Journal of Organometallic Chemistry, 61 (1973) 113–125
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOELECTRON SPECTRA AND MOLECULAR PROPERTIES

XX*. DIMETHYL ETHER, METHOXYSILANE, AND DISILOXANE

H. BOCK and P. MOLLÈRE**
Institut für Anorganische Chemie II der Universität, 6 Frankfurt/Main 70, Theodor-Stern-Kai 7 (Germany)
G. BECKER and G. FRITZ
Institut für Anorganische Chemie der Universität, Karlsruhe (Germany)

(Received March 5th, 1973)

SUMMARY

The photoelectron (PE) spectra of methyl and silyl ethers are assigned and correlated on the basis of CNDO/2-SCF-MO calculations. The dynamic behavior of the individual orbitals is discussed in terms of electronic and geometric perturbations of the ether system.

In considering the chemistry of silicon compounds, attention is often focused on the role of the Si 3*d* orbitals (see, *e.g.*, ref. 2). Thus, Almenningen *et al.*, in reporting the structure of disiloxane[3], suggest that the large bond angle at oxygen is due to the "conjugation of unshared electron pairs on the oxygen atom with *d*-orbitals from the silicon..." However, while *d*-orbital effects may indeed be important, one can readily see from Fig. 1, that in going from methyl ether to methoxysilane to disiloxane, the ether system undergoes at least three other perturbations: differences in effective nuclear charge between carbon and silicon, widening of the bond angle at oxygen, and proposedly[3] a change in the stable equilibrium conformation of the molecules.

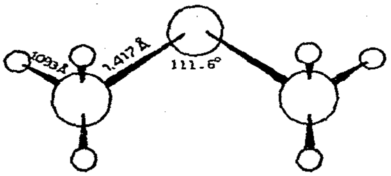
In order to study carefully patterns of change in electronic structure, which may accompany changes in composition and geometry, high resolution photoelectron (PE) spectroscopy is a most valuable technique: able to measure even small shifts in ionization energies, it affords a sensitive probe for observing the effects of various factors upon the electronic energy levels of a molecular system. Assuming the validity of the Koopmans Theorem[4], the measured ionization energies of the three title compounds may be coupled with molecular orbital calculations in order to understand the silicon compounds in terms of a perturbed ether system.

PHOTOELECTRON SPECTRA

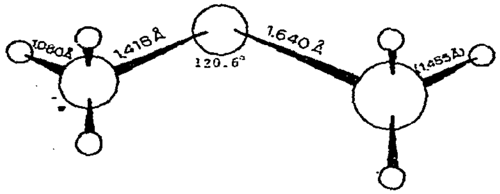
The photoelectron spectra of the three ethers are given in Fig. 2, and their

---

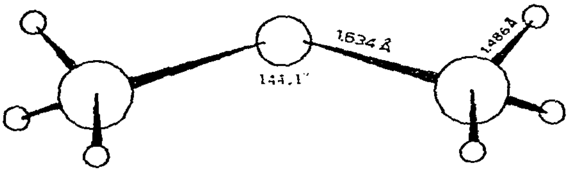
[*] For Part XIX see ref. 1.
[**] Present address: Department of Chemistry, Cornell University, Ithaca, New York, U.S.A. 14850.



H_3COCH_3
"Doubly Eclipsed"



H_3COSiH_3
"Doubly Eclipsed"



$H_3SiOSiH_3$
"Singly Eclipsed"

Fig. 1. Stable equilibrium structures of dimethyl ether, methoxysilane, and disiloxane.

ionization energies are correlated in Fig. 3. (Assignments are according to CNDO/2 MO calculations. *Vide infra.*) The indicated change in orbital sequences (an allowed crossing) may be surprising at first. Indeed, a simple sequential correspondence of the peaks in the spectra of methyl ether and disiloxane has been suggested[5]; however, as is shown below, such a naïve correlation ignores the complexities of the system and involves patterns of change which cannot be rationalized. We believe that molecular orbital calculations provide a more sound basis for the assignments presented in Figs. 2 and 3 and in Table 1.

TABLE 1

ASSIGNED IONIZATION ENERGIES (eV)

Compound	*Orbital assignments and energies*							
	$2b_1$	$4a_1$	$3b_2$	$1a_2$	$2b_2$	$3a_1$	$1b_1$	$2a_1$
H_3COCH_3	10.04	11.93	13.42	14.17	16.2	16.2		
H_3COSiH_3	10.61	11.48	12.48	12.80	15.4	15.4	18.2	
$H_3SiOSiH_3$	11.19	12.42	11.37	12.70	14.45	14.75	17.2	19.5

