

THEORETICAL STUDIES OF DISILABENZENES *

KIM K. BALDRIDGE and MARK S. GORDON

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105 (U.S.A.)

(Received January 24th, 1984)

Summary

Ab initio calculations have been carried out on the three isomers of disilabenzene. All three structures display significant delocalization, with the most delocalized and most stable being predicted to be the *meta* (1,3) isomer. The relative stabilities are rationalized with the aid of contour plots of the occupied π molecular orbitals and the contributions of various Kékulé structures to each isomer.

I. Introduction

In the past few years there has been an increased interest, both experimental [1] and theoretical [2,3], in unsaturated silicon-containing compounds but, relatively few papers have appeared on the subject of aromatic silicon species. Blustin [2] and Schlegel [3] found silabenzene to be somewhat less delocalized (aromatic) than benzene, and Gordon, Boudjouk, and Anwari [4] analyzed the isoelectronic cyclic anions. Because several groups are attempting to synthesize aromatic silicon species [1], it is of interest to pursue calculations on a variety of potentially aromatic structures. The major goal of the present work is to investigate the possibility of the aromaticity in the three silicon-disubstituted benzene molecules: 1,2- 1,3- and 1,4-disilabenzene. The $4n + 2\pi$ electron network in each of these three molecules may be compared with the isoelectronic reference molecule benzene.

II. Computational methodologies

All geometries have been optimized with the STO-2G basis set [5], using the optimization methods in GAUSSIAN80 [6]. STO-2G has been previously shown to give reliable structures for molecules of the type of interest here [4]. Following the STO-2G geometry optimizations, single point energy calculations were performed

* Dedicated to Professor Makoto Kumada for his many years of outstanding research and teaching in the field of organometallic chemistry.

using the 3-21G basis set [7] at the optimized geometry (denoted 3-21G//STO-2G). Molecular orbital contour plots, used as an aid in the discussion of the results, were drawn using the plotting program PLTORB [8]. As for previous molecules [4], a quantitative measure of the delocalization stabilization is estimated using the appropriate bond separation reactions [9] for each of the three isomers.

III. Results and discussion

A. Geometries

The predicted angles and bond lengths for 1,2-, 1,3-, and 1,4-disilabenzene are shown in Fig. 1-3, respectively. In calculating these geometries, C_{2v} symmetry was assumed for the *ortho* and *para* isomers, while the *meta* structure was limited to C_s symmetry. Note that for two of the isomers the geometry optimization resulted in higher symmetry than originally assumed: C_{2v} for *meta* and D_{2h} for *para*.

In general, all three structures display some degree of delocalization, since all ring bond lengths are in between the corresponding isolated single and double bond lengths (see Table 1). For 1,2-disilabenzene, comparison of Fig. 1 and Table 1 superficially suggests that the geometry is closest to a Kékulé structure in which the Si-Si and two C-C bonds are "double", since these bond lengths are close to the isolated double bond lengths. More careful analysis, however, reveals that the C-Si and remaining C-C bonds are only slightly longer than the average of a single and double bond (1.818 and 1.428 Å, respectively). This implies that there is, in fact, significant delocalization of the π -electron density in this molecule.

Since it is known that the disilene molecule is nonplanar, a force field was computed for the 1,2-disilabenzene to determine if the structure was planar. This computation yielded a positive definite force constant matrix indicating that, indeed, the molecule is planar. The planarity of the Si=Si group in 1,2-disilabenzene is further evidence for conjugation within the six electron π system.

In the 1,3-structure, all of the predicted bond lengths are slightly less than the average of the corresponding isolated single and double bonds. Indeed, the carbon-carbon bond lengths are the same as those predicted for benzene. This suggests strong delocalization in this structure. Similarly, the silicon-carbon bonds in the 1,4-isomer are closer to double than single in length, and the carbon-carbon bonds are actually shorter than those in benzene.

