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Ultraviolet and Charge-Transfer Spectra of Benzylsilanes

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The frequencies of low-energy charge-transfer bands (CT-II) of 14 benzylsilane-tetracyanoethylene complexes were correlated with σ^I constants of substituents on silicon. The CT-II frequencies of benzylsilanes and other related compounds were also linearly related to their ^1L_a absorption frequencies, a σ-π conjugation mechanism being discussed.

In a previous paper from this laboratory,[1] it was described that in simple benzylic compounds, $PhCH_2X$, the charge-transfer energies with tetracyanoethylene (TCNE) can be reasonably related to parameters of inductive effect of XCH_2, i.e., $\sigma^*_{XCH_2}$. However, at the same time it was noted that the charge-transfer energies of benzyltrimethylsilane was exceptional, indicative of a hyperconjugative interaction of a carbon-silicon bond with the π-electron system (σ-π conjugation).[2,3] At that time, Traylor and coworkers reported that a carbon-metal bond can stabilize a neighboring cationic center by σ-π conjugation rather than nucleophilic participation.[4,5] Thus, carbon-metal bonds display stabilizing influeneces on vertical processes such as charge-transfer spectra of benzyl-metal derivatives, as evidenced by a linear correlation of charge-transfer frequencies of $PhCH_2HgX$-TCNE complexes with σ^I_X.[5]

We report here ultraviolet and charge-transfer spectra of 14 benzylsilanes of the type $PhCH_2SiX^1X^2X^3$ and some related compounds. These data demonstrate the similar importance of σ-π conjugation in these compounds.

Charge-transfer spectra of benzyl Group IVb derivatives with TCNE were observed in dichloromethane solution as previously described.[1] Two well-resolved maxima were recorded but the spectra were further analyzed by the method of Voigt[6] to obtain accurate frequencies of two charge-transfer bands (CT-I and CT-II). The results are listed in Table 1. The Table contains also frequencies of ^1L_a bands of these compounds.

The charge-transfer frequencies of the low-energy CT-II bands are plotted against average σ^I values[7] of these substituents on silicon and a good linear relationship was observed as shown in Figure 1. The equation is

$$\nu^{PhCH_2SiX_3}_{TCNE}\ (cm^{-1}) = 7{,}740\ \sigma^I + 20{,}370$$

Table 1
Frequencies of UV- and CT-Spectra of $PhCH_2SiX^1X^2X^3$ and Related Compounds

X^1	X^2	X^3	ν (UV), cm^{-1}		ν (CT), cm^{-1}	
			^1L_a	(ε)	CT-I	CT-II
Me	$SiMe_3$	$SiMe_3$	a		25400	19500
Me	Me	$SiMe_3$	44400	(13500)	25100	19700
Me	Me	Me	45000	(9580)	24600	20100
Me	Me	CH_2SiMe_3	44800	(8740)	25200	19900
Me	Me	H	45500	(7640)	24900	20700
Me	H	CH_2SiMe_3	45100	(8910)	25300	20400
Me	Me	CH_2Ph	44700	(18500)	25000	19900
CH_2Ph	CH_2Ph	H	44800	(23000)	25500	20700
Me	Me	OMe	45200	(9350)	25000	20500
Me	Me	Cl	b		25900	21400
Me	OMe	OMe	b		25100	21100
Me	H	Cl	b		25900	21900
OMe	OMe	OMe	b		26200	22000
H	Cl	Cl	b		26800	22900
($PhCH_2GeMe_3$)			44400	(7200)	25200	19600
($PhCH_2SnMe_3$)			42400	(5520)	25100	17900

a. End absorption. b. Not determined.

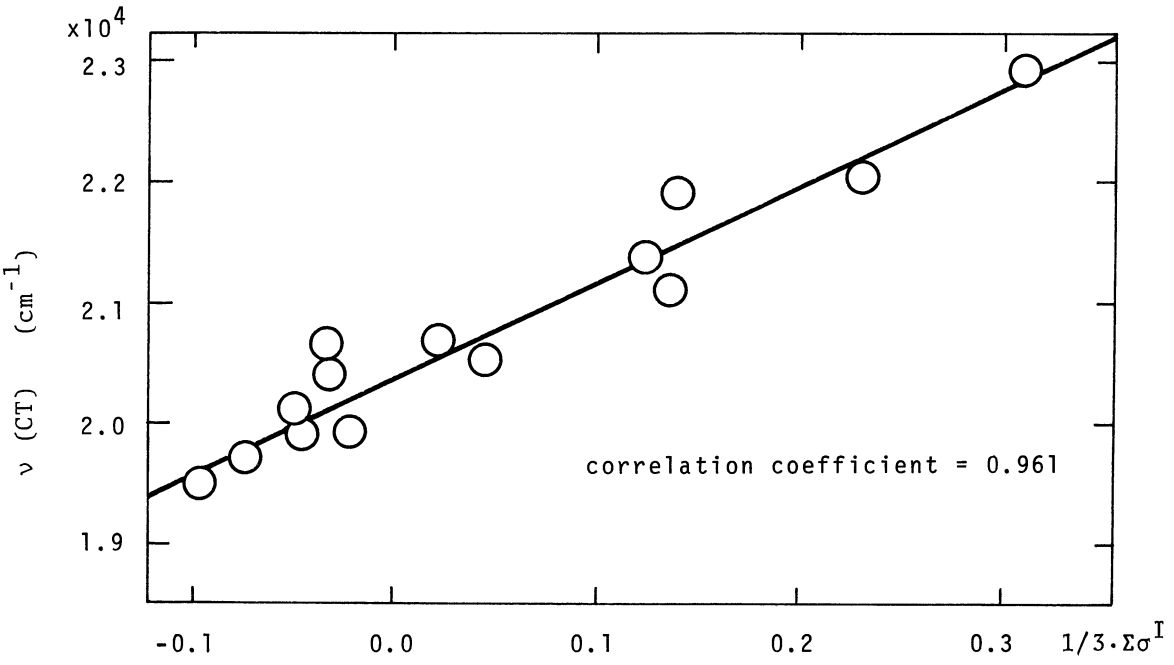

Figure 1. Plots of charge-transfer frequencies of $PhCH_2SiX^1X^2X^3$- TCNE complexes agaist σ^I constants.

