

AN AB INITIO STUDY OF SIMPLE 1,3-CYCLODISILOXANE DERIVATIVES

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ABSTRACT

Ab initio geometry optimizations on some simple cyclodisiloxane derivatives (R_2SiO)₂ ($R = CH_3$, OH and OCH_3) and on their radical cations have been carried out at the restricted Hartree-Fock (RHF) level using the basis set 3-21G*. Mayer's bond orders and valences have been calculated for all these species using the STO-3G* basis set, employing geometries determined at the RHF/3-21G* level. It was found that the geometries of the neutral and charged species are quite different, but the geometry of the ring and Mayer's bond indices are affected relatively slightly by the substituents. The small but characteristic Si···Si bond orders in neutral cyclodisiloxanes indicate a weak Si···Si bond. While this bond is considerably weaker in the molecular ions, the O···O bond orders are increased in the charged species.

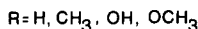
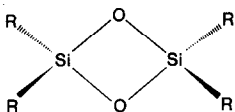
INTRODUCTION

Although 1,3-cyclodisiloxanes (R_2SiO)₂ with bulky substituents ($R = Mes$, $t-Bu$) have been isolated and their structures determined by X-ray diffraction [1,2], no detailed experimental results concerning the geometric and electronic structures of the simplest disiloxanes ($R = H$, CH_3 , OH, OCH_3 , etc.) are known to us, as these species are not stable under normal conditions. Recently, we have been involved in vacuum pyrolysis-mass spectrometry studies of some 1,3-cyclodisiloxane derivatives ($R = CH_3$ [3] and OCH_3 [4]) and have made the following observations. (a) 1,1,3,3-Tetramethyl-1,3-cyclodisiloxane can be produced by pyrolysis and its molecular ion should exist for a short time since the vast majority of ions at m/z 133 correspond to the $[M-CH_3]^+$ ions [3]. (b) In the case of 1,1,3,3-tetramethoxy-1,3-cyclodisiloxane ($R = OCH_3$) the

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molecular ion is quite stable so one can measure its ionization energy (IE). The measured IE value, 8.81 (10) eV, is considerably lower than those of methoxy-substituted linear molecules, which indicates that the electron loss from the cyclodisiloxane ring is more facile than from the methoxy substituents [4]. (c) While the loss of the $\cdot\text{CH}_3$ radical is practically the only fragmentation pathway in the case of compound with $\text{R} = \text{CH}_3$, the loss of $\cdot\text{OCH}_3$ radical from the molecular ion of the $\text{R} = \text{OCH}_3$ derivative is not the only fragmentation process, since ions formed by the loss of $\cdot\text{CH}_3$ and CH_2O species can also be detected with significant intensity in the mass spectra of this latter derivative [3,4].

The 1,3-cyclodisiloxane ring has been studied extensively by theoretical methods [5–13]. The short $\text{Si}\cdots\text{Si}$ distance in the ring raised the question of whether a bond existed between the two silicon atoms [5–11]. Almost all studies concluded that there is no such bond [5–9]. Nevertheless, by a simple extension of Dewar's model to include dibridged compounds, Grev and Schaefer suggested that this $\text{Si}\cdots\text{Si}$ bond may exist [10]. In a recently published study [11] we described the $\text{Si}\cdots\text{Si}$ bond using not only Mulliken's population analysis, as did the authors cited above, but also determined bond orders and valences according to the technique of Mayer [14–16]. Our results confirmed the suggestion of Grev and Schaefer: a small but characteristic $\text{Si}\cdots\text{Si}$ bond order was obtained. Only one paper is known to us dealing with the positively charged molecular ion of parent 1,3-cyclodisiloxane [12].



To extend our knowledge about the chemistry and mass spectrometric behaviour of 1,3-cyclodisiloxane and of its derivatives we decided to undertake an *ab initio* investigation of these systems. It seemed natural to extend our previous work [11] to the simple derivatives $\text{R} = \text{CH}_3, \text{OH}$ and OCH_3 of 1,3-cyclodisiloxane, most of which are more easily amenable to experiment. In the present paper, optimized structures for these derivatives and for their respective radical cations in their ground state are presented. These results enable us to investigate how the substituents affect the electronic structure of the cyclodisiloxane ring. Bond orders and valences were also calculated for all neutral species and cations using Mayer's technique [14–16].