TABLE 1
PROTOTYPE BOND LENGTHS

Prototype	Bond	Length (Å)
Si ₂ H ₄ ^a	Si=Si	2.109
Si ₂ H ₆	Si-Si	2.348
SiH ₂ CH ₂	C=Si	1.707
SiH ₃ CH ₃	C-Si	1.929
C ₂ H ₄	C=C	1.318
C ₂ H ₆	C-C	1.538
C ₆ H ₆	CC	1.398

^a Assumed planar.

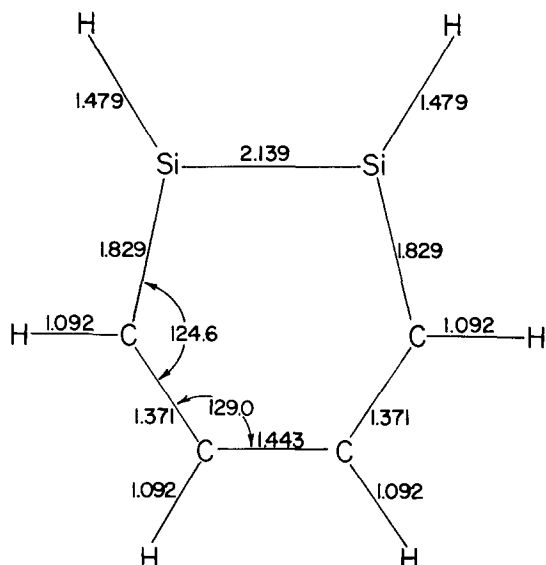


Fig. 1. Molecular structure of 1,2-disilabenzene (bond lengths in Å, angles in degrees).

B. Energetics

The total and relative energies for the disilabenzene isomers are listed in Table 2. While the generally less reliable minimal basis set predicts the *ortho* isomer to be well below the other two, the more extensive split valence basis set finds the three structures to be much closer to each other in energy, with the *meta* isomer slightly more stable than *ortho*. Indeed, the 3-21G predictions are more consistent with the strong delocalization in the *meta* and *para* structures, as noted in the preceding subsection.

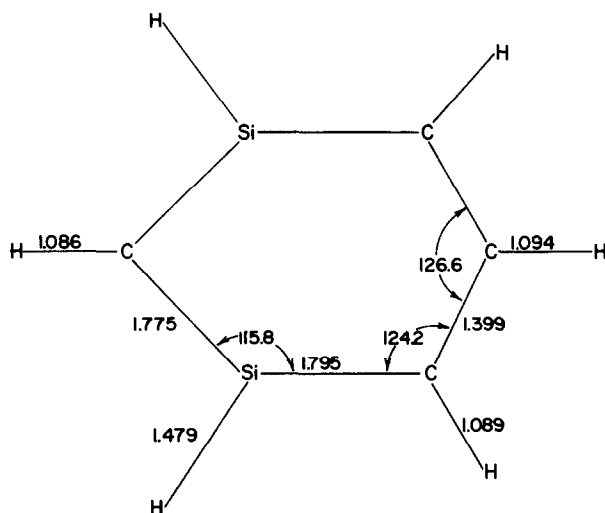


Fig. 2. Molecular structure of 1,3-disilabenzene (bond lengths in Å, angles in degrees).

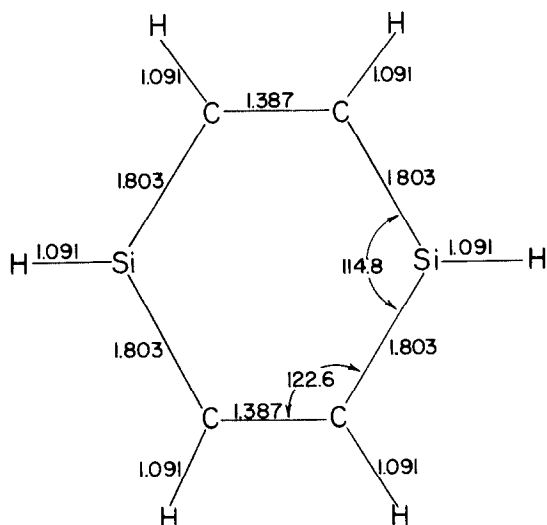


Fig. 3. Molecular structure of 1,4-disilabenzene (bond lengths in Å, angles in degrees).




