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THE RING STRAIN ENERGIES OF CYCLOPOLYSILANES, $[R^1R^2Si]_n$ (n=3-6)

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Approximate estimation for the ring-strain energies of peralkylcyclopolysilanes, $[R^1R^2Si]_n$ where n = 6, 5, 4, and 3, gave $\Delta\Delta E$ = 0, 6, 23, and 41 kcal·mol^{-1}, respectively.

Previously, we found that the lowest energy transitions in the electronic spectra for a series of peralkylcyclopolysilanes, $[R^1R^2Si]_n$ where n = 6, 5, 4, 3, and 2, occur at ca. 250-270, 260-275, 270-310, 290-330, and 390-440 nm regions with varying extinction coefficients, respectively.[1] West and coworkers pointed out that decreasing the ring size in permethylcyclopolysilanes destabilizes the σ(Si-Si) bond levels and shifts the absorptions to longer wavelengths.[2] Our result shows that this interpretation holds well in the series of cyclic catenation system bearing various sets of alkyl substituents. The bathochromic shifts with decreasing ring size for the peralkylcyclopolysilanes also parallel the decreasing trend in the first oxidation peak potentials (by Cyclic Voltammetry).[3]

It is of special interest to evaluate the ring-strain energy in each size of rings and to correlate the result with other properties of cyclopolysilanes. Fortunately, the UV absorption spectra for a series of linear permethylpolysilanes have been reported and the lowest transition absorption bands for $Me(Me_2Si)_nMe$, where n = 6, 5, 4, 3, and 2, have been shown to appear at 260, 250, 235, 216.3, and 193.5 nm, respectively.[4] Thus, it is possible to estimate approximately the ring-strain energy of the cyclopolysilanes as the difference in the transition energies between the two series of polysilanes in the same silicon number. Table 1 lists the two series of the longest wavelength absorptions and the corresponding transition energies (ΔE), and also the ring-strain energies ($\Delta\Delta E$) which are the differences between the transition energies, ΔE(linear)-ΔE(cyclic). The trend in the strain energies suggests that the reactivities of the series of cyclopolysilanes toward various reagents increase with decreasing the ring size. This was clearly demonstrated by the relative rates in the ring-opening reaction of the cyclopolysilanes with iodine.[5]

Interestingly, the ring-strain energies of the cyclopolysilanes are in good agreement with those of the corresponding cycloalkanes, $(CH_2)_2$,[6] except the case of n=2 (Table 1). Finally, it should be pointed out that the present result provides a quite significant information about the fundamental properties of the cyclopolysilanes.

Table 1. Ring-strain energies of cyclopolysilanes, $[R^1R^2Si]_n$ (R^1, R^2; alkyl groups; n=6-3), estimated from the longest wavelength absorptions of the polysilanes and of the corresponding linear permethylpolysilanes, relative rates in the ring-opening reactions of the cyclopolysilanes with iodine, and ring-strain energies of cycloalkanes, $(CH_2)_n$ (n=6-2)

Polysilane	n:	6	5	4	3	2
λ_{max}^{lin} /nm[a]		260	250	235	216.3	193.5
	$\Delta E(lin)$[b]:	110	114	122	132	148
λ_{max}^{cyc} /nm[c]		260	265	290	315	400[d]
	$\Delta E(cyc)$[b]:	110	108	99	91	71
$\Delta\Delta E$[e] /kcal·mol^{-1}		0	6	23	41	..[f]
k_{rel}[g]		1	8 11	241 237 58	5500[h]	
Cycloalkane Ring-strain energy[i] /kcal·mol^{-1}		0	6.5	26.5	45.6	38.4

a) For $Me(Me_2Si)_nMe$; see Ref. 4. b) Lowest transition energies corresponding to the absorption bands; kcal·mol^{-1}. c) For $[R^1R^2Si]_n$; see Ref. 1. d) This band is assigned to be due to the π-π^* transition; see Ref. 7. e) Ring-strain energy, $\Delta E(lin)-\Delta E(cyc) \doteqdot \Delta\Delta E$. f) The value can be estimated when the assignment to the σ-σ^* transition in the Si=Si bonding of peralkyldisilenes is done in future. g) Relative rates in the ring-opening reactions with iodine; see Ref. 5. h) Value estimated from the regression line (correlation coefficient, γ=0.94) obtained on the basis of the relative rates in the larger rings, n=4-6. i) Value on the basis of the heat of combustion; see Ref. 6.

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