiol (Figure 4e) and thiolsilabenzene (Figure 4g), –SH is clearly an ortho–para director. Upon rotation of the thiol hydrogen by 90°, however, the substituent becomes a meta director (Figure 4f,h). The meta effect is clearly weak in both benzene and silabenzene since a very small increment between contours is required for it to become apparent. Also, note the depletion of electron density within the ortho Si–C and C–C bonds and in the para position and the buildup of charge density in the ortho C–H bonds in this orthogonal conformation.

NH_2, PH_2. The density difference plots for aniline, phosphinobenzene, and their silabenzene analogues are shown in Figure 5. NH_2 is clearly an ortho–para director in both the Py1 (Figure 5a) and Py2 (Figure 5b) conformations. The lower energy Py2 conformation has a stronger ortho–para effect, and the meta positions actually show a large amount of charge depletion. It is in this conformation that the nitrogen lone pair can conjugate to a greater extent with the π system of the ring. NH_2 is also an ortho–para director in the Py1 (Figure 5c), Py2 (Figure 5d), and planar (Figure 5e) conformations of aminosilabenzene.

On the other hand, PH_2 is a meta director in the Py1 conformations of phosphinobenzene and phosphinosilabenzene. In the Py2 conformation, PH_2 is apparently more ortho–para directing in silabenzene than on benzene.

CH_3, SiH_3. Figure 6a shows toluene to be an ortho–para director as expected, and the effects are similar in methylsilabenzene (Figure 6b). In contrast (Figure 6c,d), the silyl substituent is apparently a meta director, the effect in silyl-substituted silabenzene being more pronounced than in silyl-substituted benzene.

CN, NO_2, COOH. For benzene, these three substituents appear to be meta directors (COOH is shown as an example in Figure 7a). In all three plots it is interesting to observe the buildup of charge density within the ortho C–H bonds. The substituents appear to be withdrawing strongly from the ortho and para positions and polarizing the C–H bonds. Similar behavior is noted in the silabenzene-substituted species (Figure 7b). In both nitrosilabenzene and carboxysilabenzene, the meta-directing tendencies are notably less than in the analogous substituted-benzene species.

Substitution at Other Ring Positions. When a substituent is placed in one of the other three positions of the silabenzene ring, behavior is observed which is qualitatively similar to that described above for ipso substitution. One important observation can be made in these other cases, however: It is generally found to be the case that if the substituent is an ortho–para (meta) director and the silicon is at one of the ortho or para (meta) positions with respect to the substituent, no charge buildup

