acetate and water and dried, yield 221 mg. This material was deblocked in anhydrous TFA saturated with HBr (2 ml) in the usual manner and the reaction product was precipitated with ether, washed with ether, and dried, yield 238 mg. This material was dissolved in 40% formic acid (3 ml) and the solution was applied to a Sephadex G-25 column (2 × 150 cm) which was developed with 40% formic acid. Fractions (7 ml each) were collected at a flow rate of approximately 7 ml/15 min and small aliquots of individual fractions were subjected to tlc using the chlorine test for visualization. The content of tubes containing single spot material (R_f^{III} 0.6) were pooled and lyophilized: 69 mg (36%); $[\alpha]D^{29}$ −33.7° (*c* 1.0, 90% formic acid); amino acid ratios in 48 hr acid hydrolysate, $\mathrm{Val_{2.0}Ile_{1.0}Thr_{3.1}His_{1.0}Gly_{2.1}Ala_{1.0}Ser_{0.8}Asp_{2.0}Phe_{1.0}}$-$\mathrm{Glu_{1.0}Cys_{0.9}}$ (82%); ratio Ile/Phe = 1.0; amino acid analysis in performic acid oxidized sample, $\mathrm{Val_{2.0}Ile_{1.0}Thr_{2.9}His_{1.1}Gly_{2.1}Ala_{1.1}}$-$\mathrm{Ser_{0.8}Asp_{2.1}Phe_{1.0}Glu_{1.0}Cys(SO_3H)_{0.8}}$ (92%); ratio Ile/Phe = 1.0.

Synthesis of Fragment G (Positions 81–104). Route a. From Subfragment G_4 Azide and Subfragment G_5. Subfragment G_4 hydrazide bistrifluoroacetate (50 mg) was dissolved in 90% TFA (1 ml) and the solution was cooled at −10°. A 1% solution of *tert*-butyl nitrite in DMF (0.3 ml) was added and the solution was stirred at −10° for 10 min when ether was added. The precipitate was collected, washed with ice-cold ether, and dried at 4°. The azide (46 mg) was added to a solution of subfragment G_5 (25 mg) in DMSO (1 ml) and 10% TEA in DMF (0.12 ml) and the mixture was stirred at room temperature for 24 hr. Ethyl acetate was added and the precipitate was collected, washed with ethyl acetate and water, and dried (70 mg). This material was dissolved in anhydrous TFA saturated with HBr (3 ml) containing anisole (0.1 ml) and HBr was passed through the solution at 0° for 5 min and at room temperature for 40 min. Ether was added and the precipitate was washed with ether and dried (69 mg). This material was stirred for 12 hr at room temperature in water (70 ml) and the insoluble material was removed by centrifugation. The clear supernatant was added to a column of Biorex 70 H^+ form (1.5 × 5 cm) which was eluted with water (350 ml), 0.5 *N* acetic acid (280 ml), 1 *N* acetic acid (280 ml), 2 *N* acetic acid (70 ml), and 5 *N* acetic acid (280 ml). The 5 *N* eluates were evaporated to a small volume and lyophilized: 14 mg (22%); R_f^{III} 0.5; amino acid ratios in 48 hr acid hydrolysate, $\mathrm{Asp_{5.0}Glu_{3.1}Leu_{1.05}Ala_{2.0}Gly_{3.1}Val_{1.8}Ile_{0.98}Thr_{3.0}}$-$\mathrm{His_{1.0}Ser_{1.0}Phe_{0.95}Cys_{0.6}}$ (76%); ratio Ile/Phe = 1.03.