COMPUTATIONAL DETAILS

Ab initio geometry optimizations were carried out at the restricted Hartree-Fock (RHF) self-consistent-field (SCF) level. Brenstein and Scheiner [12]

showed that the smallest basis set which seems to perform in a consistent manner for cyclodisiloxane is the 3-21G* basis. The calculations for all closed- and open-shell species performed by us thus employed the 3-21G* basis set (using even this medium quality basis set the RHF/3-21G* calculations on $R=OCH_3$ were rather expensive due to the 152 CGTOs). Calculations employing the 3-21G and 6-31G* basis sets were also performed for the neutral species $R=CH_3$ and OH, to test the basis set dependence of the theoretical results obtained. The program GAUSSIAN 86 [17] was used for these calculations.

All geometry optimizations were performed assuming D_{2h} symmetry. In support of this choice we note that a comparison of the total energies obtained from calculations employing other symmetry restrictions shows that (a) the lowest energy structure for neutral singlet $(H_2SiO)_2$ ($R=H$) has D_{2h} symmetry [12], (b) in the case of $R=OH$ the C_{2h} structure [5,6] is slightly less stable than the D_{2h} one, (c) for $R=OCH_3$ the energies of the D_{2h} and C_{2h} species are equal within 1×10^{-7} a.u.† The calculated electronic states of the neutral and cationic species are $^1A_{1g}$ and $^2B_{1u}$ respectively.

In the case of the parent cyclodisiloxane the bond indices calculated according to Mayer [14–16] were found to be practically independent of the geometry applied [11]. As in our previous study [11] the STO-3G* basis was used in the Mayer population analysis calculations. The RHF/3-21G* optimized geometries were taken as references. In these calculations the unrestricted Hartree–Fock (UHF) formalism [18] was applied for the open-shell cations, using the program MONSTERGAUSS [19]. For purposes of comparison, bond orders and valences for $R=H$ were also determined by the RHF method.

RESULTS AND DISCUSSION

Optimized geometries

Parameters of the optimized geometries for the cyclodisiloxane ring of the neutral (M) derivatives ($R=H, CH_3, OH$ and OCH_3) and their radical cations (M^+) are presented in Table 1. In general the Si–O and Si···Si distances decrease while the O···O distance increases by extension of the one-particle basis. The significant changes between the 3-21G and 3-21G* results indicate the necessity of using *d* functions in the calculations. The data obtained with the 3-21G* and 6-31G* basis sets usually differ insignificantly. Therefore, the

†It should, nevertheless, be noted that D_{2h} symmetry is probably not the best symmetry assumption for all species. It is known, for example, that because of the anomeric effect the gauche conformation is preferred in the case of $Si(OH)_4$ [22]. Therefore the assumption of gauche conformations for our species with $R=OH$ and OCH_3 seems to be reasonable. Unfortunately, limitations in computer time prevented us dealing with the anomeric effect in these derivatives. Nevertheless, we thank the reviewer for calling our attention to the importance of this effect.

TABLE 1

Optimized geometry parameters for the 1,3-cyclodisiloxane ring of neutral (M) and radical cationic (M⁺) forms^a

R	Basis	$r(\text{Si-O})$	$\alpha(\text{O-Si-O})$	$r(\text{Si}\cdots\text{Si})$	$r(\text{O}\cdots\text{O})$
Neutral M					
	3-21 ^b	171.7	84.6	254.1	231.2
H	3-21G ^{*c}	167.2	87.3	242.0	230.9
	6-31G ^{*b}	167.1	88.5	239.4	233.2
	3-21	172.0	84.4	254.9	231.0
CH ₃	3-21G [*]	167.9	87.2	243.2	231.6
	6-31G [*]	167.8	88.1	241.2	233.2
	3-21G	169.7	84.3	251.7	227.9
OH	3-21G [*]	166.5	87.5	240.6	230.3
	6-31G [*]	166.4	87.8	239.8	230.7
OCH ₃	3-21G [*]	166.7	87.5	240.8	230.5
Radical cation M ⁺					
H	3-21G ^{*c}	172.0	73.9	274.8	206.8
CH ₃	3-21G [*]	172.6	72.6	278.1	204.4
OH	3-21G [*]	169.8	74.8	269.8	206.2
OCH ₃	3-21G [*]	170.4	74.5	271.2	206.3

^aBond lengths in pm, bond angles in degrees. All results were obtained at the ab initio restricted Hartree-Fock level. In all calculations D_{2h} symmetry was assumed.

^bTaken from ref. 8.

^cTaken from ref. 12.

use of the less expensive 3-21G^{*} basis set for the largest system (R=OCH₃) and for the radical cations seems to be well founded.

