

Effect of a Weak Donor on the Intramolecular Charge Transfer of Molecules Containing Two Neighboring Silicon Atoms

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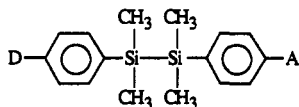
The role of a weakly donating group has been investigated when conjugated to a strong donor through two neighboring silicon atoms. A second harmonic signal, on powder, of the order of potassium titanium phosphate (KTP) has been evidenced for one of the disilane compounds.

I. Introduction

The search for new organic and organometallic materials for quadratic nonlinear optics has led to the elaboration of a large variety of molecules, based on the principle of intramolecular charge transfer (ICT), mediated by a conjugated electronic system, from donor to acceptor substituents.^{1,3} However, most of these molecules possessing a high β value exhibit limited transparency in the blue or near-UV spectral range, owing to the presence of an electronic π - π^* ICT transition mainly responsible for the nonlinearity. Consequently, the search for new compounds with increased transparency, in keeping with the high nonlinear efficiency specific of organic materials, remains a crucial challenge for various applications in the field of optical signal processing and information storage.³

A possible strategy for optimizing this transparency/nonlinearity "trade-off" consists in reducing the electronic transmitting character of the conjugated path between the donor and acceptor groups. The introduction of silicon atoms within this conjugated chain, for example, in between two phenyl rings, may reduce but not fully cancel the strength of the ICT owing to a nonnegligible σ delocalization over the Si-Si bonds, sizable σ - π interaction between sp^3 silicon and sp^2 carbon atoms, and an increased electronic polarizability as compared to sp^3 carbon bonds.⁴

In a previous paper,⁵ we reported the influence of the silicon atom chain length on the quadratic hyperpolarizability β . We also investigated the role of the disilane moiety -Si-Si- on the ICT process in molecules of the following type:



where D (respectively A) is an electron donor (respectively electron acceptor) substituent.^{6,7} Strong donor (MeO, Me₂N) and acceptor (dicyanovinyl) groups were chosen for β optimization.

In the present work, the influence of a much weaker donor substituent is studied through a fluorinated derivative (D = F, compound 1), a hydrogenated compound (D = H, compound 2), and a thiophenic derivative (compound 3). Both fluorophenyl and thiophene groups are supposed to act as weak electron donors when conjugated to the dicyanovinyl group through the silicon electronic pathway.

The fluorine atom itself is a strong electronic acceptor. In the ground state, it may significantly modify the elec-

tronic structure and the dipole moment of the molecules in which it is being introduced as a substituent. However, when the fluorine is substituted on an aromatic system, the presence of its three nonbonding electron pairs induces a conjugation with the delocalized electrons of the aromatic ring. From this point of view, fluorine plays the role of a donor (mesomeric effect). However, owing to its strong intrinsic electronegativity, the fluorine is expected to be only a weak donor group. Such electronic properties have been evidenced, both theoretically and experimentally, in various earlier studies.⁸⁻¹⁰

II. Experimental Section

All manipulations were performed under a dry nitrogen or dry argon atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) and Et₂O were distilled under N₂ from sodium benzophenone ketyl. All other solvents were nitrogen-saturated and dried according to standard procedures. Dimethylformamide (DMF) was allowed to stand over 3-Å molecular sieves (activated by heating to 360 °C for 5 h and cooling in a desiccator). ClSiMe₂SiMe₂Cl (Rhône-Poulenc) was distilled under nitrogen before use.

(1) Chemla, D. S.; Zyss, J. *NLO Properties of Organic Molecules and Crystals*; Academic Press: Orlando, FL, 1987.

(2) Hann, R. A.; Bloor, D., Eds. *Organic Materials for Nonlinear Optics*; Royal Society of Chemistry: London, 1989.

(3) Zyss, J. In *Organic Crystals and Quadratic Nonlinear Optics: the Transparency-Nonlinearity Trade-off in Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Microelectronics*; Bredas, J. L., Chance, R. R., Eds.; Kluwer Academic Publishers: Amsterdam, 1990; p 545.