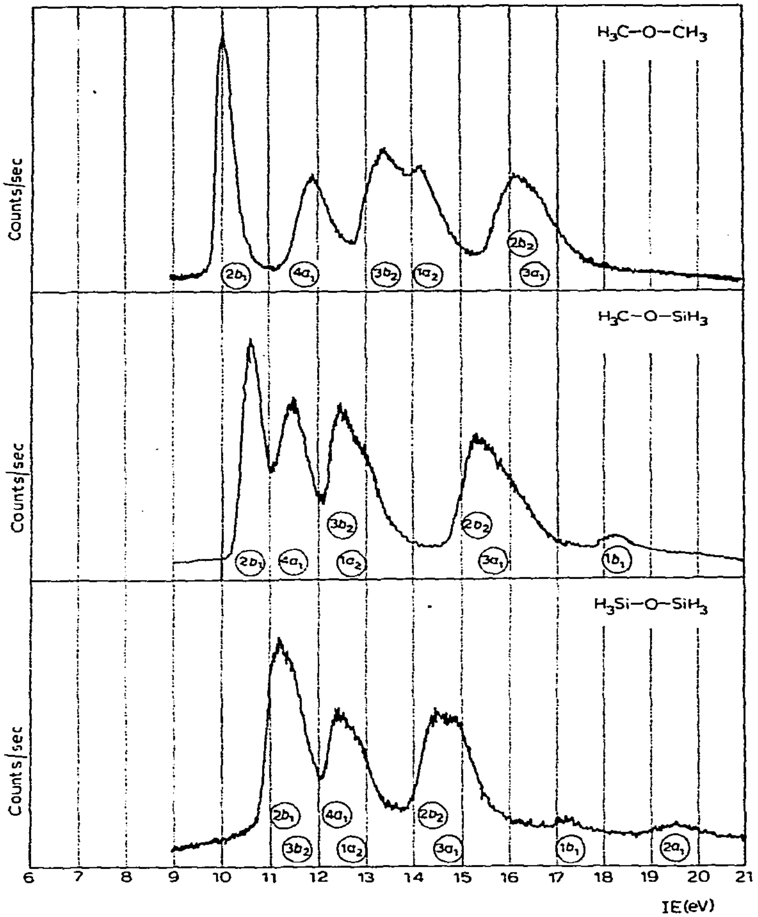


Fig. 2. Photoelectron spectra of dimethyl ether, methoxysilane, and disiloxane.

CALCULATED ORBITAL BEHAVIOR

The observable properties of molecules represent a composite of multiple, inseparable influences. Therefore, the interplay of effects in a progression of related compounds involving several simultaneously changing factors requires judicious analysis. Although it is seldom possible to achieve a real factorization of effects, molecular orbital calculations afford a means for scrutinizing the respective effects of individual factors by artificially constraining all but one. In order to examine thoroughly the series of title compounds [H_3COCH_3 (I), H_3COSiH_3 (II), $H_3SiOSiH_3$ (III)], CNDO/2 calculations[6] (including Si 3*d* orbitals) and extended Hückel calculations[7] (with and without *d*-orbitals in the silicon basis set) were used to obtain orbital sequences for the known geometries of the ethers, as well as to observe separately the effects of conformational change, central angle widening, and the substitution of silicon for carbon*.

---

* A full complement of calculations was only obtained by the CNDO/2 method. Spot checks were made using EHT in order to determine that the CNDO/2 results were not just artifacts of that method; qualitative agreement was found in all cases where both types of calculation were employed.

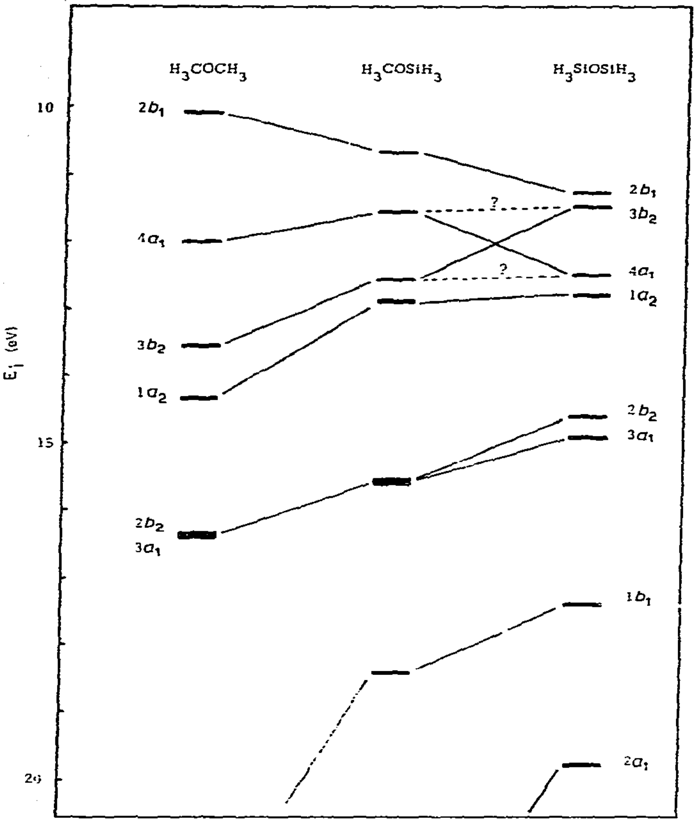


Fig. 3. Correlation of the experimental ionization energies.