In the neutral forms the geometry of the ring is only slightly affected by the substituents. The changes are somewhat larger in the cations. Still, the Si-O distances and O-Si-O angles deviate from their averages by less than 2 pm and 2° respectively.

Our data confirm the previous observation [12] that the HOMO in 1,3-cyclodisiloxanes is mainly an oxygen lone pair in character. Removal of an electron from this orbital significantly decreases the O \cdots O lone pair repulsion. This explains the considerable increase in the Si \cdots Si distances and decrease in the O \cdots O distances in the cations compared to the neutral species.

Mayer's valences and bond orders

Mayer's valences and bond orders calculated for the neutral and radical cationic species are listed in Tables 2 and 3 respectively.

Substituents have no great effect on Mayer's indices. It should, however, be noted that in the cases of the O-linked substituents R=OH and OCH₃ the

TABLE 2

Mayer's valences and bond orders (STO-3G**/3-21G*) in 1,3-cyclodisiloxanes^a

	R			
	H	CH ₃	OH ^b	OCH ₃
Valence				
Si	4.19	4.25	4.71	4.73
O	2.26	2.25	2.26	2.26
X ^c	0.99	3.93	2.14	2.20
Bond orders				
Si-O	1.069	1.057	1.048	1.047
Si-X ^c	0.936	0.940	1.178	1.169
Si...Si	0.168	0.162	0.159	0.158
	(-0.110)	(-0.100)	(-0.098)	(-0.098)
O...O	0.071	0.072	0.080	0.080
	(-0.038)	(-0.038)	(-0.042)	(-0.042)

^aSi...Si and O...O Mulliken's overlap populations are also given in parentheses.^bMayer's indices calculated at the C_{2h} equilibrium geometry published by O'Keefee and Gibbs [5,6] deviate by about ±4% from those listed here.^cX denotes that atom of R which is bonded to silicon.

TABLE 3

Mayer's valences and bond orders (STO-3G**/3-21G*) in radical cationic 1,3-cyclodisiloxanes^a

Para-meter	R					
	H		CH ₃		OH	OCH ₃
	Vert. (UHF)	Adiab. (UHF)	Adiab. (RHF)	Adiab. (UHF)	Adiab. (UHF)	Adiab. (UHF)
Valence						
Si	3.91 [0.01]	3.81 [0.01]	3.80 [0.01]	3.96 [0.01]	4.62 [0.01]	4.68 [0.01]
O	2.42 [0.35]	2.39 [0.33]	2.39 [0.24]	2.37 [0.33]	2.40 [0.33]	2.39 [0.33]
X ^b	1.00 [0.00]	1.00 [0.00]	1.00 [0.00]	3.94 [0.00]	2.25 [0.00]	2.32 [0.00]
Bond order						
Si-O	0.912	0.882	0.888	0.863	0.868	0.859
Si-X ^b	0.953	0.954	0.955	0.995	1.335	1.352
Si...Si	0.158	0.117	0.110	0.107	0.106	0.103
	(-0.018)	(-0.068)	(-0.080)	(-0.066)	(-0.068)	(-0.066)
O...O	0.205	0.260	0.342	0.267	0.271	0.271
	(-0.020)	(-0.044)	(-0.044)	(-0.048)	(-0.052)	(-0.050)

^aSi...Si and O...O Mulliken's overlap populations and free valences are also given in parentheses and square brackets respectively.^bX denotes that atom of R which is bonded to silicon.

valences on silicon atoms are larger than in the $R=H$ and CH_3 derivatives. This is due mainly to the somewhat "stronger" $Si-OH$ and $Si-OCH_3$ bonds (compare these bond orders to those of the ring $Si-O$ bonds). The small but characteristic $Si\cdots Si$ bond orders suggest that, as in the parent compound [11], a partial $Si-Si$ bond exists in these (and probably in other) 1,3-cyclodisiloxane derivatives.

To study the effect of ionization in more detail, calculations have been carried out on the parent compound ($R=H$) for both the "vertical" and "adiabatic" ionic structures. Data for the vertically ionized molecule show a significantly increased $O\cdots O$ bond order and a decreased $Si\cdots Si$ bond order. This suggests the formation of a partial $O\cdots O$ bond in the cations. (Bond formation thus cannot be simply attributed to the shorter $O\cdots O$ distance calculated for the "adiabatic" structure.) It is worth noting that the RHF and UHF methods lead to a similar qualitative picture, in spite of the fact that the $O\cdots O$ bond order is estimated to be about 30% larger when using the RHF method.