(4) (a) Sakurai, H. *J. Organomet. Chem.* 1980, 200, 261. (b) Bassindale, A.; Taylor, P. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 14, p 893. (c) Fujino, M. *Chem. Phys. Lett.* 1987, 136, 451. (d) Kepler, R. *Synth. Met.* 1989, 28, C573. (e) Zeigler, J. *Synth. Met.* 1989, 28, C581. (f) Yokoyama, K.; Yokoyama, M. *Solid State Commun.* 1989, 70, 241.

(5) Mignani, G.; Krämer, A.; Puccetti, G.; Ledoux, I.; Soula, G.; Zyss, J.; Meyrueix, R. *Organometallics* 1990, 9, 2640.

(6) Mignani, G.; Barzoukas, M.; Zyss, J.; Soula, G.; Balegroune, F.; Grandjean, D.; Josse, D. *Organometallics*, in press.

(7) Mignani, G.; Krämer, A.; Puccetti, G.; Ledoux, I.; Soula, G.; Zyss, J. *Molec. Eng.* 1991, 1, 11.

(8) Levine, B. F. *J. Chem. Phys.* 1975, 63, 115.

(9) Oudar, J. L.; Chemla, D. S.; Batifol, E. *J. Chem. Phys.* 1977, 67, 1626.

(10) Zyss, J. *J. Chem. Phys.* 1979, 1, 334.

(11) Oudar, J. L. *J. Chem. Phys.* 1977, 67, 446.

(12) Levine, B. F.; Bethea, C. G. *Appl. Phys. Lett.* 1974, 24, 445.

(13) Ledoux, I.; Zyss, J. *Chem. Phys.* 1982, 73, 203.

(14) Barzoukas, M.; Fremaux, P.; Josse, D.; Kajzar, F.; Zyss, J. *Mat. Res. Soc. Symp. Proc.* 1988, 109, 171.

(15) Hedestrand, G. *Z. Phys. Chem.* 1929, B2, 428.

(16) Morley, J.; Docherty, V. J.; Pugh, D. *J. Chem. Soc., Perkin Trans 2* 1987, 1351.

(17) Morley, J.; Docherty, V. J.; Pugh, D. *J. Chem. Soc., Perkin Trans 2* 1987, 1357.

* Centre de Recherches des Carrières, Rhône-Poulenc.

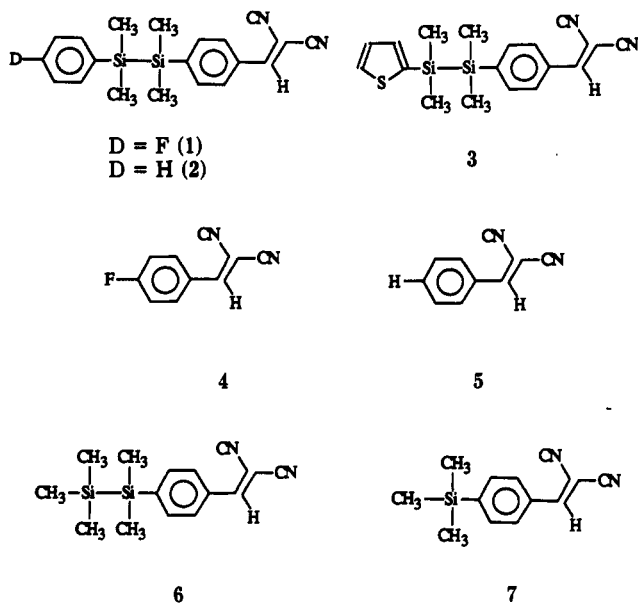
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Malonodinitrile (Aldrich), 1,4-dibromobenzene (Aldrich), 1-bromo-4-fluorobenzene (Aldrich), 2-bromothiophene (Aldrich), ethanol (Prolabo), iodine (Prolabo), and magnesium (turnings, 98%, Aldrich) were used as obtained from their commercial sources.

Column chromatography was performed with silica gel (230–400 mesh ASTM, Merck). Preparative HPLC was carried out on a Waters Prep/LC 500 with two silica gel columns (50 cm³/min). All melting points are uncorrected. The FTIR spectra (KBr) were taken on a Perkin-Elmer PE/750 spectrophotometer. The UV-visible spectra were recorded on a Varian Cary 219 spectrophotometer. ¹H NMR spectra were taken on a 360-MHz Bruker spectrometer. ¹³C NMR, ²⁹Si NMR, and ¹⁹F NMR spectra were recorded on a 250-MHz Bruker OAM spectrometer. Chemical shifts refer to HMDS (¹H NMR), TMS (²⁹Si NMR, ¹³C NMR), and FC₆H₅ (¹⁹F NMR) as internal standards. The mass spectra were measured on a AEILS30 spectrometer.