Route b. From Subfragment G_1G_2 Azide and Subfragment G_3. Subfragment G_1G_2 hydrazide bistrifluoroacetate (60 mg) was dissolved in 90% TFA (1.2 ml) and the solution was cooled at −20°. A 10% solution of *tert*-butyl nitrite in DMF (0.042 ml) was added and the solution was stirred at −20° for 10 min when ether was added. The precipitate was collected, washed with ether and 1% TEA in ether, and dried at 4°. This azide dissolved in DMSO (0.8 ml) was added at 4° to a solution of subfragment G_3 hydrobromide (37 mg) in DMSO (1 ml), DMF (0.8 ml), and 10% TEA in DMF (0.044 ml). The mixture was stirred for 36 hr at 4° and ethyl acetate was added. The precipitate was washed with ethyl acetate and water and dried (90 mg). The material was deprotected with HBr in TFA in the manner described above and the reaction product dissolved in 20% acetic acid (60 ml) was applied to a column (1 × 12 cm) of Amberlite IRA-400 and the column was eluted with 20% acetic acid. Chlorine positive eluates were pooled and lyophilized (92 mg). The desired product was isolated by Sephadex G-50 chromatography using 30% formic acid as the solvent: 11 mg (13%) of the lyophilized product was obtained; R_f^{III} 0.5; amino acid ratios in 48 hr acid hydrolysate, $\mathrm{Asp_{4.9}Glu_{3.0}Leu_{1.06}Ala_{2.1}Gly_{3.0}Val_{2.0}Ile_{1.03}Thr_{2.9}His_{1.0}Ser_{1.0}Phe_{1.06}}$-$\mathrm{Cys_{0.7}}$ (92%); ratio Leu/Phe = 1.0.

Route c. From Subfragment G_1 Azide and Subfragment G_2G_3. Subfragment G_1 hydrazide trifluoroacetate (84 mg) was dissolved in DMSO (1.0 ml) and DMF (0.7 ml) was added. The clear solution was cooled at −10° and 6.7 *N* hydrogen chloride in dioxane diluted (1:10) with DMF (0.34 ml) was added followed by 10% *tert*-butyl nitrite in DMF (0.11 ml). The reaction mixture was stirred at −10° for 15 min and cooled at −20° and TEA (10% in DMF, 0.44 ml) was added followed by a solution of subfragment G_2G_3 hydrobromide (94 mg) in DMSO (0.7 ml) and 10% TEA in DMF (0.14 ml). The precipitate was collected, washed with ethyl acetate and water, and dried (131 mg). This material was deprotected in 2 ml of anhydrous TFA–HBr in the manner described above, and the product was precipitated with ether, washed with ether, and dried (138 mg). The desired product was isolated by gel filtration on a column of Sephadex G-50 (1.8 × 145 cm) using 30% formic acid as the solvent. The contents of tubes containing single spot material by tlc (R_f^{III} 0.5) were pooled and the product was isolated by lyophilization: 38 mg (28%); $[\alpha]^{25}D$ −42.5° (*c* 0.98, 90% HCOOH); R_f^{III} 0.5, ninhydrin, Pauly, Ellman + NH_3 positive spot; amino acid ratios in 48 hr acid hyrolysate, $\mathrm{Asp_{5.0}Glu_{2.9}}$-$\mathrm{Leu_{1.05}Ala_{2.1}Gly_{3.0}Val_{2.0}Ile_{0.99}Thr_{2.9}His_{1.0}Ser_{1.0}Phe_{1.01}Cys_{0.5}}$ (92%); ratio Ile/Phe = 0.98.

Fragment G was also isolated by chromatography on AG1-X2 in the following manner. Crude fragment G (294 mg) prepared from 168 mg of G_1 hydrazide and 188 mg of G_2G_3 in the manner described above was lyophilized twice from aqueous formic acid and dissolved in DMF–H_2O (3:2; 60 ml). The solution was applied to an AG1-X2 column (2 × 7 cm) that was developed with the following solvents: DMF–H_2O (150 ml), DMF–0.01 *N* AcOH (150 ml), DMF–0.02 *N* AcOH (100 ml), DMF–0.05 *N* AcOH (150 ml), and DMF–1 *N* AcOH (100 ml). The ratio of DMF to aqueous AcOH was 3:2. Fractions (5 ml each) were collected and chlorine positive tubes from the DMF–0.05 *N* AcOH eluates containing the desired material were pooled, evaporated, and lyophilized from aqueous formic acid: 50 mg (19%); R_f^{III} 0.5; amino acid ratios in 48 hr acid hydrolysate, $\mathrm{Asp_{4.8}}$-$\mathrm{Glu_{3.1}Leu_{1.02}Ala_{2.1}Gly_{3.2}Val_{1.8}Ile_{0.93}Thr_{3.2}His_{0.9}Ser_{0.9}Phe_{1.05}Cys_{0.9}}$ (88%); ratio Leu/Phe = 0.97; amino acid ratios in 48 hr acid hydrolysate of performic acid oxidized sample, $\mathrm{Asp_{4.8}Glu_{2.9}Leu_{1.01}}$-$\mathrm{Ala_{2.0}Gly_{3.1}Val_{2.1}Ile_{1.14}Thr_{3.1}His_{1.1}Ser_{0.8}Phe_{1.01}Cys(SO_3H)_{0.9}}$ (92%); ratio Leu/Phe = 1.0.