A method used previously [3,4] to provide a quantitative measure of the delocalization stabilization in potentially aromatic compounds is the calculation of the ΔE for the appropriate bond separation reaction [9]. These bond separation reactions and the calculated stabilization energies are summarized in Table 3. While 3-21G consistently predicts smaller bond separation energies, the trends are basically the same for the two basis sets: By this measure 1,3-disilabenzene is the most stabilized by delocalization, and the 1,2-isomer is the least stabilized relative to the corresponding isolated prototype bonds. To place these results in the perspective of related molecules, the ratios of the calculated bond separation energies to that of benzene are listed in the last two columns of Table 3. At the 3-21G level, the *meta*-, *para*-, and *ortho*-isomers are 80, 62, and 38% as stable as benzene. Note also that mono-silabenzene [4] has nearly the same bond separation energy as *meta*-disilabenzene at this same level of computation.

The philosophy of the bond separation reaction is to measure the stability of a parent molecule relative to its simplest isolated prototypes. From this point of view, it is worth noting that the 1,3- and 1,4-isomers are measured against identical products, while the products for the 1,2-isomer are different and more stable (i.e., disilene + ethylene vs. two silaethylenes). This is the source of the quantitative

TABLE 2
TOTAL AND RELATIVE ENERGIES FOR SILABENZENES

Isomer	Total energy (Hartree)		Relative energy (kcal/mol)	
	STO-2G	3-21G	STO-2G	3-21G
<i>ortho</i>	-703.75147	-728.84107	0.0	0.0
<i>meta</i>	-703.70280	-728.84426	30.5	-2.0
<i>para</i>	-703.69859	-728.82702	33.2	8.8

TABLE 3
BOND SEPARATION REACTIONS^a

		$\Delta E(3-21G)$		$\Delta E(STO-2G)$		R^b	
		X = C	X = SI	X = C	X = SI	3-21G	STO-2G
(A)	 $+ 2XH_4 + 4CH_4 \rightarrow 1X_2H_4 + 2C_2H_4 + 1C_2H_6 + 2CH_3XH_3$	59	22.5	73	37.3	0.38	0.51
(B)	 $+ 2XH_4 + 4CH_4 \rightarrow 2XH_2CH_2 + 1C_2H_4 + 1C_2H_6 + 2CH_3XH_3$	59	47.2	73	57.8	0.80	0.79
(C)	 $+ 2XH_4 + 4CH_4 \rightarrow 2XH_2CH_2 + 1C_2H_4 + 1C_2H_6 + 2CH_3XH_3$	59	36.4	73	55.1	0.62	0.75

^a Energies in kcal/mol.

^b R = ratio of $\Delta E(X = SI)/\Delta E(X = C)$.

difference between the two measures of relative stabilities presented in Tables 2 and 3. Both approaches, however, predict the most stable isomer to be *meta*.

C. Molecular orbitals

Schematics of the π -molecular orbitals, with their appropriate LCAO coefficients, for the three molecules considered here are presented in Fig. 4–6, and actual contour plots of the same orbitals are displayed in Fig. 7–9. In these silicon disubstituted benzenes, the introduction of the silicon atoms splits the benzene e_{1g} pair in D_{6h} symmetry into b_1 and a_2 orbitals in C_{2v} symmetry. Since the lowest π -MO is also b_1 in C_{2v} , we will refer to the higher energy orbital as b'_1 .

To the extent that the lowest $\pi(b_1)$ -MO is localized, one would expect strong polarization of the electron density in this orbital toward the carbons. Examination of the LCAO coefficients (Fig. 4) and contour plot (Fig. 7) demonstrate this strong polarization for the *ortho* isomer. While the same orbital is clearly polarized in the other isomers as well (Fig. 5, 6, 8, 9), the delocalization is much more apparent here.