Molecular coordinates

Structure determinations of all three molecules have been reported in the literature[3,8,9], and the results are illustrated in Fig. 1. The electron diffraction studies of dimethyl ether [8a] and disiloxane[3] were able to establish the indicated stable equilibrium conformations ("doubly eclipsed" and "singly eclipsed," respectively), but methoxysilane was merely reported to have C_s symmetry[9]. Given the known bond lengths and angles, it was found that both CNDO/2 and EHT calculations correctly predicted the preferred conformations of (I) and (III) on the basis of minimum total molecular energy, although the sensitivity of the total energy to changes in conformation did not prove to be great. Four distinct conformations were considered for methoxysilane. Both MO methods indicated the "doubly eclipsed" conformer to be the most stable, and this geometry was assigned to (II).

Orbital sequences

The sequences of occupied orbitals obtained from the CNDO/2 calculations for the stable equilibrium geometries of (I), (II), and (III) are presented in Fig. 4. The overall similarity in the three MO schemes is to be anticipated: the regular

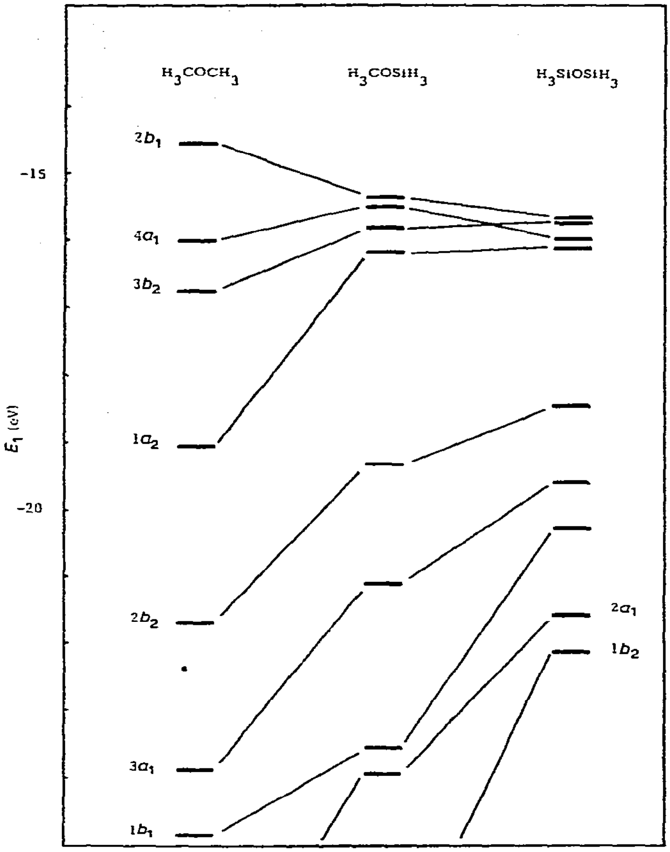


Fig. 4. Calculated orbital sequences for the preferred conformations of the methyl and silyl ethers.

pattern of destabilization on going from the dimethyl to the disilyl compound is a mere reflection of the smaller valence state ionization potentials of silicon, as compared to carbon[10]. The interesting behavior is manifested by the sinking $2b_1$, as well as by the crossing $4a_1$ and $3b_2$ orbitals*. When the measured ionization energies are assigned according to these results, the qualitative agreement between calculations and experiment is excellent. (Compare Figs. 3 and 4, and note that the naïve alternative correlation of the spectra destroys any similarity between predicted and observed behavior in the three highest occupied orbitals.)

All further attention is now directed toward analyzing the patterns of change in the $2b_1$, $4a_1$ and $3b_2$ orbitals.

Conformational changes

The influence of conformational change affords a prime example of how an

---

* In their strictest sense, the symmetry designations of the point group C_{2v} are not applicable to methoxysilane (C_s or C_1). However, the orbitals of H_3COSiH_3 sufficiently resemble those of (I) and (III), that there is virtually no chance of incorrect correlation.

ostensibly superficial effect may have far reaching consequences: although the effect of altering conformation on the total molecular energy is small, the molecular orbitals of interest ($2b_1$, $4a_1$ and $3b_2$) were found to be highly sensitive to such changes*. Thus, in all three cases, changing from a "doubly eclipsed" to a "singly eclipsed" conformation resulted in stabilizing the $4a_1$ orbital and destabilizing the $2b_1$ and $3b_2$ orbitals; moreover, a $4a_1$–$3b_2$ cross-over was found in each case! These patterns are shown for methyl ether in Fig. 5.