The description of the synthesis of compounds 1 and 3 is shown in Figure 1. Compounds 2, 6, and 7 were described previously.⁷ Compounds 4 and 5 were prepared by a literature method.¹⁸



1-Chloro-2-(4-fluorophenyl)tetramethyldisilane (8). To a suspension of 13.2 g (0.54 mol) of magnesium in ether (200 mL) was added one crystal of iodine and slowly (1 h) a solution of 4-bromo-1-fluorobenzene (95 g, 0.54 mol) in ether (100 mL). During this procedure, the temperature was maintained at 35–37 °C. Subsequently, the mixture was heated at reflux for 12 h and then was allowed to cool to room temperature. During the addition of the Grignard reagent to 1,2-dichlorotetramethyldisilane (117 g, 0.62 mol), a slight exothermic reaction took place. The resulting mixture was heated at reflux overnight and was then cooled to room temperature and filtered. The solvent was removed at 30 °C/30 mmHg, and the residue was distilled under reduced pressure. A colorless liquid (85.8 g, bp 80 °C/2 Torr (64.5% yield)) was obtained. This material was used without further purification.

Mass spectrum (CI): *m/e* 246 (M⁺). ¹H NMR (CDCl₃): δ 0.47 (s, Si(CH₃)₂, 6 H), 0.49 (s, Si(CH₃)₆, 6 H), 6.98–7.56 (AA'BB', FC₆H₄, 4 H).

1-(4-Bromophenyl)-2-(4-fluorophenyl)tetramethyldisilane (9). To a solution of 82 g (348 mmol) of *p*-dibromobenzene in hexane/toluene (150 mL/150 mL) was slowly added 217 mL of BuLi (1.6 M solution in *n*-hexane). This mixture was kept at 45 °C and stirred overnight. To this organolithium compound (yellow precipitate in hexane/toluene) was slowly added a solution of 85.8 g (348 mmol) of 1-chloro-2-(4-fluorophenyl)tetramethyldisilane. An exothermic reaction occurred, and the resulting mixture was heated at reflux for 12 h. After cooling to room temperature, the reaction mixture was hydrolyzed with H₂O and neutralized (pH = 7.5). The organic layer was separated and the aqueous layer

washed three times with water. After the organic layer was dried over Na₂SO₄, the solvent was evaporated and the crude product was purified by column chromatography (silica gel, hexane) to give 76 g (59.5% yield) of a colorless oil that was used without further purification.

Mass spectrum (CI): *m/e* 366 (M⁺). ¹H NMR (CDCl₃): δ 0.41 (s, Si(CH₃)₂, 6 H), 0.45 (s, Si(CH₃)₂, 6 H), 7.03–7.47 (AA'BB', BrC₆H₄, 4 H), 7.3–7.56 (AA'BB', FC₆H₄, 4 H).

1-[4-(2,2-Dicyanoethenyl)phenyl]-2-(4-fluorophenyl)-tetramethyldisilane (1). To a solution of 60.5 g (165 mmol) of 1-(4-bromophenyl)-2-(4-fluorophenyl)tetramethyldisilane in 300 mL of hexane was added 115 mL of BuLi (1.6 M, 184 mmol). This mixture was kept at 55 °C for 12 h, and then 15 g (205 mmol) of DMF was added and a slightly exothermic reaction occurred. After another 6 h of stirring, the mixture was hydrolyzed with HCl (0.1 N). The organic layer was separated and the aqueous phase washed three times with hexane. All organic layers were unified and dried over Na₂SO₄. The solvent was evaporated, and the residue was used without further purification. Twelve grams (182 mmol) of malonodinitrile, dissolved in 100 mL of ethanol was added as well as 2 drops of piperidine. Stirring overnight gave a yellow precipitate that was filtered. This crude product was purified by column chromatography (silica gel), eluting with 90/10 (hexane/ethyl acetate). The final product was isolated as a yellow powder and twice recrystallized from hexane (15.2 g/25% yield), mp 85–86 °C.