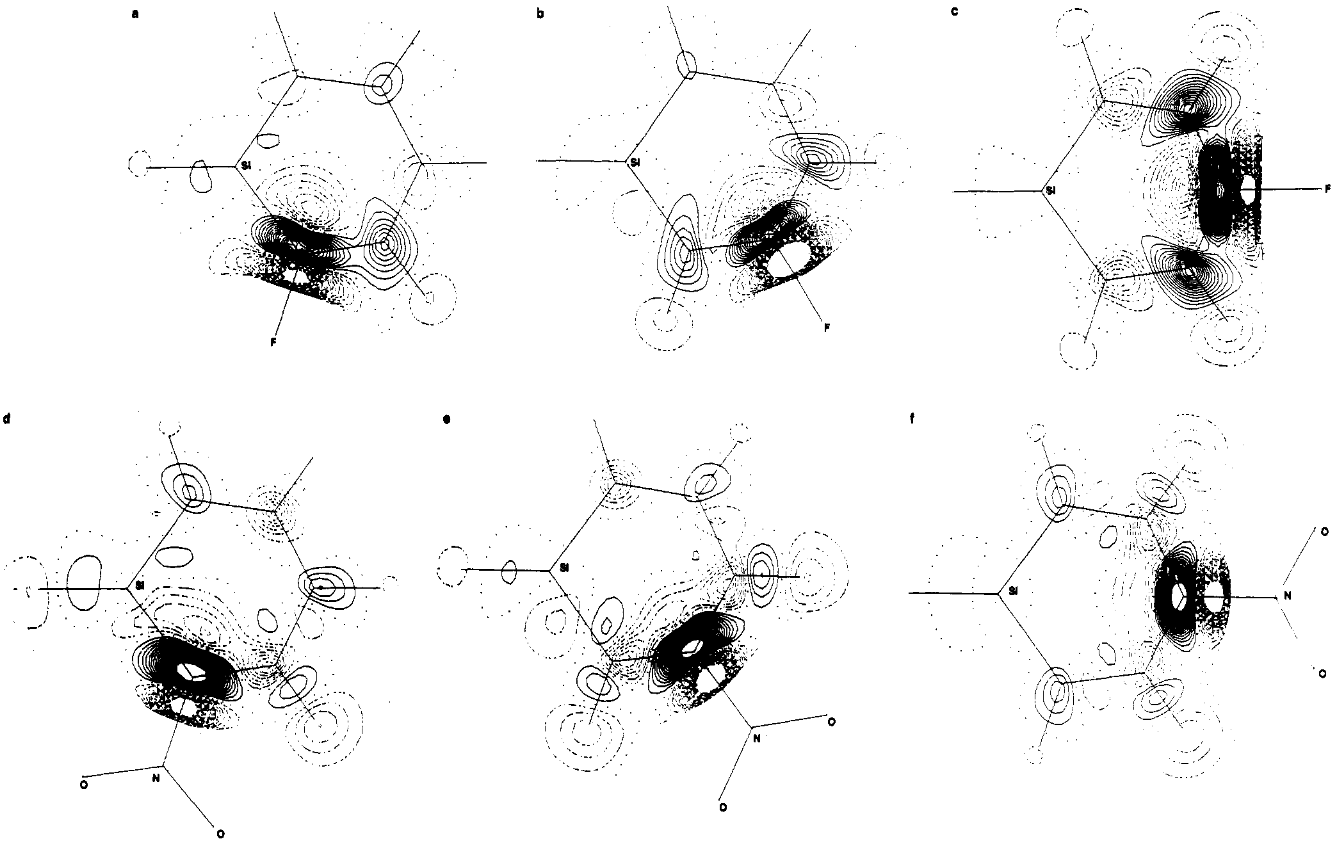


Figure 8. 3-21G//STO-2G density difference plots taken in a plane 0.7 B above the plane of the ring. Value in parentheses refers to the increment between consecutive contours, in electrons/bohr^3: (a) 2-fluorosilabenzene minus silabenzene (0.001); (b) 3-fluorosilabenzene minus silabenzene (0.001); (c) 4-fluorosilabenzene minus silabenzene (0.0005); (d) 2-nitrosilabenzene minus silabenzene (0.0005); (e) 3-nitrosilabenzene minus silabenzene (0.0005); (f) 4-nitrosilabenzene minus silabenzene (0.0005).

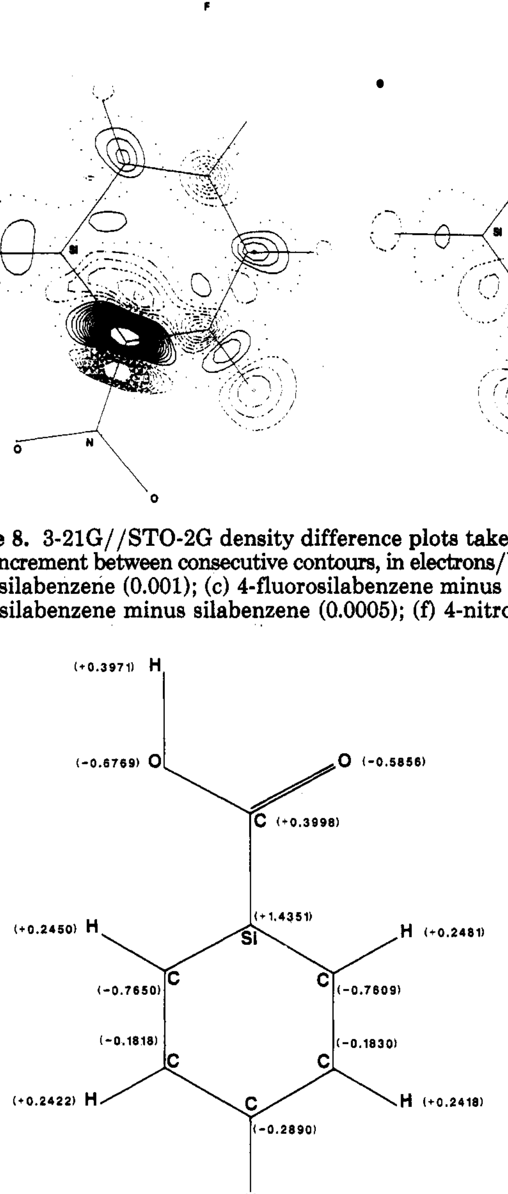
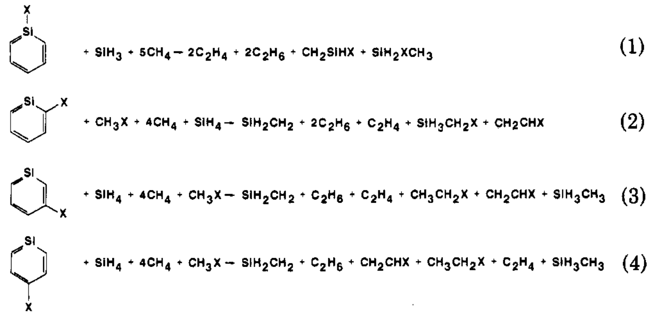


Figure 9. 3-21G Mulliken charge distribution for COOH.

is observed directly on the silicon. This is a result of electropositive nature of silicon. Examples of this are shown in Figure 8.