Two questions now pose themselves: how should changing conformations affect the orbitals, and why have the molecules adopted their respective conformational attitudes?

Since conversion from one conformer to another simply involves the rotation of H_3C- or H_3Si- groups and does not alter any bonds (in the sense of two-center valence-bond formalism), it may be assumed that the governing effect consists of formally nonbonded interactions which are not invariant to conformational change (see also ref. 12). The interactions which satisfy these criteria are those between 1*s* atomic orbitals of two hydrogens bonded to different heavy atoms, and those between a hydrogen 1*s* orbital and one of the 2*p* atomic orbitals of oxygen which lie in the plane of the molecule. These interactions may be given a quantitative basis according to their overlap integrals[13]. The nonbonded interactions may also be designated as stabilizing (+) or destabilizing (−), depending upon the relative phases of the atomic orbitals within the molecular orbital under consideration.

The behavior of the $3b_2$ orbital of disiloxane is taken as a representative case in

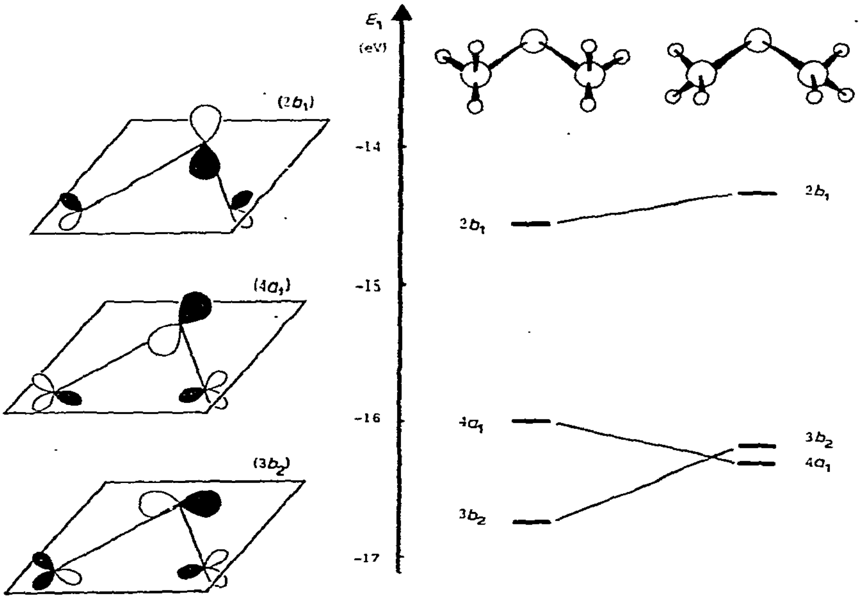


Fig. 5. Conformation dependence of the three highest occupied orbitals of dimethyl ether.

---

* Other strong conformational consequences have been reported by R. Hoffmann *et al.*[11].

point. The significant non-bonded interactions for the two possible C_{2v} conformations ("doubly eclipsed" and "singly eclipsed") are indicated in Fig. 6, and their weighted contributions (positive or negative overlap integrals) are tabulated in Table 2. It is clear that the net effect of all non-bonded interactions in the "doubly eclipsed" conformer is stabilizing, whereas it is destabilizing in the other, thereby accounting for the rise in energy of the $3b_2$ orbital on going from the one conformation to the other. In similar fashion, the conformational dependence of the $2b_1$ and $4a_1$ orbitals may also be explained.

Finally, there is a demonstrable correlation between the stability of a given

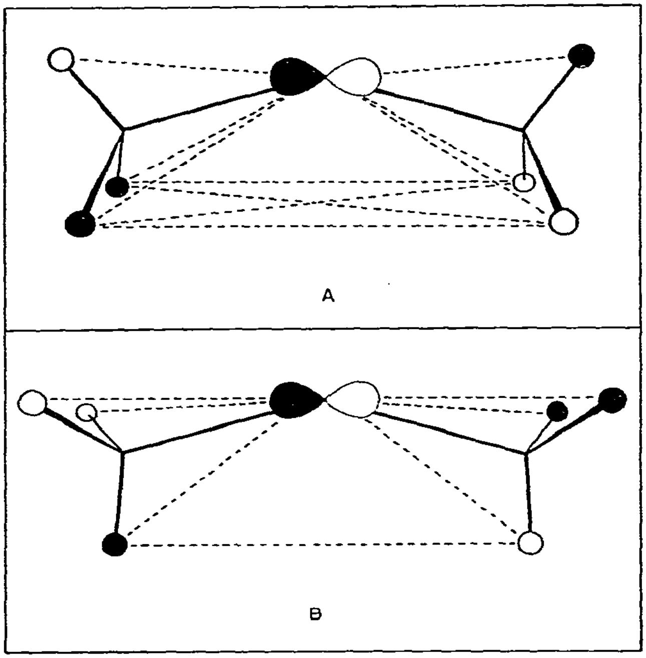


Fig. 6. Significant nonbonded interactions in the $3b_2$ orbital of disiloxane: "doubly eclipsed" conformation (A), and "singly eclipsed" conformation (B).