Such a linear relationship and rather large effects to stabilize the charge-transfer complexes by the groups X on $PhCH_2SiX_3$ can be taken another evidence for the Si-C σ-π conjugation. Thus, the substituent effects of CH_2SiX_3 groups may be best explained in terms of inductive effects of X to stabilize the positive charge developed on the SiX_3 groups in charge-transfer complexes. As a result, X changes the conjugating abilities of a Si-CH_2 bond with a π-electron system.

The ρ^I value of the similar equation for $PhCH_2HgX$-TCNE complexes was reported to be 11,200 (cm^{-1}).[5] The difference in ρ^I values of two cases seems to be interesting, since the availability of conjugating σ electrons may parallel to the cationic stability of the metal center. Such cationic stabilities should be directly related to electronegativity of metals. The lower ρ value observed for benzylsilanes in the present study is in accord with less electropositive nature of silicon than of mercury. It is interesting, therefore, to examine the same sort of relationship for various benzylmetal(loid) compound, a related work being in progress.

The ultraviolet spectra of benzyl Group IVb derivatives disclosed intense absorption maxima in the π→π* transition region.[8] The ^1L_a transition of these benzylmetals is at a significantly longer wavelength than that of phenyl derivatives. Although this red shift has been explained usually in terms of inductive effects[9] or dπ-pπ interactions,[10] a recent recognition of σ-π conjugation of organometallic compounds led to suggest that the red shift is due to the importance of conjugation between the metal-carbon σ bond and the π electron system.[11] However, since the electronic transitions depend upon energies of both ground and excited state, these data alone can not be taken as a proof of σ-π conjugation.[12] In this connection, it is worthwhile to note that the ultraviolet transition frequencies of benzyl Group IVb metals are linearly related to their charge-transfer frequencies as shown in Figure 2. The equation is

$$\nu\ (^1L_a) = 1.09\ \nu\ (CT) + 22{,}900 \quad (cm^{-1})$$

The slope of this linear relationship was approximately unity. Therefore, it is concluded that the major decrease in the ^1L_a transition energy in the series of $PhCH_2MX_3$ is due to the importance of σ-π conjugation to raise the energy of the π orbitals. The energy levels of the π* orbitals are little affected in these compounds.

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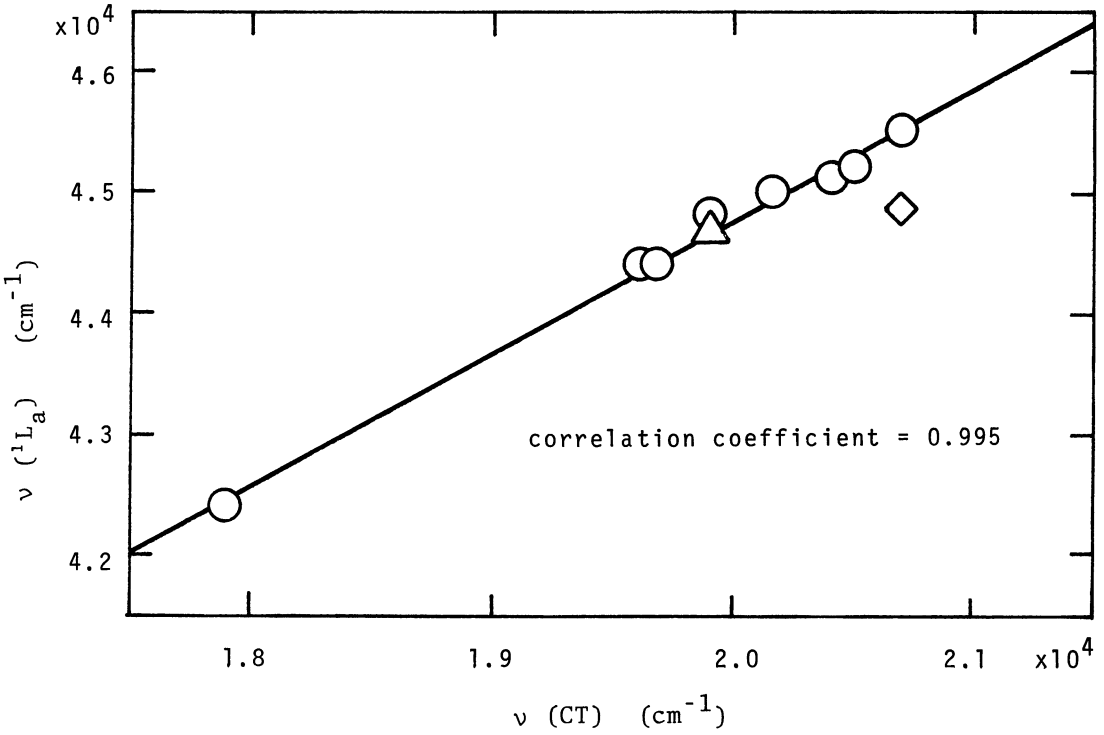

Figure 2. Plots of UV absorption maxima of benzyl Group IVb derivatives against their CT frequencies. $(PhCH_2)_2SiMe_2$ (△) and $(PhCH_2)_3SiH$ (◇) are excluded from the least squares plot because of a possible interaction between benzyl groups.

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