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Dibenzo[*c*,*h*]-1,6-diisopropyl-1,6-disilabicyclo[4.4.0]deca-3,8-dienes

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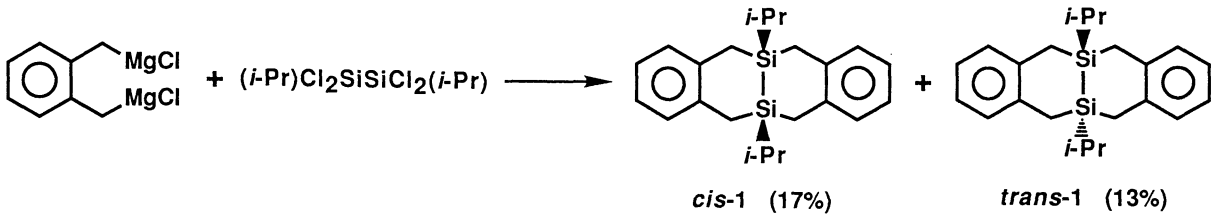
cis- and *trans*-Dibenzo[*c*,*h*]-1,6-diisopropyl-1,6-disilabicyclo[4.4.0]deca-3,8-dienes were prepared. Strong σ-π conjugation was found to operate in both isomers, which was shown in UV spectra, cyclic voltammetry, and charge-transfer spectra with TCNE.

Recently, the chemistry of cyclic polysilanes with a fused ring system has been investigated extensively by us[1] and other groups.[2] These compounds exhibit the σ-σ or σ-π interaction of Si-Si σ bonds and π systems, and in some cases act as precursors of reactive intermediates. We report herein the synthesis and characterization of *cis*- and *trans*-dibenzo[*c*,*h*]-1,6-diisopropyl-1,6-disilabicyclo[4.4.0]-deca-3,8-dienes (*cis*-**1** and *trans*-**1**), which have not yet been described in the literature. Judging from the structures of **1** optimized by the MM2 calculation,[3,4] properties and reactivity due to σ-π conjugation are expected in this system. Since the degree of σ-π conjugation depends on the dihedral angle between the benzylic C-Si bond and the π-orbital,[5] σ-π conjugation might operate more effectively in *cis*-**1**.

The title compounds were prepared by the reaction of a di-Grignard reagent derived from α,α'-dichloro-*o*-xylene[6] with 1,2-diisopropyl-1,1,2,2-tetrachlorodisilane in THF at room temperature. After usual work-up, a mixture of two isomers (*cis*- and *trans*-**1**) was separated by recycle-type HPLC (ODS, MeOH-THF). *cis*- and *trans*-**1** were obtained as colorless crystals in 17 and 13% yields, respectively.[7] The geometrical isomerism of each isomer was confirmed by NOE difference experiments at 200 MHz. Thus, saturation of the methyl protons in the isopropyl groups produced a positive NOE of only one (2.20 ppm) of two kinds of benzylic protons in the case of *cis*-**1**, while a positive NOE was observed for both benzylic (2.08 and 2.21 ppm) protons in the case of *trans*-**1**.



cis-1 (17%) *trans*-1 (13%)

The oxidation potential of *cis*-**1** (E_p^{ox} = 1.35 V vs. SCE, in MeCN) is smaller than that of *trans*-**1** (E_p^{ox} = 1.59 V vs. SCE, in MeCN). The results indicate that the highest occupied molecular orbital (HOMO) of *cis*-**1** is higher in energy than *trans*-**1** because of more effective σ-π conjugation. UV

spectra of *cis*- and *trans*-**1** are shown in Fig. 1. Although the ^1L_a band does not appear as a clear single peak, it extends to the longer wavelength region with larger intensity than the corresponding bands for benzene and benzyltrimethylsilane. Similar tendency is observed in the ^1L_b bands of *cis*-**1** ($\lambda_{max} = 280$ nm (ε 2070)) and *trans*-**1** ($\lambda_{max} = 277$ nm (ε 1030)). The bathochromic shifts and marked increase in intensity are attributed to the destabilization of the HOMO due to σ-π conjugation. It is noted that increments of the wavelength and the extinction coefficient of the absorption maximum are larger in the case of *cis*-**1**, in which σ-π conjugation operates more effectively.