TABLE 2

CONFORMATION-DEPENDENT NONBONDED INTERACTIONS IN THE $3b_2$ ORBITAL OF DISILOXANE

"Double eclipsed"			*"Singly eclipsed"*		
Type	*Number*	*Weighted effect*	*Type*	*Number*	*Weighted effect*
H–H	2	−0.0086	H–H	1	−0.0186
H–H	2	−0.0022			
H–O(p_y)	2	−0.0286	H–O(p_y)	4	−0.0260
H–O(p_y)	4	+0.0210	H–O(p_y)	2	+0.0185
Net		+0.0052	Net		−0.0856

conformation and the achievement of optimum charge distribution, in so far as the average deviation from electrostatic neutrality (per atom) may be taken as a measure of charge delocalization. That is, minimum average deviation from neutrality represents the situation in which concentration of localized charge is best alleviated (*i.e.*, Pauling's concept of electroneutrality[14]). The data in Table 3 reveal that the known stable equilibrium conformations of dimethyl ether and disiloxane both correspond to conditions of optimal electroneutrality although the calculated differences are rather small.

Incidental to the charge distribution data is one last point of interest: the residual negative charge of the hydrogen atoms, deriving both from inductive effects and from hyperconjugative electron transfer from the oxygen center. These charges are fully an order of magnitude greater in disiloxane (Table 3). It is well imaginable that the central angle widening in the silyl derivatives may as much be a mechanism to relieve coulombic repulsions owing to critical charge concentration within the interior angle of the heavy atom skeleton[15], as it is partially a result of oxygen–silicon $p\pi$–$d\pi$ interaction. (The adoption of the “singly eclipsed” conformation in the case of disiloxane may also be viewed as making a secondary contribution in this connection.)

Central angle widening

By adopting the measured values for all other structural constants and allowing

TABLE 3

CALCULATED CHARGE DISTRIBUTIONS

Compound	*Atom*	*Charge per atom*		
		“Doubly eclipsed”	*“Staggered”*	*“Singly eclipsed”*
H_3COCH_3	O	−0.2070	−0.2085	−0.2089
	C	+0.1370	−0.1406	+0.1376
	H	−0.0051	−0.0070	−0.0142
	H	−0.0142	−0.0151	−0.0094
	H	−0.0142	−0.0151	−0.0094
	C	+0.1370	+0.1366	+0.1375
	H	−0.0051	−0.0147	−0.0143
	H	−0.0142	−0.0084	−0.0094
	H	−0.0142	−0.0084	−0.0094
	Ave.	0.0609	0.0616	0.0611
$H_3SiOSiH_3$	O	−0.2200	−0.2211	−0.2201
	Si	+0.5459	+0.5461	+0.5453
	H	−0.1417	−0.1419	−0.1484
	H	−0.1471	−0.1473	−0.1434
	H	−0.1471	−0.1473	−0.1434
	Si	+0.5459	+0.5464	+0.5453
	H	−0.1417	−0.1486	−0.1484
	H	−0.1471	−0.1432	−0.1434
	H	−0.1471	−0.1432	−0.1434
	Ave.	0.2426	0.2427	0.2423

only the central angle at oxygen to vary, it is now possible to examine the relationship between this lone factor and the energies of the three orbitals in question. Disiloxane provides a propitious illustration here, for the inclusion of *d*-orbital effects allows some critical comment concerning their influence on geometry. The behavior of the $2b_1$, $4a_1$, and $3b_2$ orbitals as a function of the central angle is displayed in Fig. 7. The $2b_1$ orbital is seen to be essentially independent, whereas the $3b_2$ and $4a_1$ react in strong but opposite manners. These results closely parallel those of Gimarc regarding AB_2 systems, and may be explained in terms of his arguments[16,*].