Energetics. Total electronic energies and dipole moments for the substituted benzenes and silabenzenes are available as supplementary material. A comparison of the dipole moments indicates that the 3-21G, MB, and CNDO/2 values for the substituted benzenes are generally larger than the experimental values. The 3-21G dipole moments, in particular, reproduce the observed trends. The STO-2G and STO-3G dipole moments, on the other hand, are typically lower than the corresponding experimental values.

Scheme I. Bond Separation Reactions



$$+ \mathrm{SiH_3} + 5\mathrm{CH_4} \longrightarrow 2\mathrm{C_2H_4} + 2\mathrm{C_2H_6} + \mathrm{CH_2SiHX} + \mathrm{SiH_2XCH_3} \quad (1)$$

$$+ \mathrm{CH_3X} + 4\mathrm{CH_4} + \mathrm{SiH_4} \longrightarrow \mathrm{SiH_2CH_2} + 2\mathrm{C_2H_6} + \mathrm{C_2H_4} + \mathrm{SiH_3CH_2X} + \mathrm{CH_2CHX} \quad (2)$$

$$+ \mathrm{SiH_4} + 4\mathrm{CH_4} + \mathrm{CH_3X} \longrightarrow \mathrm{SiH_2CH_2} + \mathrm{C_2H_6} + \mathrm{C_2H_4} + \mathrm{CH_3CH_2X} + \mathrm{CH_2CHX} + \mathrm{SiH_3CH_3} \quad (3)$$

$$+ \mathrm{SiH_4} + 4\mathrm{CH_4} + \mathrm{CH_3X} \longrightarrow \mathrm{SiH_2CH_2} + \mathrm{C_2H_6} + \mathrm{CH_2CHX} + \mathrm{CH_3CH_2X} + \mathrm{C_2H_4} + \mathrm{SiH_3CH_3} \quad (4)$$

Calculation of the energy difference for the appropriate bond separation reaction, using the 3-21G single-point energies, provides a quantitative measure of the stabilization energy. These bond separation reactions and the calculated stabilization energies, ΔE, are summarized in Scheme I and Tables V and VI for both the substituted silabenzenes and substituted benzene molecules.

Let B, SB, BX, and SBX represent benzene, silabenzene, X-substituted benzene, and X-substituted silabenzene, respectively. Then, one may calculate the following ratios:

$$R = [\Delta E(\mathrm{BX\ or\ SBX})/\Delta E(\mathrm{B})] \times 100$$

$$R' = [\Delta E(\mathrm{SBX})/\Delta E(\mathrm{SB})] \times 100$$

$$R'' = [\Delta E(\mathrm{SBX})/\Delta E(\mathrm{BX})] \times 100$$

In the case of benzene, the value of R relates the aromaticity of the substituted compound to that of unsub-

Table V. Calculated Bond Separation Energies and R for Substituted Benzene Using 3-21G Single-Point Energies

substituent	ΔE^a	R^b
F	66.3	110.5
Cl	56.4	94.0
OH	55.3	92.2
SH	56.9	94.9
NH_2	60.6	95.3
PH_2	58.9	97.2
CN	58.1	96.8
NO_2	56.5	94.2
CH_3	59.0	98.4
SiH_3	60.0	99.9
OCH_3	51.7	86.2
COOH	45.9	76.5

[a] ΔE, stabilization energies (kcal/mol). [b] $R = [\Delta E(BX)/\Delta E(B)] \times 100$, where BX represents substituted benzene and B represents benzene.

Table VI. Calculated Values of ΔE, R, R', R'' for Substituted Silabenzene Using 3-21G Single-Point Energies