Acknowledgment. The authors wish to express their appreciation to Mr. Guirguis Rizk for the amino acid analyses.

Communications to the Editor

Charge-Transfer Complexing between Permethylpolysilanes and Tetracyanoethylene[1]

Sir:

Excited-state charge transfer (CT) complexes between aromatic hydrocarbons and π acceptors are well known,[2] and CT complexes are also formed between lone pair donors and π acceptors. In studying the spectral properties of permethylpolysilanes we find that compounds with Si–Si bonds appear to form CT complexes with the π acceptor tetracyanoethylene (TCNE), even though these silanes lack either π bonds or lone electron pairs.

Solutions of permethylpolysilanes, 0.1–0.5 *M* in chloroform containing 0.015 *M* TCNE, are colored, and the color deepens as the number of silicon atoms in the chain increases. In the visible spectrum new CT bands appear, sometimes rather broad and unsymmetrical

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[1] This work was supported in part by the Air Force Office of Scientific Research (NC) O.A.R., USAF, Grant No. AF-AFOSR, 70-1904.

[2] R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969; R. S. Mulliken and W. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969.

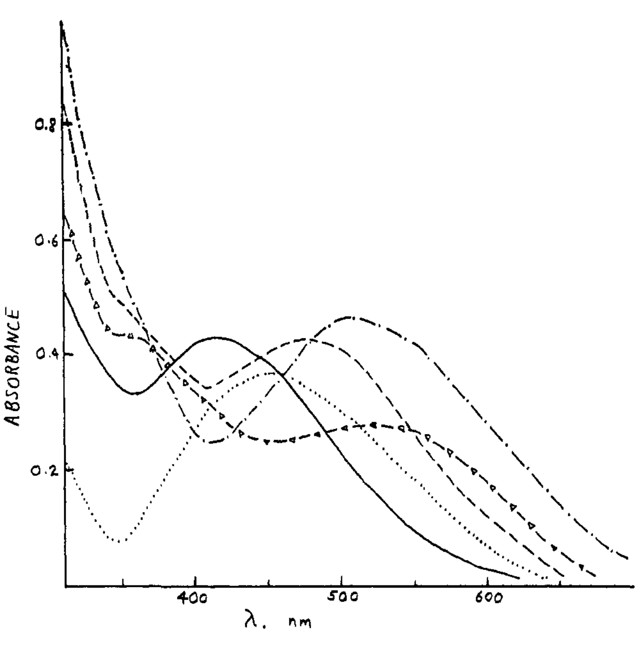

Figure 1. Spectra of charge-transfer complexes of TCNE, 0.015 *M* in chloroform, with permethylpolysilanes: (——) $Me_3SiSiMe_3$, 0.35 *M*; (----) Si_3Me_8, 0.40 *M*; (.....) $(Me_3Si)_4Si$, 0.35 *M*; (-Δ-Δ-Δ-) Si_4Me_{10}, 0.40 *M*; (-·-·-·-) $(SiMe_2)_6$, 0.40 *M*.