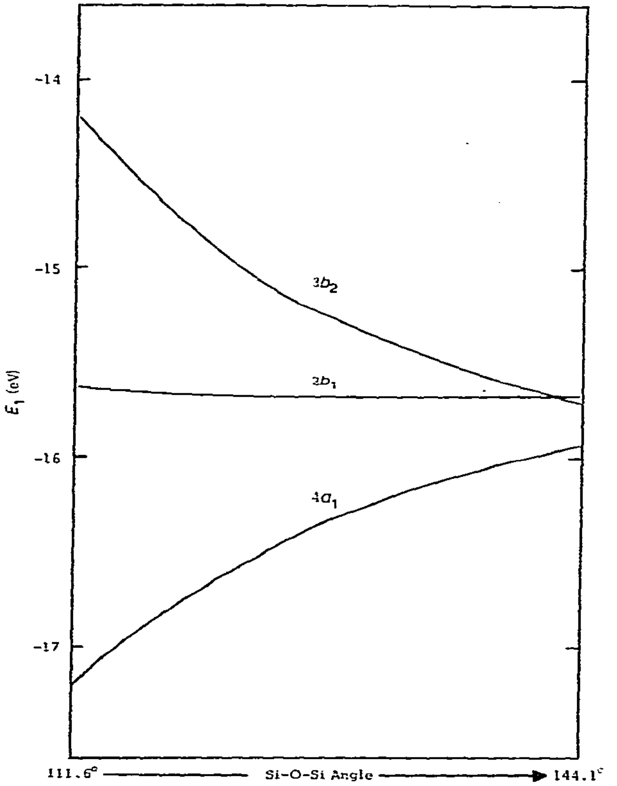


Fig. 7. Correlation diagram for angle widening in disiloxane.

The involvement of the vacant *d*-orbitals on silicon warrants further comment. The acceptor capacity of these atomic orbitals (d_{xz}, d_{xy}) certainly operates in the $2b_1$ molecular orbital to delocalize the "lone pair" at oxygen (p_x) via a $(p \rightarrow d)\pi$-interaction, although without bearing on the size of the central angle. The $3b_2$, the one orbital which is significantly stabilized upon widening of the angle, possesses a symmetry which precludes any such π-interaction. Only in the case of the $4a_1$ orbital can the enlargement of the bond angle at oxygen be expected to enhance any benefit derived

---

[*] That the $2b_1$ orbital is not entirely independent of geometry is due to the fact that the electron pair at oxygen is not a true "lone pair," but is partially delocalized through direct conjugation and hyperconjugation; *cf.* ref. 17.

from *d*-orbital participation: as the central angle increases, the $O(p_z)$–$Si(d_{yz})\pi$-interaction increases; in the limit of linearity, the $4a_1$ and $2b_1$ orbitals would be degenerate, and would enjoy equivalent $p \rightarrow d\pi$ conjugation. Nevertheless, the $4a_1$ orbital is the very one which is strongly destabilized by widening the angle at oxygen. Thus, while the presence of *d*-orbitals may be expected to contribute to the enlarging of the central angle, they probably do not play the dominant role.

Silicon effects

It is now appropriate to consider the energetic consequences stemming solely from the replacement of carbon atoms by silicon. The most obvious difference introduced is the more positive potential energy of the silicon valence orbitals, whose influence within the actual molecular milieu was indicated earlier (Figs. 3 and 4), and may be associated with the "inductive effect". A second and equally significant change is the expansion of the valence basis set by the presence of vacant 3*d*-orbitals, whose acceptor capacity serves to modify the electron-donating inductive effect; in accordance with the maxim of energy matching[18], the involvement of these acceptor *d*-orbitals is greatest in the higher occupied molecular orbitals. The first three orbital sequences of Fig. 8 display the calculated effects due to the introduction of silicon atoms into an ether system with fixed central angle and conformation. However, a complication necessarily arises from the conformational perturbation inherent within a "doubly eclipsed" disiloxane; to eliminate this extraneous factor and thereby simplify the consideration of silicon effects alone, a fourth orbital sequence was calculated, which differs from the third only in that disiloxane has assumed its preferred conformation. Thus, for the series, dimethyl ether ("doubly eclipsed"), methoxysilane ("doubly eclipsed"), and disiloxane ("singly eclipsed"), the $2b_1$ orbital is seen to ex-