substituent	position	ΔE^a	R^b (SBX/B)	R'^c (SBX/SB)	R''^d (SBX/BX)
H	1	47.8	80.0	100.0	79.7
F	1	42.9	71.5	89.7	64.7
	2	48.1	80.2	100.6	72.5
	3	55.9	93.3	117.1	84.4
	4	53.0	88.3	110.8	79.9
Cl	1	44.2	73.7	92.5	78.4
	2	47.8	79.7	100.0	84.8
	3	48.7	81.2	101.9	86.3
	4	44.4	74.0	92.9	78.7
OH	1	46.1	76.8	96.4	83.4
	2	42.2	70.3	88.3	76.3
	3	45.1	75.2	94.4	81.6
	4	40.6	67.7	84.9	73.4
SH	1	45.9	76.5	96.0	80.6
	2	45.7	76.2	95.6	80.2
	3	45.5	75.8	95.2	79.9
	4	43.3	72.2	90.6	76.0
NH_2	1	48.2	80.3	100.8	84.3
	2	47.8	79.7	100.0	83.6
	3	45.4	75.7	95.0	79.4
	4	44.1	73.5	92.3	77.1
PH_2	1	48.4	80.7	101.3	83.0
	2	44.0	73.3	92.1	75.5
	3	45.1	75.2	94.4	77.4
	4	45.5	75.8	95.2	78.0
CN	1	45.4	75.7	95.0	78.1
	2	50.2	83.7	105.0	86.4
	3	45.0	74.9	94.1	77.4
	4	47.7	79.5	99.8	82.1
NO_2	1	40.1	66.8	83.9	71.0
	2	51.9	86.5	108.6	91.9
	3	44.1	73.5	92.3	78.1
	4	48.3	80.5	101.0	85.5
CH_3	1	47.7	79.5	99.8	80.8
	2	47.9	79.8	100.2	81.1
	3	46.5	77.5	97.3	78.8
	4	45.2	75.3	94.6	76.6
SiH_3	1	49.9	83.2	104.4	83.2
	2	47.2	78.7	98.7	78.7
	3	46.5	77.5	97.3	77.6
	4	47.2	78.7	98.7	78.7
OCH_3	1	44.3	73.8	92.7	85.7
	2	40.3	67.2	84.3	77.9
	3	40.2	67.0	84.1	77.8
	4	36.9	61.5	77.2	71.4
COOH	1	34.3	57.2	71.8	74.7
	2	42.7	71.2	89.3	93.0
	3	37.7	62.8	78.9	82.1
	4	41.8	69.7	87.5	91.1

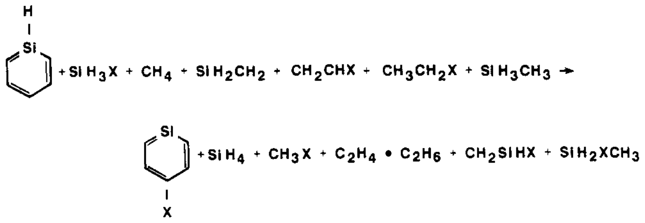
[a] ΔE, stabilization energies (kcal/mol). [b] $R = [\Delta E(\text{BX or SBX})/\Delta E(B)] \times 100$. [c] $R' = [\Delta E(SBX)/\Delta E(SB)] \times 100$. [d] $R'' = [\Delta E(SBX)/\Delta E(BX)] \times 100$. BX represents substituted benzene, SBX represents substituted silabenzene, and B represents benzene.

stituted benzene. For silabenzenes, the value of R relates the aromaticity of the substituted silabenzene to that of benzene. When X = H, one finds silabenzene to be 80% as aromatic as benzene,[12] using the bond separation energies as a measure.

The substituted benzenes are predicted, on the average, to be 95% as aromatic as benzene with benzoic acid being the least aromatic (76.5%) and fluorobenzene being actually more aromatic than benzene (R = 110). The substituted silabenzenes range from 57 to 93% as aromatic as benzene, with most R values being in the range of 70–80%. Since R(SB) = 80%, the predicted trends for BX and SBX are similar. However, while only fluorine has an $R > 100\%$ for substituted benzenes, several substituents effect an increased stabilization relative to silabenzene (see R' in Table VI).

As noted for the substituted benzenes, the fluorosilabenzenes show the greatest aromaticity and carboxysilabenzenes, the least. Note that for the substituted fluorosilabenzenes the values of R decrease in the order 3- > 4- > 2-fluorosilabenzene. One would expect greater stability in 3- than in the 2- or 4-position since fluorine directs electron density to the ortho–para positions. Thus, only when the fluorine is in the 3-position can electron density buildup at silicon be avoided without violating the normal directing tendency. Analogous comments apply to the other strong ortho, para directors. For similar reasons all of the second-period meta directors (CN, NO_2, and COOH) have a large R for the 2-substituted position. For the two third-period meta directors (PH_2 and SiH_3), however, the ipso-substituted molecule is the most aromatic of all positions.

It is apparent from Scheme I that differences among bond separation energies for substituents at the 2-, 3-, and 4-positions are readily analyzed. The products of these reactions for 3- and 4-substitution are the same, and those for 2-substitution are related isodesmically (i.e., $SiH_3CH_2X + CH_3CH_3 \rightarrow CH_3X + SiH_3CH_3$ is an isodesmic reaction). Because substitution at the ipso(1–) position leads to a different set of products in the bond separation reaction, a similar analysis here is not as straightforward. For example, subtracting eq 4 from 1 in Scheme I leads to the following relationship:



Thus, the relative resonance stabilization of 1- and 4-substitution is a complicated balance of many interactions.