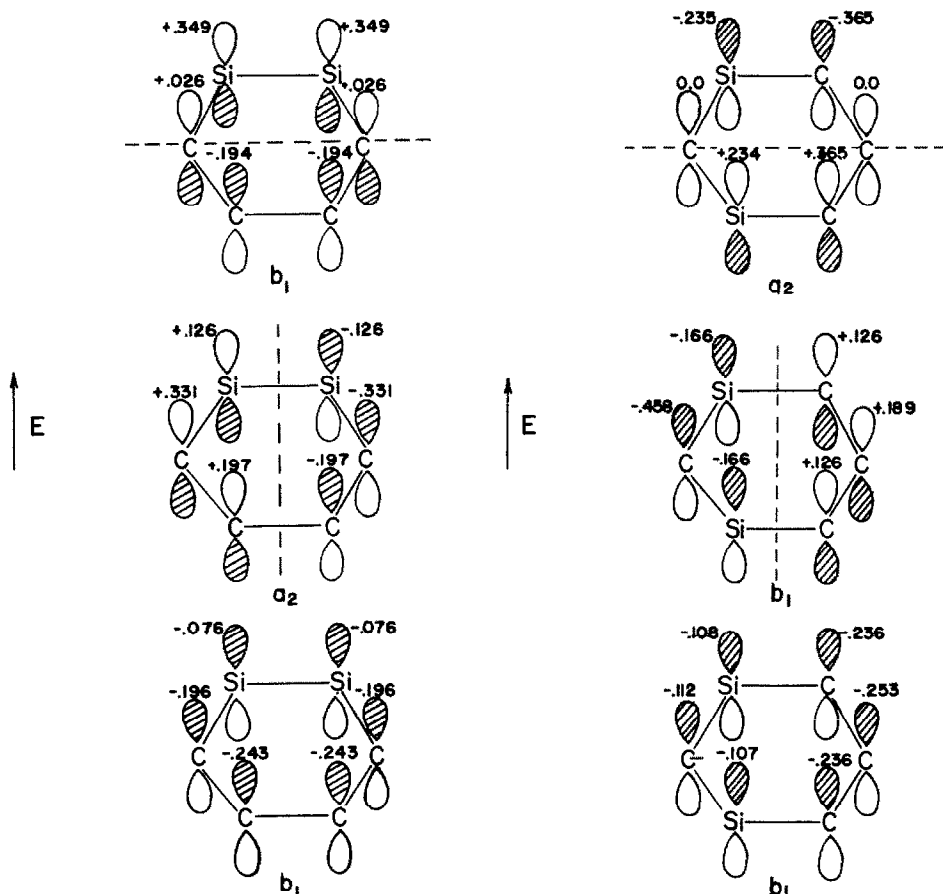


Fig. 4. Schematics of π -MO's in 1,2-disilabenzene. Coefficients are from 3-21G outer valence π -AO's.

Fig. 5. Schematics of π -MO's in 1,3-disilabenzene. Coefficients are from 3-21G outer valence π -AO's.