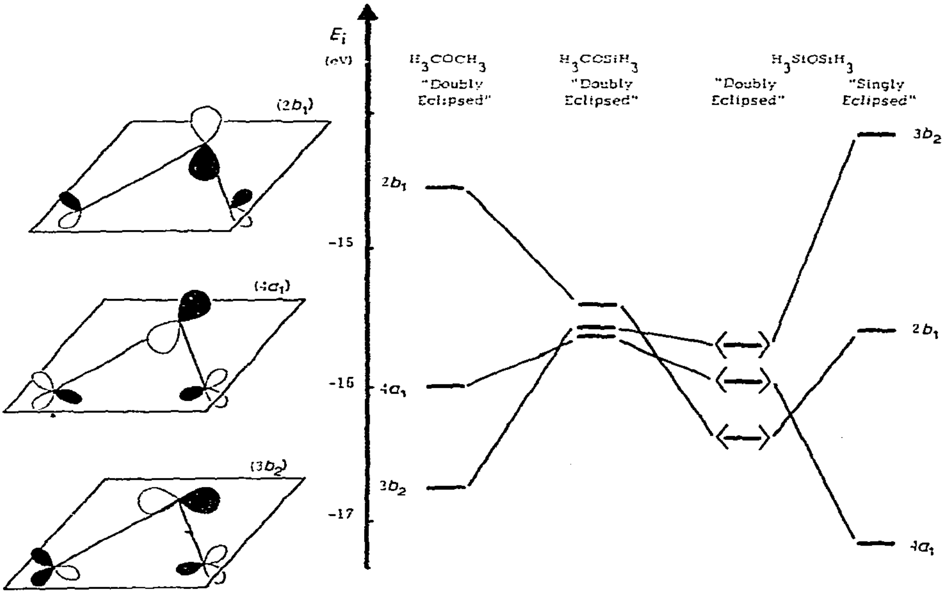


Fig. 8. The effects of substituting silicon for carbon. The bond angle at oxygen is fixed at 111.6°.

perience a monotonic stabilization; this trend may be straightforwardly interpreted as owing to the dominance of the effect of delocalizing the O(p_x) "lone pair" into the d-orbitals of silicon, an interaction which both energy and symmetry criteria favor most in this particular molecular orbital. On the other hand, the $3b_2$ orbital undergoes regular destabilization, and the inductive effect is clearly the controlling factor here. By contrast, the behavior of the $4a_1$ orbital is ambivalent. This may well be due to a more delicate balance of the mutually opposite inductive and mesomeric effects of silicon substitution. In this case, where the bent geometry of the molecule constrains the extent of $p\pi$–$d\pi$ interaction, it appears that the inductive effect is initially dominant (H_3COSiH_3), but is subsequently overridden ($H_3SiOSiH_3$).

Composite orbital behavior

To recapitulate, the artificial factorization of effects has allowed the assessment of the individual contribution of each. The deceptively minor differences in conformation proved to exert a profound influence on the higher occupied molecular orbitals, even to the point of changing their order (Fig. 3). Indeed, the assumption of identical conformational attitudes for the three ethers (*i.e.*, all "doubly eclipsed" or all "singly eclipsed"), while offering only inacceptable correlations with the PE spectra, never requires an orbital crossing, so that the $4a_1$–$3b_2$ inversion in disiloxane must be due to conformation (Fig. 2). The effect of widening the angle at oxygen (Fig. 5) was found to be just that predicted by simple Walsh diagrams[16,19], and appears to be in no way peculiar to these compounds. Lastly, the substitution of silicon for carbon was observed to produce a general inductive destabilization which is countermanded to varying degrees in the higher molecular orbitals through mesomeric electron acceptance by vacant $3d$-orbitals (Fig. 2); in particular, the trend exhibited by the $2b_1$ orbital is primarily a function of $p\pi$–$d\pi$ delocalization of the "lone pair."

Viewed in sequence, the separate effects of silicon substitution and conformational change (Fig. 8), coupled with that of angle widening (Fig. 7), clearly describe the composite behavior of the three highest orbitals presented in Figs. 3 and 4.

The qualitative compatibility between measurements and calculations is undeniable here. Nevertheless, the correctness of the spectral assignments should be viewed within the framework of certain limitations. It should be particularly considered, that while the calculated orbital sequences are for preferred conformations, actual gaseous samples of the compounds might consist of mixtures of conformers. The question of these assignments could well be further elucidated by a study of the analogous sulfur compounds. The structures of dimethyl sulfide and disilyl sulfide have already been determined[20,21], and the smaller ionization energy of the sulfur "lone pairs" should provide a clear separation of the peaks in the first band of the disilyl derivative.

SOME REMARKS ON ELECTRONIC INTERACTIONS IN COVALENT MOLECULES

It is characteristic of many derivatives of non-metallic elements, that they suffer from high electron density at given centers; the alleviation of this unfavorable condition clearly requires some means for optimizing the distribution of negative charge and reducing coulombic electronic repulsions. In this connection, the above set of three ethers may be exemplary of a broader class of covalent compounds, as it illustrates how a variety of model mechanisms may operate to correct electron concentrations. Angle widening may reduce bond–bond repulsions, as well as serving to better distribute localized electron density over the "surface" of a central atom. Conformational change can optimize nonbonded interactions and lead to improved charge delocalization. Finally, the transfer of electron density to nearby sites is achievable both by hyperconjugation and by direct conjugation with vacant atomic orbitals. In general, these factors may be broadly classified as those involving some type of conjugation and those involving structural change. However, these classes are not necessarily independent, and the overriding point of this work may simply be the complexity of the interplay of effects which ultimately determines the properties of molecular states.

EXPERIMENTAL

Molecular orbital calculations were carried out using the CNDO/2[6] and extended Hückel[7] methods.