Generally, the trends noted above for R are similar to those found in Table VI for R'. The latter compares the aromaticity of substituted silabenzenes with that of the parent silabenzene. The fluorosilabenzenes show the overall largest value of R', with the 3-fluorosilabenzene being over 17% more aromatic than silabenzene, since it is in this position that fluorine directs electron density in the ortho and para positions and thus away from the silicon. All of the meta directors, except for COOH, also show increased aromatic character relative to silabenzene. Of these, the second-period meta directors, CN and NO_2, show considerably more aromaticity in the ortho position than any other. Here again, electron density is being directed away from the silicon.

Table VII. 3-21G Single-Point Relative Energies of the Four Isomers of Each Silabenzene (kcal/mol)

substituent	directing tendency[a]	postition of substitution 1	2	3	4
F	o–p	0.0	45.2	35.2	38.1
Cl	o–p	0.0	33.8	31.9	32.6
OH	o–p	0.0	38.8	29.1	33.6
SH	m	0.0	24.0	22.3	24.3
NH_2	o–p	0.0	31.7	27.3	28.6
PH_2	m	0.0	11.7	13.3	12.9
CN	m	0.0	8.6	12.9	10.2
NO_2	m	0.0	6.9	10.7	6.4
CH_3	o–p	0.0	14.0	13.0	14.2
SiH_3	m	0.0	2.3	6.2	5.6
OCH_3	o–p	0.0	35.2	29.4	32.7
COOH	m	0.0	−7.0	−2.3	−6.4

[a] The directing tendencies given here, as predicted by density difference plots, consider only the lowest energy structures: o–p, ortho–para-directing substituent; m, meta-directing substituent.

Table VII compares the relative energies of the four isomers of each substituted silabenzene. Among all substituents, with the exception of COOH, the 1-substituted species is the most stable, especially for the ortho–para directors. The degree of stability appears to be a reflection of the electronegativity of the substituent; i.e. the more electronegative the substituent, the more stable the 1-substituted species relative to the other isomers. In the case of COOH, the 1-substituted molecule is the highest rather than the lowest in energy relative to the other three positions. This appears to be the result of the strong π-withdrawing ability of this substituent.

Among all ortho–para directors, the 3-substituted species is the next lowest in energy. This may be due to the fact that in this position the substituent is directing electron density away from the silicon. Among all meta directors except NO_2, the 2-substituted species is the second most stable. Again, in this position, the substituent directs the π-electron density toward positions other than the silicon.

Comparison with Previous Results. Most of the previous studies have involved only substituted benzenes. In this section we compare our results for substituted benzenes with results obtained from two extensive studies of substituted benzenes, those by HRP[21a] and MG,[22] and compare these with the silabenzene results.

To characterize the effect of the substituent X on the stability of the ring, HRP proposed the following reaction:

$$C_6H_5X + CH_4 \rightarrow C_6H_6 + CH_3X \qquad (5)$$

The ΔE for this reaction compares the effect of the substituent X on the stability of benzene with its effect on the stability of methane. For silabenzene, the analogous reaction is

$$SiXC_5H_5 + SiH_4 \rightarrow SiC_5H_6 + SiH_3X \qquad (6)$$

for X attached to silicon and

$$SiC_5H_5X + CH_4 \rightarrow SiC_5H_6 + CH_3X \qquad (7)$$

for X attached to carbon.

The predicted energetics for reaction 5 from this work are compared with those from HRP in Table VIIIa. The results indicate that, for all substituents considered, the stability of the substituted molecule is greater than that of the unsubstituted molecule. The third-period substituents do not stabilize the ring as significantly as those from the second period, relative to the methyl analogue. This is particularly evident for –F, –Cl, –OH, –SH, $-OCH_3$, $-NH_2$, and $-PH_2$ systems where the conformation that leaves the lone pair most accessible to the ring is the most favorable (i.e. planar conformation and Py2 conformation, respectively).

Table VIII. Stabilities[a] Calculated for Substituted Benzenes and for Ipso Substituted Silabenzenes (kcal/mol)

(a) Benzene

substituent	3-21G[b]	STO-2G	STO-3G[c]	4-31G[d]	expt[c]
F	12.9	15.3	11.4	7.8	9.6
OH					
planar	12.3	14.8	12.4	7.5	12.9
orthogonal	10.1	9.1			
OCH_3					
planar	12.5	14.4	5.5		11.7
orthogonal	11.0	11.6			
Cl	3.5	8.2			
NH_2					
Py1[e]	5.8	5.4			
Py2[e]	9.2	10.1	9.7	9.8	11.4
SH					
planar	2.7	6.3			
orthogonal	4.4	4.1			
NO_2	7.4	9.1		2.5	
PH_2					
Pyl	3.3	2.1			
Py2	4.0	5.9			
CH_3	2.1	3.2		1.3	
SiH_3	1.4	0.3			
CN	1.9	6.2	5.8	1.2	
COOH	11.3	10.8	4.5		