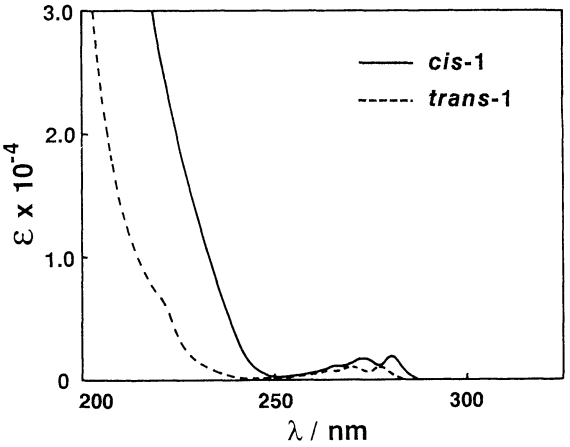


Fig. 1. UV spectra of *cis*- and *trans*-**1** in hexane.

When **1** was mixed with tetracyanoethylene (TCNE) in dichloromethane, the solution was colored violet (*cis*-**1** and TCNE) or orange (*trans*-**1** and TCNE). In UV-visible absorption spectra, broad charge-transfer (CT) bands appeared in the longer wavelength region than the absorptions of **1** and TCNE (Fig. 2). The CT bands have been curve-fitted to two skewed Gaussian peaks in each case.[8] These Gaussians have their maxima at 448 and 559 nm (*cis*-**1** and TCNE) and 422 and 503 nm (*trans*-**1** and TCNE), respectively. In Table 1, frequencies of the CT absorption maxima of **1** and related compounds are listed. The charge-transfer transition energies decrease in the order of $PhCH_2SiMe_3$ > *trans*-**1** > *o*-$C_6H_4(CH_2SiMe_3)_2$ > *cis*-**1**, and the electron-donating property seems to increase in the reverse order.[9] The result is in good accord with Mulliken's charge-transfer theory.[10]

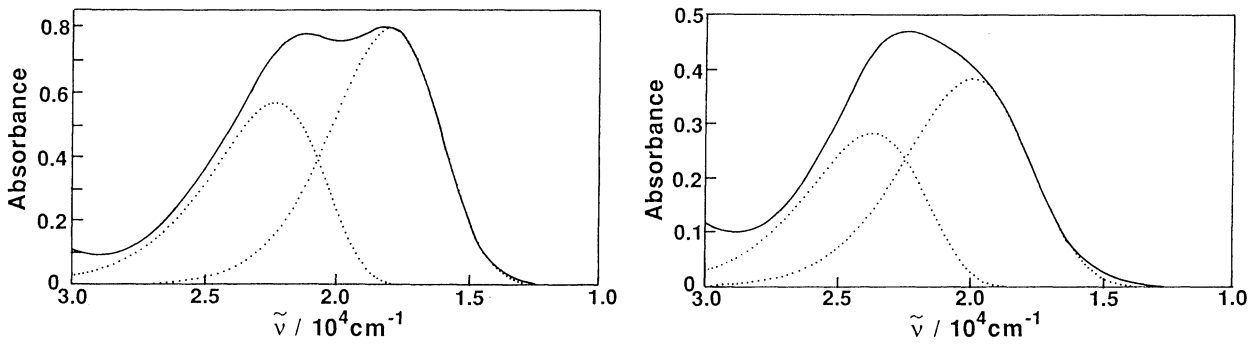
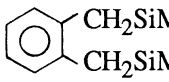


Fig. 2. Charge-transfer absorption spectra of *cis*-**1** (left) and *trans*-**1** (right) with TCNE in CH_2Cl_2. —— : **1** (0.05 M) + TCNE (0.005 M), ····· : Skewed Gaussian line (1 M = 1 mol dm^{-3}).

Table 1. Frequencies for Charge-Transfer Absorptions in Complexes of TCNE with **1** and Related Compounds in Dichloromethane at Room Temperature

Compound	$\tilde{\nu}_{max}$ (CTI) / cm^{-1}	$\tilde{\nu}_{max}$(CTII) / cm^{-1}	Reference
cis-**1**	22300	17900	this work
trans-**1**	23700	19900	this work
	22400	18700	11
$PhCH_2SiMe_3$	24050	20550	11

Relatively strong electron-donating properties of *cis*- and *trans*-**1** and the presence of two absorption bands in the CT complexes are explained as follows (Fig. 3). σ-π Conjugation between the benzene ring and the Si-C σ bond results in the destabilization and the separation of the degenerate HOMO's of benzene.[11] The two σ-π orbitals and the Si-Si σ orbital of *cis*- and *trans*-**1** can interact with the LUMO of TCNE. Among these CT interactions, the absorption of the CT complex between Si-Si σ donor and TCNE is reported to be much weaker than those of π donor.[12] Therefore, the CT bands due to two σ-π orbitals of *cis*- and *trans*-**1** appear in UV-visible spectra, and the CT band due to the Si-Si σ orbital is considered to be concealed behind the former absorptions.