Implication of the results for mass spectrometry

Total energies, vertical ionization energies ($-\epsilon_i$) determined according to Koopmans' theorem and adiabatic ionization energies (ΔE) are given in Table 4. The adiabatic ionization energy calculated for the $R=OCH_3$ derivative is probably close to the experimental value, even if one remembers that the ionization energy determined by mass spectral measurements is mainly of vertical character. Since the vertical ionization energies ($-\epsilon_i$) calculated according to Koopmans' theorem are considerably larger than the adiabatic ones, Koopmans' theorem does not seem to be applicable to these systems.

As was mentioned earlier, extensive loss of the $\cdot CH_3$ radical from the molecular ion of the tetramethyl derivative ($R=CH_3$) has been observed [3]. This easy loss of the $\cdot CH_3$ (and, in general, alkyl) radical from similar molecular ions such as siloxanes could be explained [20] by the positive charge located on the silicon atoms, which can weaken the $Si-C$ bond at the α position [20]. However, bond order data in Tables 2 and 3 and net charge densities of Table 5 do not support this explanation. Although the net positive charge on the silicon atoms is fairly large, its relative change from the neutral to the cationic species is less than that corresponding to the ring O atoms (Table 5). Additionally, it is seen from Tables 2 and 3 that the $Si-C$ bond order does not decrease but slightly increases in the charged species ($R=CH_3$). It is worth mentioning that the outer $Si-O$ bonds ($R=OH$ and OCH_3) have bond orders considerably larger than unity; this, at least in the first approximation, is in agreement with the harder loss of $\cdot OCH_3$ from the corresponding molecular ion [4].

"Static" parameters, such as bond orders and charge densities, calculated

TABLE 4

Total energies and ionization energies for neutral (M) and radical cationic (M⁺) 1,3-cyclodisiloxanes

R	Basis	Energy (u)	Ionization energies (eV)	
			$-\epsilon_i^a$	ΔE (adiabatic)
Neutral M				
H	3-21 ^b	-726.131630	11.85 (b_{1u})	9.71
	3-21G* ^c	-726.342627	12.04 (b_{1u})	
	6-31G** ^b	-730.026812	12.18 (b_{2u})	
CH ₃	3-21	-881.524832	10.82 (b_{2u})	8.84
	3-21G*	-881.761554	11.10 (b_{2u})	
	6-31G*	-886.229903	11.06 (b_{2u})	
OH	3-21G	-1024.172348	12.51 (b_{1u})	9.15
	3-21G*	-1024.491022	12.67 (b_{3g})	
	6-31G*	-1029.796224	13.28 (b_{3g})	
OCH ₃	3-21G*	-1179.729039	11.77 (b_{3g})	8.61 (8.81(10)) ^d
Radical cation M ⁺				
H	3-21G* ^c	-725.985945		
CH ₃	3-21G*	-881.436721		
OH	3-21G*	-1024.154830		
OCH ₃	3-21G*	-1179.412705		

^aObtained according to Koopmans' theorem.

^bReference geometries taken from ref. 8.

^cReference geometries taken from ref. 12.

^dExperimental value [4].

TABLE 5

STO-3G* net charges on silicon, oxygen and outer atoms (X) bonded to silicon in 1,3-cyclodisiloxanes (M) and their radical cations (M⁺)

R			Si	O	X ^b
H	M		0.645	-0.415	-0.115
		Vert. (UHF)	0.738	-0.194	-0.022
	M ⁺	Adiab. (RHF)	0.773	-0.240	-0.016
		(UHF)	0.778	-0.245	-0.016
CH ₃	M		0.744	-0.424	-0.335
	M ⁺ ^a		0.847	-0.262	-0.339
OH	M		0.802	-0.427	-0.420
	M ⁺ ^a		0.954	-0.247	-0.413
OCH ₃	M		0.808	-0.426	-0.373
	M ⁺ ^a		0.918	-0.256	-0.366

^aCharge densities were calculated at the 3-21G* optimized geometry of the corresponding cation.

^bX denotes that atom of R which is bonded to silicon.

from the wavefunctions have their limitations in describing "dynamic" fragmentation processes. Nevertheless, their usefulness for explaining and predicting the main fragmentation routes cannot be discounted. The significant decrease in the ring Si-O bond order in the radical cations (Tables 2 and 3), for example, might inspire one to carry out further calculations on open ring cationic species or other unique (e.g., diborane-like [21]) structures.

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