(b) Silabenzene[f] (3-21G)

substituent	ΔE	substituent	ΔE
F	−1.2	SH	
OH		planar	−1.0
planar	−1.5	orthogonal	−0.1
orthogonal	1.9	NO_2	−4.6
OCH_3		PH_2	
planar	−0.8	Pyl	1.9
orthogonal	1.4	Py2	3.5
Cl	−2.3	planar	−18.5
NH_2		CH_3	1.1
Pyl	3.0	SiH_3	3.4
Py2	−1.3	CN	−1.2
planar	10.4	COOH	13.1

[a] Equation 5: $C_6H_5 + CH_4 \rightarrow C_6H_6 + CH_3X$. [b] These are 3-21G single-point results using STO-2G geometries. [c] Reference 21a. [d] Charton, M.; Greenberg, A.; Stevenson, T. A. *J. Org. Chem.* **1985**, *50*, 2643. [e] See text for definitions. [f] Equation 6: $SiXC5H_5 + SiH_4 \rightarrow SiC_5H_6 + SiH_3X$.

For silabenzene (Table VIIIb), not all of the ipso substituents stabilize the ring by the measure of eq 6. Apparently F, Cl, SH, NO_2, and CN stabilize SiH_3X more than the ring. The remaining ipso substituents appear to stabilize the ring only slightly, with the exception of COOH. As observed previously, the conformational preference seen for these compounds seems to affect stability. It has previously been observed[35] that silicon is reluctant to form double bonds. This is reflected in the fact that in all substituted species where conjugation to the ring is possible through conjugation of lone pairs (F, Cl, OH, SH, OCH_3, NH_2 PH_2, NO_2, and CN), we predict a negative ΔE, i.e. a destabilizing effect. Where possible, the substituted species prefers the conformation that reduces the π interaction with the ring, with the exception of aminosilabenzene. This is observed in the preference of orthogonal conformations for OH, SH, and OCH_3 substituted silabenzene and the preference of the Pyl conformation for PH_2 substituted silabenzene. In the preferred conformations, the ΔE is positive (stabilizing). Aminosilabenzene appears to be an exceptional case in which the planar structure has a relatively large positive ΔE (i.e. significant stabilizing effect). For F, Cl, NO_2, and CN substituents, no analogous conformational changes can

Table IX. 3-21G//STO-2G Values of q_σ, q_π, and $q_{\mathrm{Ph-X}}$ for Substituted Benzenes[a,b] and Substituted Silabenzenes[a,b]

substituent	directing tendency[c]	q_σ	q_π	$q_{\mathrm{Ph-X}}$
	(a) Substituted Benzenes			
H		−	0	0
F	o,p	+	−	+
Cl	o,p	−	−	−
OH	o,p	+	−	+
SH	o,p	−	−	−
OCH_3	o,p	+	−	+
NH_2	o,p	+	−	+
PH_2	o,p	−	−	−
CH_3	o,p	−	−	−
SiH_3	m	−	+	+
CN	m	+	+	0
NO_2	m	+	+	+
COOH	m	+	+	+
	(b) Substituted Silabenzenes			
H		+	0	0
F	o,p	+	−	+
Cl	o,p	+	−	−
OH	o,p	+	−	+
SH	m	+	−	−
OCH_3	o,p	+	−	+
NH_2	o,p	+	−	−
PH_2	m	−	−	0
CH_3	o,p	+	−	−
SiH_3	m	−	+	+
CN		+	+	+
NO_2	m	+	+	+
COOH	m	+	+	+

[a] A negative value indicates charge donation by the substitutent group to the ring; a positive value indicates charge withdrawal from the ring. [b] Only minimum energy conformations are considered. [c] o,p refers to ortho–para-directing tendencies. m refers to meta-directing tendencies.

occur to alleviate the interaction and here the ΔE is negative. The small or negative ΔE's for reaction 6 are qualitatively consistent with the smaller aromaticity of silabenzenes noted earlier via examination of the bond separation reactions.

Analysis of Mulliken[38] charges for the substituted benzenes and silabenzenes can be used to support the predicted directing tendencies of the substituents. Information extrapolated from these values is limited, however, by the fact that the relative magnitude of these charges and charge differences are quite small[39] and subject to basis set variation.[40] The density difference plots give a clearer, more detailed picture of the directing tendencies.

In order to discuss the effects of the substituents on the electron density distribution of the ring, HRP[21a] defined q_σ, q_π, and $q_{\mathrm{Ph-X}}$ as follows: q_σ = total σ charge donated to the ring by substituent X; q_π = total π charge donated to the ring by substituent X; $q_{\mathrm{Ph-X}}$ = Mulliken overlap population between the adjacent π-type p orbitals in the bond joining X to the ring.