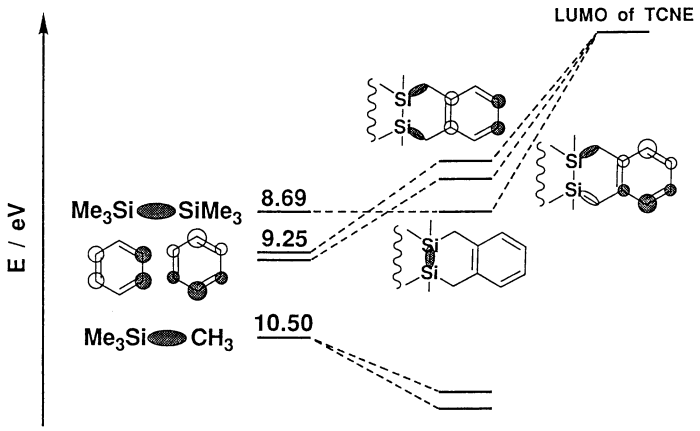


Fig. 3. Interaction of orbitals in the CT complex of **1** with TCNE.

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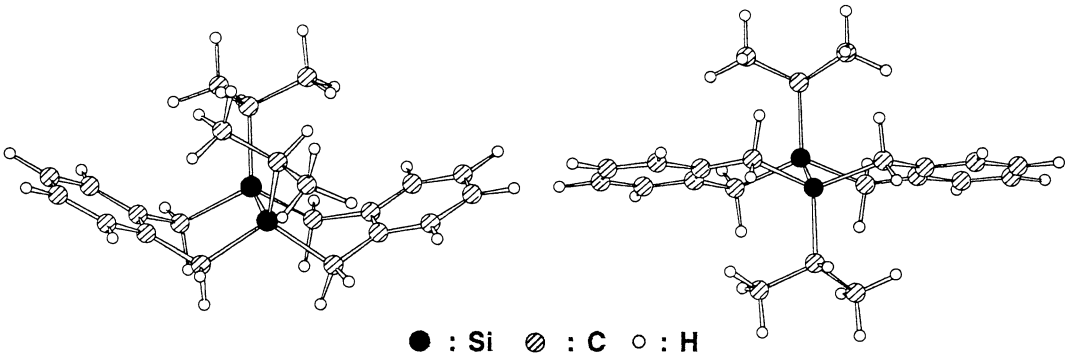
4) Structures of *cis*-**1** (left) and *trans*-**1** (right) calculated by the MM2 method are shown below. In the *cis*-**1**, the disilacyclohexene rings exist in a boat conformation and the geometry around the central Si-Si bond is eclipsed, while a chair form and an *anti* conformation is adopted in the *trans*-**1**. The dihedral angles between the Si-C (benzyl) bond and the *p* orbitals of the benzene rings are 43° (*cis*-**1**) and 66° (*trans*-**1**), respectively.



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7) *cis*-**1**: Mp 49.0-51.5 °C; ^{1}HNMR ($CDCl_3$) δ 0.96-1.10 (m, 14H), 1.85 (d, 4H, J = 13.6 Hz), 2.20 (d, 4H, J = 13.6 Hz), 6.93-7.06 (m, 8H); ^{13}CNMR ($CDCl_3$) δ 11.4, 19.1, 19.6, 125.1, 129.6, 138.1; IR (KBr, cm^{-1}) 1490, 1471, 1459, 1217, 1155, 779; MS m/z (%) 350 (M^+, 100), 307 (65), 265 (89). Anal. Found: C, 75.88; H, 8.76%. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62%. *trans*-**1**: Mp 50.0-52.0 °C; ^{1}HNMR ($CDCl_3$) δ 0.96-1.15 (m, 14H), 2.08 (d, 4H, J = 17.4 Hz), 2.21 (d, 4H, J = 17.4 Hz), 7.03 (dd, 4H, J = 5.5, 3.4 Hz), 7.17 (dd, 4H, J = 5.5, 3.4 Hz); ^{13}CNMR ($CDCl_3$) δ 13.2, 18.0, 18.8, 125.6, 128.8, 142.5; IR (KBr, cm^{-1}) 1486, 1471, 1460, 1217, 1124, 790; MS m/z (%) 350 (M^+, 63), 307 (100), 265 (96). Anal. Found: C, 75.15; H, 8.65%. Calcd for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62%.

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9) Ionization potentials of $PhCH_2SiMe_3$ and *o*-$C_6H_4(CH_2SiMe_3)_2$ have been reported to be 8.35 and 8.05 eV, respectively. See, H. Bock and B. Solouki, " The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1989), p. 555.

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