Mass spectrum (CI): *m/e* 364 (M⁺). FTIR (KBr): 1100 (ν(Si-Ph)), 1230 (ν(aryl-F)), 2230 cm⁻¹ (ν(CN)). ¹H NMR (CDCl₃): δ 0.27 (s, Si(CH₃)₂, 6 H), 0.30 (s, Si(CH₃)₂, 6 H), 6.95–7.22 (AA'BB', FC₆H₄Si(CH₃)₂, 4 H), 7.43–7.73 (AA'BB', Si(CH₃)₂C₆H₄CH=, 4 H), 7.68 (s, CH=C(CN)₂, 1 H). ¹³C NMR (CDCl₃): δ -4.41, -3.95 (Si(CH₃)₂), 115.1, 133.2, 135.5, 163.6 (FC₆H₄), 129.3, 130.7, 134.7, 149.7 (C₆H₄CH=C(CN)₂), 159.9 (CH=), 82.3 (=C(CN)₂), 112.7, 113.8 (CN). ²⁹Si NMR (CDCl₃): δ -21.2, -20.4 (s, SiMe₂). UV (CHCl₃): 344 nm (ε = 23 600). UV (CH₃OH): 28 (ε = 16 800), 333 nm (ε = 23 100). UV (*n*-hexane): 228 (ε = 17 500), 332 (ε = 26 500). ¹⁹F NMR (CDCl₃): δ 0.8.

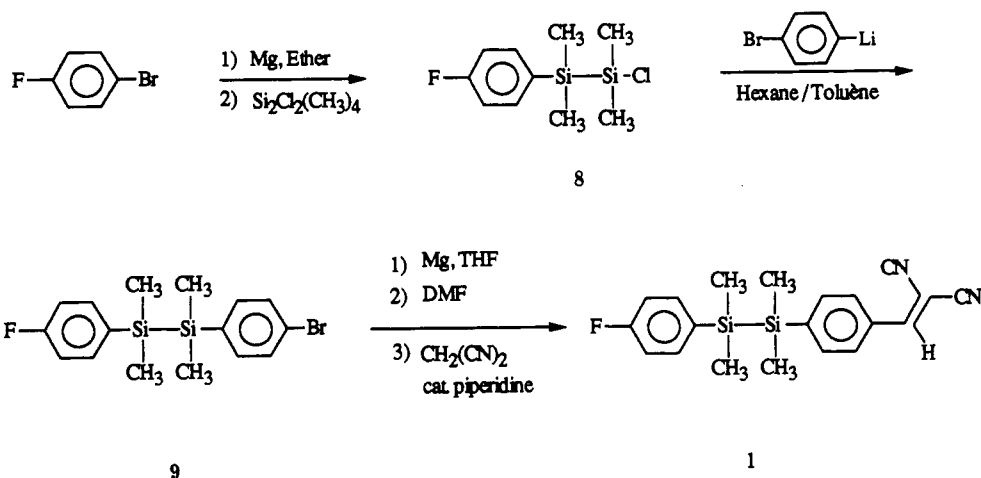
Anal. Calcd for C₂₀H₂₁FN₂Si₂: C, 65.93; H, 5.77; N, 7.69; Si, 15.38. Found: C, 66.61; H, 5.95; N, 7.39; Si, 15.30.

1-(4-Bromophenyl)-2-(2-thienyl)tetramethyldisilane (10). To 6.70 g (279 mmol) of magnesium cuttings in 300 mL of THF was slowly added 45 g (276 mmol) of 2-bromothiophene. At the end of this exothermic reaction, the mixture was stirred for 12 h at 60 °C. To the resulting brown Grignard reagent was added 83.75 g (272 mmol) of 1-(4-bromophenyl)-2-chlorotetramethyldisilane. After this addition had been completed, the reaction mixture was stirred for another 12 h at 60 °C before hydrolyzing with 0.1 N HCl. The organic layer was separated and the aqueous layer washed three times with hexane. All organic layers were unified and dried over Na₂SO₄. The solvent was evaporated, and the residue was purified by column chromatography (silica gel, hexane). After evaporating the solvent, a colorless oil was obtained (86.8 g, 89.9% yield).