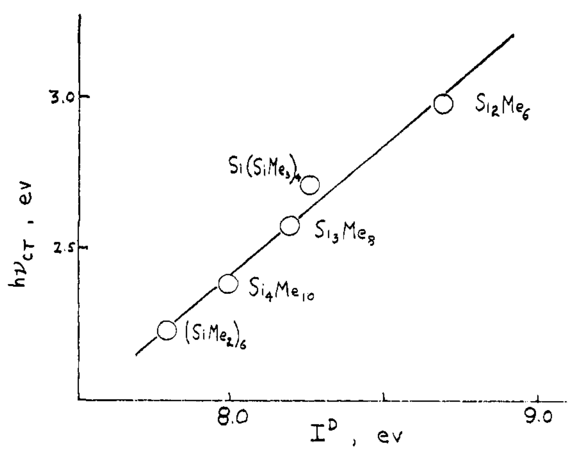

Figure 2. Plot of charge-transfer transition energies $h\nu_{CT}$ for TCNE–polysilane complexes against the first ionization potentials I^D of polysilanes.

(Figure 1). The colors and wavelength maxima for the TCNE complexes of the polysilanes of Figure 1 are hexamethyldisilane, yellow, 417 nm; octamethyltrisilane (Si_3Me_8), red, 480; tetrakis(trimethylsilyl)silane ($Si(SIMe_3)_4$, orange-red, 458; decamethyltetrasilane, violet, 370 sh, 520; dodecamethylcyclohexasilane $(SiMe_2)_6$, violet, 507. Separate solutions of polysilanes or of TCNE in chloroform are colorless and show no measurable absorption at wavelengths longer than 320 nm.

Intermolecular charge transfer seems indicated to account for the new absorption bands observed when polysilanes and TCNE are mixed. In this interaction we believe that the silicon compounds serve as donors and TCNE as the acceptor.[3] For charge-transfer complexes of various donors with the same acceptor, the energy of the charge-transfer band should be related to the ionization potential for the donor.[5] Data for our compounds are shown in Figure 2; the relationship is approximately linear as required by theory.[2] However, the relationship may be more complicated because some of the CT absorptions appear to consist of several overlapping bands.

The shape of the CT bands was studied using Briegleb's relationship,[7] $(\tilde{\nu}_h - \tilde{\nu}_l)/2(\tilde{\nu}_m - \tilde{\nu}_l)$, where $\tilde{\nu}_h$ and $\tilde{\nu}_l$ refer to the wave numbers at half the maximum intensity on the high- and low-energy side of the peak located at $\tilde{\nu}_{max}$. For aromatic donors with π acceptors this relationship has a value near 1.2. The complex of TCNE with $Si(SiMe_3)_4$ appears to give only a single CT band (Figure 1);[8] the value of Briegleb's relationship for this band is $\sim$1.1. Using this value for the asymmetry we have separated bands for complexes which appear to have overlapping CT absorptions.[9] Thus for $(SiMe_2)_6$TCNE the broad band at 507 nm can be separated into bands at 555 and 477 nm. These may be due to charge transfer from the two highest filled levels of $(SiMe_2)_6$, with ionization energies of 7.79 and 8.16 eV.[5] The difference in energies of CT transitions is the same as the difference in the ionization potentials: $\Delta h\nu_{CT} = \Delta I^D = 0.37$ eV.

The absorbance of the complexes was studied as a function of donor concentration. Straight-line plots were obtained using the Benesi–Hildebrand method,[2] but the intercepts used for calculating *K* and ϵ values were near zero (or negative) indicating that the complexes are quite weak.[10] Polysilanes also appear to form colored charge-transfer complexes with other acceptors; for example, new absorption bands appear in the spectra of solutions of $(SiMe_2)_6$ with chloranil (yellow, λ_{max} 430 nm) and Si_3Me_8 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (violet, λ_{max} 535 nm).

Relatively few examples of CT complexing involving σ-electron donors are known,[11] and none appear to have been reported for π acceptors. In the light of our observations it is reasonable that other metal compounds with low ionization potentials should also form CT complexes with π acceptors; preliminary experi-

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(3) A referee suggested that charge-transfer might occur in the opposite direction, from TCNE as donor to polysilanes as acceptors. However, the first ionization potential of TCNE is about 10.1 eV[4] while those of polysilanes are less than 9.0 eV.[5] Moreover the electron affinity of polysilanes is comparable with that of benzene and far lower than for TCNE.[6]

(4) H. Kuroda, T. Amano, I. Ikemoto, and H. Akamatu, *J. Amer. Chem. Soc.*, **89**, 6056 (1967).