These values have been calculated for both substituted benzenes and silabenzenes and tabulated along with those of HRP in tables (available as supplementary material). Qualitative magnitudes of these values are given in Table IX. Charge transfer in the σ space for third-period substituents is from substituent group to the benzene ring, while, except for methyl, charge transfer for second-period substituents is just the opposite. Values of q_π illustrate that all ortho–para directing substituents are π donors, while all meta directors withdraw π-electron density from the ring. π overlap populations, $q_{\mathrm{Ph-X}}$, indicate that all third-period substituents except X = SiH_3 have negative values of $q_{\mathrm{Ph-X}}$, an antibonding effect, while all second-period substituents except methyl have positive overlap populations.

Similar observations can be made for the q_π and $q_{\mathrm{Ph-X}}$ populations for substituted silabenzenes with the exception of X = NH_2. In the latter case, the π overlap is found to be negative. More differences are noted for the σ charges. Only two substituents (PH_2 and SiH_3) exhibit σ donation into the ring. The remaining substituents withdraw σ electron density from the ring.

Conclusions

Several points should be noted from the comparison of substituent effects in benzene with those in silabenzene.

(1) π electron direction by substituents on these aromatic systems can be determined from density difference plots. The substituents have the same directing tendencies in both benzene and silabenzene systems. Conformation of the substituents appears to determine the magnitude of the effect for OH, SH, OCH_3, NH_2, and H_2. Third-period substituents were determined to have the same effect as their second-period counterparts for the two systems, with the exception of SiH_3 versus CH_3 and the lower energy conformations of NH_2 versus PH_2.

(2) The variations in aromaticity in these compounds are generally minor. By use of the appropriate bond separation reactions as a guide, most substitutions result in a predicted aromaticity about the same or slightly less than that in unsubstituted benzene (60 kcal/mol) or silabenzene (47 kcal/mol). Exceptions to this are fluorobenzene (which has a 3-21G predicted aromaticity of 66.3 kcal/mol) and, for silabenzene, cyano and nitro substituents in the ortho position, silyl substitution in the ipso position, and fluoro substitution in both the meta and para positions. The latter group has 3-21G predicted aromaticities of 50–55 kcal/mol.

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Registry No. 1-Fluorosilabenzene, 110851-72-4; 2-fluorosilabenzene, 110851-73-5; 3-fluorosilabenzene, 110851-74-6; 4-fluorosilabenzene, 110851-75-7; 1-chlorosilabenzene, 110851-76-8; 2-chlorosilabenzene, 110851-77-9; 3-chlorosilabenzene, 110851-78-0; 4-chlorosilabenzene, 110851-79-1; 1-hydroxysilabenzene, 110851-80-4; 2-hydroxysilabenzene, 110851-81-5; 3-hydroxysilabenzene, 110851-82-6; 4-hydroxysilabenzene, 110851-83-7; 1-thiolsilabenzene, 110851-84-8; 2-thiolsilabenzene, 110851-85-9; 3-thiolsilabenzene, 110874-16-3; 4-thiolsilabenzene, 110851-86-0; 1-aminosilabenzene, 110851-87-1; 2-aminosilabenzene, 110851-88-2; 3-aminosilabenzene, 110851-89-3; 4-aminosilabenzene, 110851-90-6; 1-phosphinosilabenzene, 110851-91-7; 2-phosphinosilabenzene, 110851-92-8; 3-phosphinosilabenzene, 110851-93-9; 4-phosphinosilabenzene, 110851-94-0; 1-cyanosilabenzene, 110851-95-1; 2-cyanosilabenzene, 110851-96-2; 3-cyanosilabenzene, 110851-97-3; 4-cyanosilabenzene, 110851-98-4; 1-nitrosilabenzene, 110851-99-5; 2-nitrosilabenzene, 110852-00-1; 3-nitrosilabenzene, 110852-01-2;

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4-nitrosilabenzene, 110852-02-3; 1-methylsilabenzsene, 63878-65-9; 2-methylsilabenzene, 110852-03-4; 3-methylsilabenzene, 110852-04-5; 4-methylsilabenzene, 110852-05-6; 1-silylsilabenzene, 110852-06-7; 2-silylsilabenzene, 110852-07-8; 3-silylsilabenzene, 110852-08-9; 4-silylsilabenzene, 110852-09-0; 1-methoxysilabenzene, 110852-10-3; 2-methoxysilabenzene, 110852-11-4; 3-methoxysilabenzene, 110852-12-5; 4-methoxysilabenzene, 110852-13-6; 1-carboxysilabenzene, 110852-14-7; 2-carboxysilabenzene, 110852-15-8; 3-carboxysilabenzene, 110852-16-9; 4-carboxysilabenzene, 110852-17-0; silabenzene, 289-77-0.