Mass spectrum (CI): *m/e* 354 (M⁺). ¹H NMR (CDCl₃): δ 0.30 (s, Si(CH₃)₂, 12 H), 7.19–7.59 (AA'BB', BrC₆H₄, 4 H), 7.53–7.11–7.06 (m, thiophene, 3 H). ¹³C NMR (CDCl₃): δ -4.1, -2.6 (Si(CH₃)₂), 137.3–135.4–130.9–123.4 (C₆H₄Br), 130.6–126.2–134.5–137.6 (thiophene).

1-[4-(2,2-Dicyanoethenyl)phenyl]-2-(2-thienyl)tetramethyldisilane (3). To 5.95 g (245 mmol) of magnesium cuttings in 200 mL of THF was slowly added 86.8 g (245 mmol) of 1-(4-bromophenyl)-2-(2-thienyl)tetramethyldisilane. At the end of this exothermic reaction, the mixture was heated at 60 °C and stirred overnight. To this Grignard reagent was added 20 g (274 mmol) of DMF dissolved in THF. After this addition, the mixture was stirred for another 6 h at 60 °C and then hydrolyzed with 0.1 N HCl until the aqueous layer became slightly acidic. The organic layer was separated and the aqueous layer washed three times with hexane. All organic layers were unified and dried over Na₂SO₄. The solvent was evaporated, and the residue was used without further purification. Eighteen grams (272 mmol) of malonodinitrile dissolved in 100 mL of ethanol was added as well as 2 drops of piperidine. After this mixture was stirred for 5 h, the product was allowed to crystallize in the refrigerator. A crude yellow product was isolated that was twice recrystallized from hexane (yellow solid, mp 98.5–99.5 °C, 9 g, 10.4% yield).

Compound 1



Compound 3

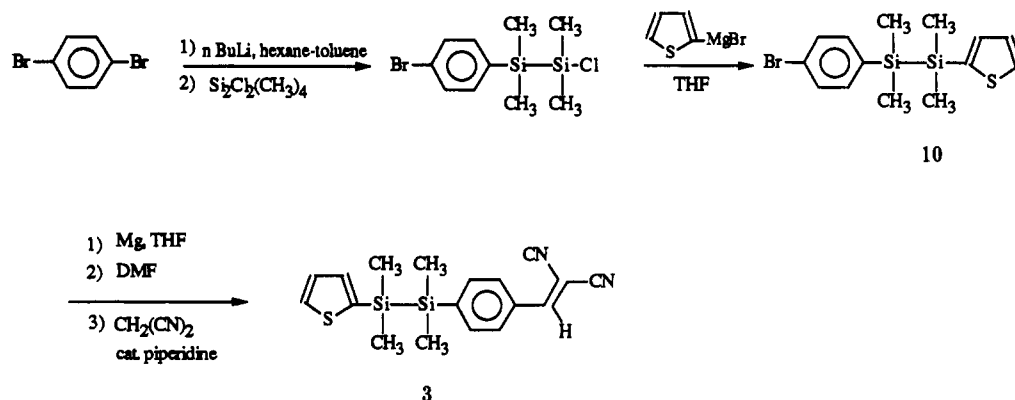


Figure 1. Synthesis of compounds 1 and 3.

Mass spectrum (CI): m/e 352 (M^+). FTIR (KBr): 1586–1538–1495 ($\nu(\text{C}=\text{C}$ aryl)), 1248 ($\nu(\text{Si}-\text{CH}_3)$), 792 ($\nu(\text{Si}(\text{CH}_3)_2)$), 718 (thiophene), 2226 cm^{-1} ($\nu(\text{CN})$). ^1H NMR (CDCl_3): δ 0.32 (s, $\text{Si}(\text{CH}_3)_2$, 6 H), 0.34 (s, $\text{Si}(\text{CH}_3)_2$, 6 H), 7.48–7.74 (AA'BB', $\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{CH}=\text{C}(\text{CN})_2$, 4 H), 7.53–7.11–7.05 (m, thiophene, 3 H), 7.67 (s, $\text{CH}=\text{C}(\text{CN})_2$, 1 H). ^{13}C NMR (CDCl_3): δ -2.8, -4.53 ($\text{Si}(\text{CH}_3)_2$, 134.7–129.3–149.3–150.6 (ArCH=), 130.9–128.3–134.5 (thiophene), 160.0 (CH=), 82.3 ($=\text{C}(\text{CN})_2$), 112.6–113.8 (CN). ^{29}Si NMR (CDCl_3): δ -23.8, -20.4 (s, $\text{Si}(\text{CH}_3)_2$). UV (CHCl_3): 344 nm ($\epsilon = 22000$).

Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{S}_1\text{N}_2\text{Si}_2$: C, 61.31; H, 5.71; S, 9.05; N, 7.94; Si, 15.93. Found: C, 61.00; H, 5.82; S, 8.45; N, 7.55; Si, 16.4.

Second-order polarizability measurements are performed by using a Q-switched mode-locked Nd^{3+} :YAG laser emitting at 1.34 μm by the electric field induced second harmonic generation (EFISH) method.^{11–13} The molecules are dissolved in acetone at various concentrations and the solutions placed in a wedge-shaped cell. A high voltage pulse, synchronized with the laser pulse, breaks the centrosymmetry of the liquid by dipolar orientation of the molecules. Translation of this cell perpendicular to the beam direction modulates the second harmonic signal into Maker fringes. The amplitude and periodicity of the fringing pattern are related to the macroscopic quadratic susceptibility, $\gamma(x)$, and to its coherence length, $l_c(x)$ (where x is the mass concentration). Calibrations are made with respect to the pure solvent. $\gamma(x)$ is related to the microscopic hyperpolarizabilities of the solvent, γ_s , and of the dissolved molecule, γ_c , by

$$\gamma(x) = \frac{Nf\rho}{1+x} \left(\frac{\gamma_s}{M_s} + x \frac{\gamma_c}{M_c} \right)$$

where ρ is the density of the solvent, N is Avogadro's number,

f is the local field factor, and M_s (respectively M_c) is the molecular mass of the solvent (respectively of the dissolved molecules).

$$\gamma_c(-2\omega; \omega, \omega, 0) = \gamma(-2\omega; \omega, \omega, 0) + \frac{\mu\beta(-2\omega; \omega, \omega)}{5kT}$$

μ is the ground-state dipole moment.

Carrying-out measurements at various concentrations ($x = 10^{-2}$ – 10^{-3}), neglecting the third-order contribution $\gamma(2\omega; \omega, \omega, 0)$,¹⁴ and assuming a two-level model for the frequency dispersion of β ,¹¹ one can derive a frequency-independent value, β_0 :

$$\beta_0 = \left(\frac{\omega_1^4}{(\omega_1^2 - \omega^2)(\omega_1^2 - 4\omega^2)} \right)^{-1} \beta(-2\omega; \omega, \omega)$$

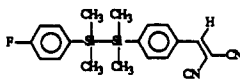
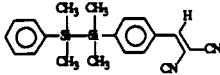
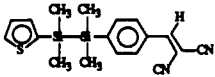
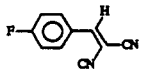
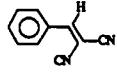
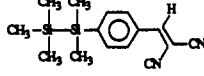
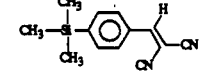
Dipole moments are separately measured in a nonpolar solvent (dioxane), using a dipole meter and applying the Hedestrand method.¹⁵ Absorption spectra are made in chloroform with a Lambda 9 spectrophotometer.

SHG powder tests are performed by using a Q-switched Nd^{3+} :YAG laser source emitting at 1.06 μm . A qualitative comparison is made, at constant laser emission power, between the visible SHG signal of the sample of interest and those from several reference powders (quartz, KDP, urea, POM, NPP).