(5) Ionization potentials for polysilanes (Figure 2) were determined by photoelectron spectroscopy: H. Bock and W. Ensslin, *Angew. Chem. Int. Ed. Engl.*, 10, 404 (1971).

(6) E. Carberry and R. West, *J. Amer. Chem. Soc.*, **91**, 5446 (1969).

(7) G. Briegleb and J. Czekalla, *Z. Phys. Chem.* (*Frankfurt am Main*), **24**, 37 (1960).

(8) Only a single CT band is expected because $Si(SiMe_3)_4$ has only a single low-energy ionization potential; see ref 5.

(9) The details of the analysis of charge-transfer spectra will be given elsewhere; for example, see E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, **86**, 3930 (1964).

(10) The relatively low values of K_c and ϵ presumably account for the fact that these complexes have not been detected earlier. For example, Pitt reports that polysilanes do not form detectable CT complexes with TCNE (unpublished work reported by C. G. Pitt and H. Bock, *J. Chem. Soc., Chem. Commun.*, 28 (1972)). Our earlier attempts to detect such complexes were also unsuccessful.

(11) Saturated hydrocarbons and alkyl metal compounds form weak CT complexes with strongly electron-deficient halides such as NbF_5, MoF_5, and WF_6; see R. R. McLean, D. W. A. Sharp, and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 676 (1972); P. R. Hammond, *J. Phys. Chem.*, 74, 647 (1970). Saturated hydrocarbons also form charge transfer complexes with iodine, in which the energy of the CT band is related directly to the ionization potential for the hydrocarbon donor: see S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Amer. Chem. Soc.*, **75**, 2900 (1953).

ments with alkyl polygermanes and polystannanes show that they also appear to form CT complexes with TCNE. Work on these and other organometallic donors is in progress.

(12) Soviet participant of IREX (International Research Exchange Board) program in 1972–1973.

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Intermolecular Donation of a σ-Electron from Group IVb Catenates to Tetracyanoethylene. Evidence of Electron Paramagnetic Resonance and Charge-Transfer Spectra

Sir:

During the course of the study on σ–π conjugation in arylpolysilanes,[1,2] we have found that σ electrons of low ionization energy, such as of the Si–Si and Ge–Ge bonds, can be donated to certain π acceptors such as tetracyanoethylene (TCNE). For example, permethylpolysilanes, Me(SiMe$_2$)$_n$Me ($n \geq 2$), form charge-transfer complexes with TCNE in dichloromethane. Such complexes were identified by both photoinduced epr signals of TCNE anion radicals and characteristic charge-transfer bands in the visible region. Although $\pi \rightarrow \pi$ or n $\rightarrow \pi$ electron donor–acceptor interactions have been well known,[3] relatively few examples of σ donors are found in the literature.[4,5] This fact appears to be related to the high ionization potentials of σ electrons, relative to n and π electrons, in most molecules.

Solutions (*ca.* 0.1 *M*) of TCNE and permethylpolysilane (*ca.* 0.1 *M*) in dichloromethane were placed in a Pyrex tube, degassed as thoroughly as possible by freeze–thaw cycles, and sealed. The samples were cooled to −60 to −70° and examined for a spontaneous epr signals using a Varian E 12 spectrometer. No signal was observed without irradiation;[6] however, when the sample was irradiated with a focused 500-W super-high-pressure mercury lamp, an immediate and strong nine-line epr photosignal of the TCNE radical anion was observed. The splitting constant (a_N = 1.556 G) agreed with that recorded for the sodium salt in tetrahydrofuran (a_N = 1.56 ± 0.02 G).[7] The epr photosignal reached a maximum within 3 sec after the ultraviolet light was turned on and decayed to zero during periods of prolonged irradiation. Although the countercation (or a radical cation) is not identified,[8] the TCNE radical anion should arise from charge-transfer interaction with polysilanes.

The intensities of photosignals depend upon the length of the polysilane chain: the weakest signal was observed for hexamethyldisilane and the strongest signals were observed for the longer polysilanes. Therefore, higher polysilanes form charge-transfer complexes more easily. Tetramethylsilane did not give the photosignal under the same experimental conditions.