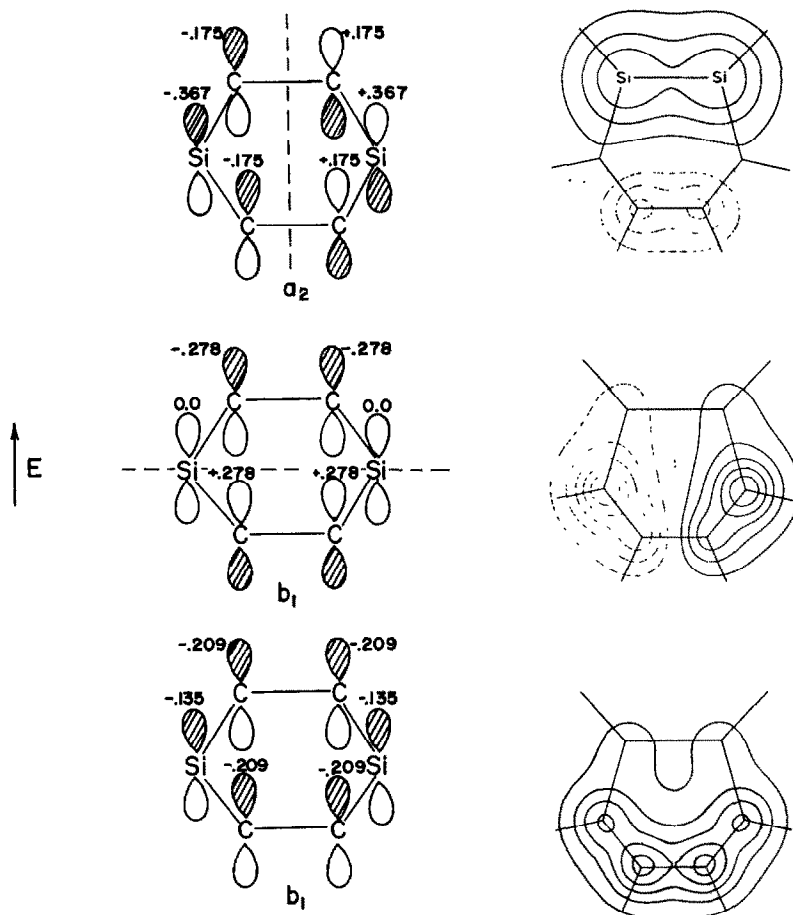


Fig. 6. Schematics of π -MO's in 1,4-disilabenzene. Coefficients are from 3-21G outer valence π -AO's.

Fig. 7. Contour plots for π -MO's in 1,2-disilabenzene. Plots taken at 0.7 Å above the molecular plane.

The relative ordering of the a_2 and b'_1 orbitals is largely determined by their nodal characteristics. In the 1,2-isomer the a_2 MO has a node separating the two silicons, so this orbital lies lower in energy. In contrast, the b'_1 node passes through the two silicons in the 1,4-isomer. This causes b'_1 to lie lower than a_2 in which the node separates two pairs of carbon atoms. In 1,3-disilabenzene the lower lying b'_1 MO has a node separating two silicon-carbon pairs. As one might expect, the 3-21G a_2 - b'_1 orbital energy splitting is much larger in the 1,4-isomer (0.16 Hartree) than in the 1,2- and 1,3-species (0.025 and 0.049 Hartree, respectively). In all three isomers, the highest lying MO (b'_1 in 1,2- and a_2 in 1,3- and 1,4-) has the largest silicon contribution. In the 1,2- and 1,4-isomers this orbital is strongly polarized toward the silicons, while the 1,3-MO is more delocalized. Indeed, the delocalization is most apparent in all orbitals of the latter isomer, and this is consistent with its stability.