III. Discussion

The thiophene derivative (molecule 3 in Table I) exhibits a significant harmonic signal in powder, similar to that of KTP. This is the first occurrence, to our knowledge, of any quadratic nonlinear response in the crystalline state for an organosilicon derivative. The extended transparency

Table I. Values of Peak Absorption Wavelengths (λ_{\max}),^a Dipole Moments (μ),^b and Frequency-Independent Second-Order Polarizabilities (β_0)^c for Several Silicon Derivatives^d

compd	λ_{\max} (CHCl ₃), nm	μ , D	β_0 , 10 ⁻³⁰ esu
1	 344	5.8	9.1
2	 345	5.6	8.5
3	 344	6.2	8.2
4	 317	4.8	4.0
5	 312	6.5	3.76
6	 342	6.1	8.8
7	 322	5.0	9.0

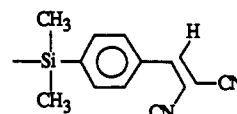
^a Measured in chloroform. ^b Measured in dioxane. ^c Measured in acetone. ^d The maximal relative error on β_0 is about 6%. Compounds 2 and 6 are described in ref 7, while compound 7 is from ref 6.

of the molecule ($\lambda_{\max} = 344$ nm in chloroform) in the blue and near-UV spectral range qualifies this material for frequency doubling within this transparency domain, provided the material is able to form macroscopic single crystals of good quality. The values of λ_{\max} , μ , and β_0 of the thienyl and fluorine derivatives are given in Table I and compared to those of several compounds already measured in previous studies.^{6,7}

Comparisons of λ_{\max} , μ , and β_0 values between compounds 1–3 and 6 suggest that, as far as the intramolecular charge transfer is concerned, the fluorine atom is almost as inactive as a hydrogen atom. This is confirmed by the similar β values for compounds 4 and 5. Compounds 1 and 2 exhibit similar maximum absorption wavelengths, dipole moments, and hyperpolarizabilities when experimental errors are taken into account. The thiophene derivative presents also similar linear and nonlinear optical properties to those of the fluorinated and the hydrogenated ones (1 and 2). The usual “inductive” attractive character of fluorine, leading to substantial changes in the dipole mo-

ment for “classical” ICT compounds as illustrated by compounds 4 and 5, seems to be strongly reduced by the presence of silicon atoms in the para position (see 1 and 2). The dipole moment of 1 is almost the same as for 2 and only slightly weaker than for 6.

The remarkably similar β_0 values of compounds 1–3 and 6 clearly give evidence that, for an identical attractor (dicyanovinyl), the addition of weak electron-donating groups such as Me₃Si, phenyl, thienyl, or fluorophenyl does not significantly alter the β_0 value of the organosilicon ICT molecule. A red shift of 20 nm is also noted in this case. The large increase of the molecular volume resulting from the addition of the abovementioned substituents would lower the “hyperpolarizability density” $\rho_h = \beta/V^{16}$ and therefore weaken the efficiency of the corresponding macroscopic systems. The “inactive” character of weakly electron-donating substituents when conjugated to a strong attractor through the disilane chain may probably be accounted for by the predominance of a more “local” ICT limited to the following moiety:



as confirmed by the similar β_0 values when comparing 1–3, 6, and 7. In ref 7, on the contrary, we have evidenced an ICT extending over the whole system, by involving more electron-donating groups such as MeO or (CH₃)₂N. This charge transfer is made possible by the stronger electron-donating nature of these substituents as compared to the silane group, resulting in limited electron transfer, through the disilane chain. In the present work, the fluorophenyl or the thienyl groups are not strong enough to withdraw any substantial amount of electronic charge toward the acceptor through the disilane chain. Therefore, the ICT remains limited to the silane/dicyanovinyl system through the phenyl ring.

In conclusion, we have investigated the role of weakly donating groups when conjugated to a strong attractor through two silicon atoms. The negligible influence of such substituents is accounted for by the predominance of local ICT between the silane and the dicyanovinyl group. However, the evidence of a significant SHG emission in the crystalline state for compound 1 may simulate further investigations in the field of organosilicon derivatives to find new transparent and efficient organic materials for optical signal processing in the blue and near-UV range.

Registry No. 1, 135734-07-5; 3, 135734-08-6; 4, 2826-22-4; 5, 2700-22-3; 8, 130104-13-1; 9, 135734-09-7; 10, 135734-10-0; F-*p*-C₆H₄Br, 460-00-4; Br-*p*-C₆H₄Br, 106-37-6; CH₂(CN)₂, 109-77-3; Si₂Cl₂(CH₃)₄, 4342-61-4; 2-bromothiophene, 1003-09-4; 1-(4-bromophenyl)-2-chlorotetramethyldisilane, 129620-61-7.