After Lagercrantz and Yhland used epr to demonstrate the photoinduced transfer of an electron from donors to acceptors in solution,[9] several workers have reported on the existence of epr signals arising from donor–acceptor interactions, both in the presence and absence of irradiation.[10–12] Many π donors, such as benzene and its derivatives, and n donors, such as THF and amines, give rise to epr signals involving TCNE radical anions in the presence and/or absence of irradiation. However, the photoinduced transfer of an electron from compounds with only a σ framework to a π acceptor has not been known to date.

The donor properties of permethylpolysilanes have been further demonstrated by appearance of charge-transfer bands when permethylpolysilane and TCNE were dissolved in dichloromethane.[13] Table I lists the frequencies of band maxima and ionization potentials of polysilanes as determined by electron impact[14] (EI) and photoelectron spectroscopic (PE) methods.[15]

Table I. Frequencies for Charge-Transfer Absorptions in Complexes of TCNE with Permethylpolysilanes, Me(SiMe$_2$)$_n$Me, in Dichloromethane at Room Temperature

	ν_{max}			
n	cm^{-1}	eV	IP(EI),[a] eV	IP(PE),[b] eV
2	24,000	2.97	8.00	8.69
3	21,100	2.61	7.53	8.19
4	19,600	2.43	7.29	7.98
5	18,400	2.28	7.11	(7.79)[c]

[a] Reference 14. [b] Reference 15. [c] Calculated from the relationship between IP(EI) and IP(PE) for linear permethylpolysilane: IP(PE) = 1.009 IP(EI) + 0.613 (r = 0.999).

Although charge transfer interactions between permethylpolysilanes and TCNE are weak, well-defined charge-transfer spectra were observed. Interestingly, a good linear relationship between charge-transfer frequencies and ionization potentials of the respective polysilanes was obtained.[16]

$$\nu_{CT}\,(\text{eV}) = (0.77_1)\text{IP(PE)} - 3.71_6 \; (r = 0.999)$$

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(1) H. Sakurai, S. Tasaka, and M. Kira, *J. Amer. Chem. Soc.*, **94**, 9285 (1972).

(2) H. Sakurai and M. Kira, *J. Amer. Chem. Soc.*, submitted for publication.

(3) (a) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969; (c) R. S. Mulliken and W. Person, "Molecular Complexes," Wiley, New York, N. Y., 1969.

(4) S. H. Hastings, J. L. Franklin, J. C. Schilker, and F. A. Matsen, *J. Amer. Chem. Soc.*, 75, 2900 (1953).

(5) R. R. McLean, D. W. A. Sharp, and J. M. Winfield, *Chem. Commun.*, 452 (1970); *J. Chem. Soc., Dalton Trans.*, 676 (1972).

(6) In some cases weak dark signals were observed, but unidentified.

(7) W. D. Phillips, J. C. Rowell, and S. I. Weissmann, *J. Chem. Phys.*, **33**. 626 (1960).

(8) After the ultraviolet light was turned off, the epr signal disappeared immediately. Therefore, there exists free radicals or radical cations which can combine with TCNE·$^-$

(9) C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, **16**, 1013, 1799, 1807 (1962).

(10) D. F. Ilten and M. Calvin, *J. Chem. Phys.*, **42**, 3760 (1965).

(11) F E. Stewart and M. Eisner, *Mol. Phys.*, **12**, 173 (1967).

(12) N. S. Isaacs and J. Paxton, *Photochem. Photobiol.*, **11**, 137 (1970).

(13) V. F. Traven and R. West, *J. Amer. Chem. Soc.*, **95**, 6824 (1973), have observed similar charge-transfer complexing between permethylpolysilanes and TCNE in chloroform.

(14) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *J. Amer. Chem. Soc.*, **92**, 519 (1970).

(15) H. Bock and W. Ensslin, *Angew. Chem.*, **83**, 404 (1971).

(16) However, this linear relation has only a limited accuracy since unsymmetrical shapes of CT bands indicate overlapping multiple transitions. The separation of the two highest occupied molecular orbitals for decamethyltetrasilane is, for example, only 0.78 eV[15] or 6300 cm^{-1}. Nevertheless, the relation is important enough to indicate the $\sigma \rightarrow \pi$ intermolecular charge transfer.