Supplementary Material Available: Geometries, electronic energies and dipole moments, and q_σ, q_π, and $q_{\mathrm{Ph-X}}$ values for substituted compounds of both benzene and silabenzene (17 pages). Ordering information is given on any current masthead page.

Four- and Five-Coordinate Tin(II) (Stannylene) Compounds: Crystal and Molecular Structures of $W(CO)_5\{SnCl_2(OC_4H_8)\}$ and $W(CO)_5\{SnCl_2(OC_4H_8)_2\}$

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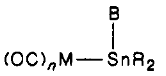
Photolysis of a tetrahydrofuran (THF) solution of tungsten hexacarbonyl and tin(II) chloride gives $W(CO)_5\{SnCl_2(OC_4H_8)_2\}$ which loses THF on heating to produce $W(CO)_5\{SnCl_2(OC_4H_8)\}$. Both complexes have been characterized by X-ray crystallography. Crystals of $W(CO)_5\{SnCl_2(OC_4H_8)\}$ belong to the triclinic space group $P\bar{1}$ (No. 2) with $a = 6.668$ (2) Å, $b = 9.791$ (4) Å, $c = 12.583$ (2) Å, $\alpha = 70.49$ (2)°, $\beta = 89.03$ (1)°, $\gamma = 77.67$ (2)° at 130 K, $Z = 2$, $R = 0.045$, and $R_w = 0.051$. The structure consists of a six-coordinate tungsten and an irregular, four-coordinate tin. Yellow crystals of $W(CO)_5\{SnCl_2(OC_4H_8)_2\}$ belong to the triclinic space group $P\bar{1}$ (No. 2) with $a = 9.589$ (9) Å, $b = 10.704$ (5) Å, $c = 10.856$ (8) Å, $\alpha = 69.06$ (6)°, $\beta = 86.03$ (7)°, $\gamma = 66.41$ (6)° at 130 K, $Z = 2$, $R = 0.052$, and $R_w = 0.057$. The structure consists of a six-coordinate tungsten and a five-coordinate tin with distorted trigonal-bipyramidal geometry (pseudoaxial O–Sn–O angle = 160.1 (2)°). The major change in adding THF to $W(CO)_5\{SnCl_2(OC_4H_8)\}$ is an ca. 0.13 Å increase in the Sn–O bond length; the Sn–W bond length shows only a slight elongation (0.02 Å). Very little change in the angular distribution of ligands about tin accompanies the change in tin coordination number. The THF appears to add to a vacant tin coordination site in $W(CO)_5\{SnCl_2(OC_4H_8)\}$.

Introduction

Initial attempts to prepare stannylene complexes 1 of group 6 and other transition-metal carbonyls resulted in the isolation of compounds that contained donor solvent molecules (B) coordinated to tin.[1] Only with bulky or donor substituents (R) was it possible to isolate examples of structure 1.[2] The majority of characterized stannylene complexes with additional donor groups bonded to tin involve four-coordinate tin with structure 2.[2,3] The few examples of stannylene complexes of type 3 with five-coordinate tin involve polydentate ligands (for example, a porphyrin dianion,[4] acetylacetonate[5]) bound to tin.

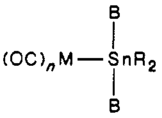
$(OC)_nM—SnR_2$

1



$(OC)_nM—SnR_2(B)$

2



$(OC)_nM—SnR_2(B)_2$

3

In the course of our studies of main group/transition metal interactions,[6] we had occasion to examine the structural nature of the $W(CO)_5\{SnCl_2(THF)_n\}$ (THF is tetrahydrofuran) system. Previous reports indicated that photolysis of tungsten hexacarbonyl in tetrahydrofuran in the presence of tin(II) chloride yields products formulated as the solvent-free $W(CO)_5\{SnCl_2\}$ ($n = 0$)[7] or as the solvate $W(CO)_5\{SnCl_2(THF)\}$.[8] Studies of the ^{119}Sn NMR spectra of the latter complex in benzene solution indicated that there was a marked change produced by adding THF (chemical shift altered from −54.6 to −209.4 ppm; ^1J (^{119}Sn, ^{183}W) changed from 1440 to 1594 Hz) and that a second species, formulated as $W(CO)_5\{SnCl_2(THF)_n\}$, was formed.[9] Here we report on the unambiguous preparations of $W(CO)_5\{SnCl_5(THF)\}$ (4) and $W(CO)_5\{SnCl_2(THF)_2\}$ (5) and their structural characterization by X-ray crystallography. Compound 5 is the first example of a compound of type 3 in which only monodentate ligands are present on tin, and 4 and 5 are the first structurally characterized pair

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