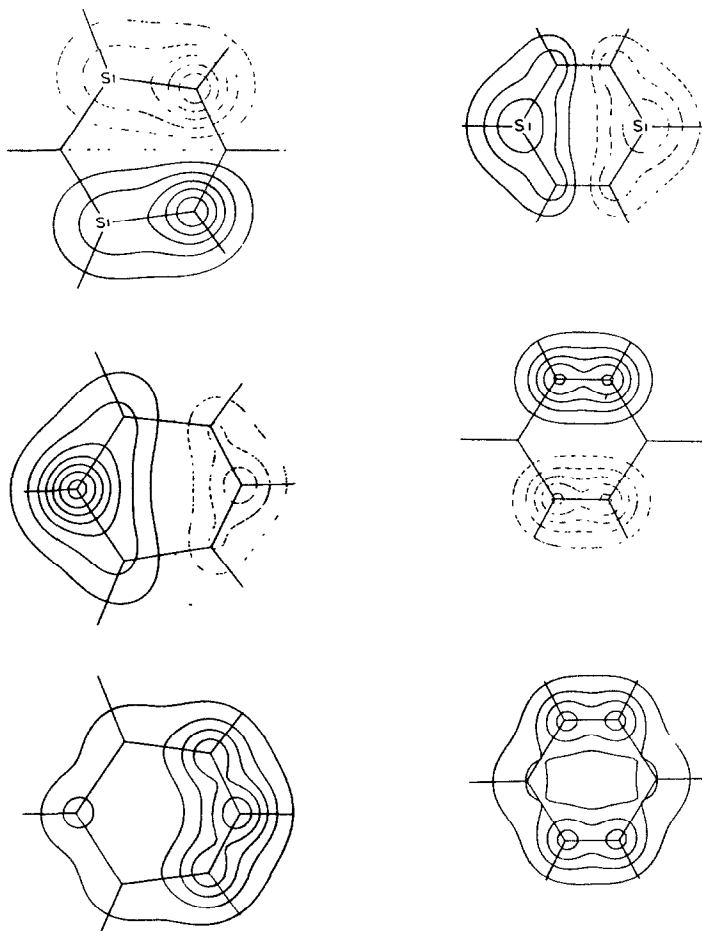


Fig. 8. Contour plots for π -MO's in 1,3-disilabenzene. Plots taken at 0.7 Å above the molecular plane.

Fig. 9. Contour plots for π -MO's in 1,4-disilabenzene. Plots taken at 0.7 Å above the molecular plane.

D. Electron densities

The 3-21G electron density distributions [10] for benzene and the three disilabenzene isomers are displayed in Fig. 10. As expected all three isomers exhibit a strong charge separation, with rather positive silicons and negative carbons, although this is less so for the *ortho*-isomer. Apparently, this polarization occurs almost exclusively in the σ space, since the π -electron density distribution is remarkably close to neutral in all three isomers. Only in the 1,3-isomer is there much π -charge separation, and here one sees charge alternation such that the carbon β to both silicons has a positive charge in the π space.

IV. Conclusions

Of the three molecules studied, 1,3-disilabenzene appears to be the most stable based on both direct energy comparisons with the other isomers and on the measure

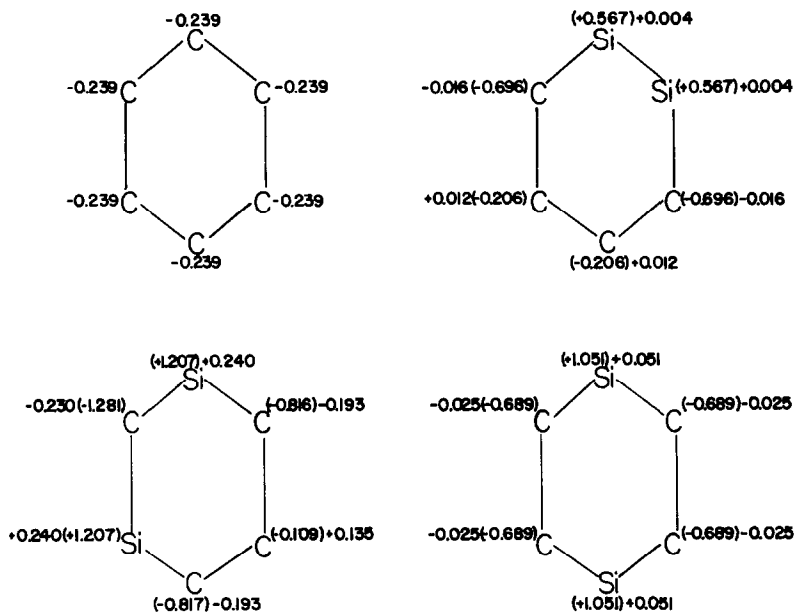


Fig. 10. 3-21G π -electron (total) charge densities in disilabenzenes.

of aromaticity using bond separation reactions. The latter is supported by the predicted structure, in which all of the bond lengths are closer to the corresponding double than single bond lengths. The 1,4-isomer is the least stable by direct energy comparison and in the middle on the scale of aromaticity. The latter is again supported by the molecular structure. It is also noteworthy that these two isomers both regain substantial symmetry upon geometry optimization in order to maximize their delocalization stabilization. Because of the Si-Si linkage, the 1,2-isomer appears to be less delocalized than the other two.