The PE spectra were measured with a Perkin–Elmer PS-16 employing a 127° electrostatic deflection analyzer.

Dimethyl ether

Dimethyl ether of the highest commercial purity (*puriss.*) was purchased from Fluka, AG.

Disiloxane[22].

Monobromosilane[23] (0.095 mole), prepared by the cleavage of phenylsilane with anhydrous HBr and purified by fractional condensation, was carefully hydrolyzed with 10 ml water in a 2 l flask. The disiloxane was washed with water and thereafter freed of residual moisture and HBr by repeated fractional condensation at −126°. The purity of the product was ascertained by means of infrared spectroscopy[24] and molecular weight determination. (Calcd.: 78.21; found: 78.8.) The yield was 48%.

Methoxysilane[25].

Iodosilane was prepared by cleaving chlorophenylsilane with anhydrous HI[26], purified by fractional condensation, and converted to the 1/1 trimethylamine adduct, $ISiH_3 \cdot N(CH_3)_3$. Methanolysis of the amine adduct (0.036 mole) gave methoxysilane which was isolated from the solid by-products by suction filtration, and purified by fractional condensation at −126°. Purity of the product was verified by infrared spectroscopy[25] and molecular weight determination. (Calcd.: 62.10; found: 62.2.) The yield was 18%.

REFERENCES

1 G. Wagner, H. Bock, R. Budenz and F. Seel, *Chem. Ber.*, 106 (1973) 1285.
2 E. Ebsworth, in A. G. MacDiarmid (Ed.), *The Bond to Carbon*, Vol. I. Part 1, Marcel Dekker, New York, 1968, pp. 56–61.
3 A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg and M. Traetteberg, *Acta Chem. Scand.*, 17 (1963) 2455.

4 T. Koopmans, *Physika*, 1 (1934) 104.

5 S. Craddock and R. Whiteford, *J. Chem. Soc., Faraday Trans., II*, (1972) 281.

6 (a) J. Pople and D. Beveridge, *Approximate Molecular Orbital Theory*, McGraw Hill, New York, 1970;
(b) D. Santry and G. Segal, *J. Chem. Phys.*, 47 (1967) 158.

7 R. Hoffmann, *J. Chem. Phys.*, 39 (1963) 1397.

8 (a) K. Kimura and M. Kubo, *Nature*, 183 (1959) 533;
(b) P. Kassai and R. Myers, *J. Chem. Phys.*, 30 (1959) 1096.

9 C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley and J. M. Freeman, *J. Mol. Struct.*, 5 (1970) 417.

10 L. Cusachs and J. Corrington, in O. Sinanoglu and K. Wiberg (Eds.), *Sigma Molecular Orbital Theory*, Yale University Press, New Haven, 1970, p. 167.

11 R. Hoffman, L. Radom, J. A. Pople, P. V. R. Schleyer, W. I. Hehre and L. Salem, *J. Amer. Chem. Soc.*, 94 (1972) 6221.

12 (a) R. Hoffmann and R. Olofson, *J. Amer. Chem. Soc.*, 88 (1966) 943; (b) R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, in press.

13 (a) R. Mulliken, *J. Phys. Chem.*, 56 (1952) 295;
(b) R. Mulliken, *J. Amer. Chem. Soc.*, 72 (1950) 4493.
(c) K. Müller, *Helv. Chim. Acta*, 53 (1970) 1112.

14 L. Pauling, *J. Chem. Soc.*, (1948) 1461.

15 R. Gillespie, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 819.

16 B. Gimarc, *J. Amer. Chem. Soc.*, 93 (1971) 593.

17 H. Bock and G. Wagner, *Angew. Chem.*, 84 (1972) 119; *Angew. Chem., Int. Ed. Engl.*, 11 (1972) 150.

18 (a) C. Coulson, *Valence*, Oxford University Press, New York, 1961, p. 71;
(b) H. Jaffe, *J. Chem. Educ.*, 33 (1956) 25.

19 A. Walsh, *J. Chem. Soc.*, (1963) 2260, 2266, 2301.

20 L. Pierce and M. Hyashi, *J. Chem. Phys.*, 35 (1961) 479.

21 A. Almenningen, K. Hedberg and R. Seip, *Acta Chem. Scand.*, 17 (1963) 2264.

22 A. Stock *et al.*, *Ber. Deut. Chem. Ges.*, 50 (1917) 1754.

23 G. Fritz and F. Kummer, *Chem. Ber.*, 94 (1961) 1143.

24 R. C. Lord, D. W. Robinson and W. C. Schumb, *J. Amer. Chem. Soc.*, 78 (1956) 1327.

25 B. Sternbach and A. MacDiarmid, *J. Amer. Chem. Soc.*, 83 (1961) 3384.

26 B. Aylett and I. Ellis, *J. Chem. Soc.*, (1960) 3415.