To rationalize the difference between the aromatic character exhibited by the 1,3- and 1,4-isomers, consider the zwitterionic contributions to the Kékulé' structures of each molecule in Fig. 11 and 12.

There are six contributing structures in the case of 1,3-disilabenzene, and only four for 1,4-disilabenzene since the structures having negative charge on silicon are unfavorable in the latter isomer. The electron density distributions for the 1,3- and 1,4-disilabenzenes reinforce this point. In 1,3-disilabenzene, there is a partial positive charge on the β carbon and a negative charge on the α carbons, as suggested in Fig. 11. In 1,4-disilabenzene, there is a negative charge on each carbon atom and positive charges on the silicons. Similarly, note that, in addition to its inability to significantly delocalize the Si-Si linkage, the 1,2-isomer will also only have four contributing zwitterionic structures (Fig. 13).

Finally, it is important to recognize that this work has considered only relative thermodynamic stabilities. Particularly in view of the rather large charge separations, kinetic stability (or instability) is quite another matter.



KEKULE STRUCTURES

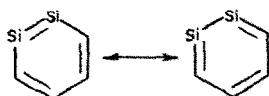


KEKULE STRUCTURES



Fig. 11. Contributing Kékulé structures in 1,3-disilabenzene.

Fig. 12. Contributing Kékulé structures in 1,4-disilabenzene.



KEKULE STRUCTURES



Fig. 13. Contributing Kékulé structures in 1,2-disilabenzene.

Acknowledgements

This work was supported by a grant (13025-AC6) from the Petroleum Research Fund, administered by the American Chemical Society. The authors have benefitted from several helpful discussions with Dr. M.W. Schmidt and Professor P. Boudjouk. The computer time made available by the North Dakota State University Computer Center is gratefully acknowledged.

References

- 1 T.J. Barton and D.S. Bonasiak, *J. Am. Chem. Soc.*, 99 (1977) 5199; T.J. Barton and G.T. Burns, *ibid.*, 100 (1978) 5246; H. Bock, A. Bowling, B. Solouki, T.J. Barton and G.T. Burns, *ibid.*, 102 (1980) 429; C.L. Kriel, D.L. Chapman, G.T. Burns and T.J. Barton, *ibid.*, 102 (1980) 841; G. Maier, G. Mihm, and H.P. Reisenhauer, *Angew. Chem. Int. Ed. Engl.*, 19 (1980) 52; B. Solouki, P. Rosmos, H. Bock and G. Maier, *ibid.*, 19 (1980) 51; T.J. Barton, and M. Vuper, *J. Am. Chem. Soc.*, 103 (1981) 6788.
- 2 P.H. Blustin, *J. Organomet. Chem.*, 166 (1979) 21.
- 3 H.B. Schlegel, B. Coleman and M. Jones, *J. Am. Chem. Soc.*, 100 (1978) 6499.
- 4 M.S. Gordon, P. Boudjouk and F. Anwari, *J. Am. Chem. Soc.*, 105 (1983) 4972.
- 5 W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.*, 51 (1969) 2657.
- 6 J.S. Binkley, R.A. Whiteside, R. Krishnan, R. Seeger, D.J. DeFrees, H.B. Schlegel, S. Topiol, L.R. Kahn and J.A. Pople, *Quantum Chemical Programme Exchange*, 13 (1980) 406.
- 7 J.S. Binkley, J.A. Pople and W.J. Hehre, *J. Am. Chem. Soc.*, 102 (1980) 939; M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro and W.J. Hehre, *ibid.*, 104 (1982) 2797.
- 8 K. Ruedenberg, M.M. Gilbert and M.W. Schmidt, Program developed at Iowa State University, unpublished.
- 9 W.J. Hehre, R. Ditchfield, L. Radom and J.A. Pople, *J. Am. Chem. Soc.*, 92 (1970) 4796.
- 10 R.S. Mulliken, *J. Chem. Phys.*, 23 (1955) 1833 and 1841.