d-Orbital Effects in Silicon-Substituted π-Electron Systems. XXIV.[1] Charge-Transfer Studies of Silyl- and Alkylbenzenes[2]

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Abstract: Information on the relative energies of the highest occupied molecular orbitals of π systems is easily obtained from charge-transfer absorptions of suitable donor–acceptor complexes. This method is used to determine the electronic effects of SiR_3, CH_2SiR_3, and CR_3 groups in 35 mono-, di-, tri-, and tetrasubstituted benzene derivatives. Steric effects on the CT excitation energies are excluded by the consistent results from tetracyanoethylene (TCNE) and iodine complexes as well as by the excellent correlation with ionization energies determined by mass spectroscopy. Extreme perturbations of the benzene π system comparable to those of alkoxy substituents are caused by CH_2SiR_3 and SiR_2SiR_3 groups. On the other hand the CT bands of SiR_3-substituted benzenes appear at even shorter wavelengths than those of the corresponding alkyl derivatives. The SiH_3 group shows no donor property at all. The experimental results, *i.e.*, number, wavelengths, and shape of the CT bands, are in agreement with the predictions of the MO perturbation treatment used. The substituent effects on the benzene e_{1g} molecular orbitals can be rationalized in terms of inductive polarization $+I_{SiR_3} > +I_{CR_3}$ as well as strong electron back-donation $Si \leftarrow C_\pi$ from the benzene π system into empty silicon atomic orbitals of π symmetry.

The perturbation of π-electron systems with well-known properties can be used to determine the unknown electronic influence of substituents. The isoconjugate alternant benzene π system is well suited for investigations of this kind: the degeneracy of the highest occupied e_{1g} molecular orbitals is removed by inductive and conjugative effects of substituents. Additional information is available from some simple relationships between different types of substitution due to distortions of the D_{6h} symmetry of benzene.

The substituent effects of SiR_3 groups on the benzene π system have been the subject of numerous investigations. For the corresponding radical anions esr data clearly demonstrate a $Si \leftarrow C_\pi$ electron delocalization into empty silicon orbitals.[3] The uv spectra of phenylsilanes are generally interpreted by excited-state interactions of similar "d–π^*" type.[4] Whether "d_π–p_π" bonding also lowers the ground-state energy of silylbenzenes cannot be determined from electronic transition energies which only represent the difference of substituent effects on both ground and excited states. Furthermore $Si \leftarrow C_\pi$ interactions should be less favored in the ground state due to the greater energy difference between occupied benzene molecular orbitals and empty acceptor orbitals of silicon. Nevertheless numerous observations have been reported in the literature which indicate "d_π–p_π" bonding also in the ground state of R_3Si-substituted benzene derivatives: dipole moments of silylbenzenes,[5] the ^{19}F nmr shielding in *m*- and *p*-fluoro derivatives,[6] ^1H nmr data of $Si(CH_3)_3$ and $Si(CH_3)_2H$ compounds,[7] p*K* values of benzoic acids, phenols, and anilines,[8] or the vibrational frequency $\tilde{\nu}_{OH}$ of silanol–ether adducts.[9] Extensive kinetic studies on the desilylation of R_3SiCH_2-substituted benzenes indicate a considerable inductive effect of the silyl group in a β position to the benzene ring,[10] whereas *ortho*- and *para*-electrophilic substitutions are only weakly activated by silyl groups in α position.[8]

Energy differences due to $Si \leftarrow C_\pi$ interactions in the ground state of silylbenzenes cannot be evaluated by the above-mentioned methods of measurement. In our investigations on silicon-substituted π-electron systems[11] besides mass spectroscopically determined ionization energies[12] charge-transfer studies[2] of suitable donor–acceptor complexes turned out to be a most valuable source of information on the relative energies of

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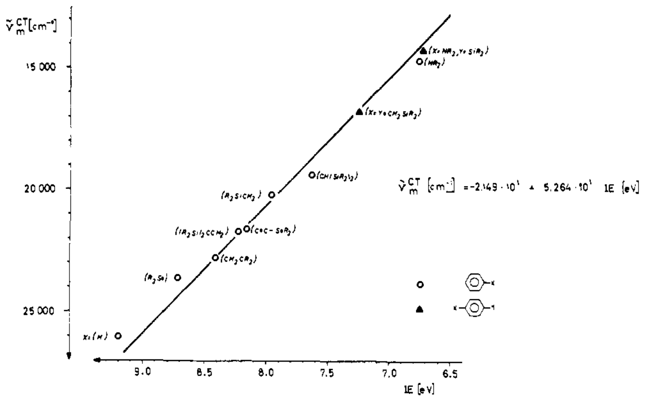


Figure 1. Correlation IE (eV)/$\bar{\nu}_m{}^{CT}$ (cm^{-1}) for 1- and 1,4-substituted benzene derivatives.

the highest occupied molecular orbitals in silyl- and alkylbenzenes.

Results and Discussion

I. CT Absorptions. Interpretation, Band Shapes, Steric Effects, and Correlation with Ionization Energies. The long-wavelength CT absorptions of donor–acceptor complexes D–A are assigned to an electron-transfer D → A leading to a radical ion pair D^+–A^-.[13] According to the Mulliken theory[14] of D–A complexes their excitation energy $E_m{}^{CT}$ depends upon the donor ionization

$$E_m{}^{CT} = IE_D - EA_A + C_1 + \frac{C_2}{IE_D - EA_A + C_1} \quad (1)$$

energy IE_D and the acceptor electron affinity EA_A. The energy term C_1 mainly comprises the difference between the Coulomb attraction D^+–A^- after excitation and the van der Waals bonding energy D···A before excitation; C_2 reflects intermolecular resonance. Under the assumption that C_1 and C_2 as well as EA_A are constants for comparable complexes between the same acceptor A and different donors D of high ionization energy,[13] eq 1 can be replaced by the linear expression[15]

$$\bar{\nu}_m{}^{CT} = aIE_D + b \quad (2)$$

Thus to a first approximation the wave numbers of the CT absorption maxima $\bar{\nu}_m{}^{CT}$ are proportional to the ionization energies IE_D of the donor molecule.

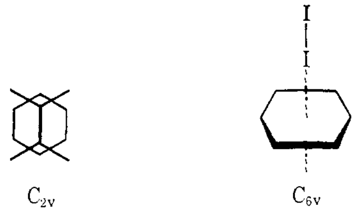
In a one-electron MO scheme the CT absorptions correspond to electron transitions from the highest occupied molecular orbital(s) $\psi_J{}^D$ of the donor into the lowest unoccupied molecular orbital(s) $\psi_J{}^A$ of the acceptor molecule. The excitation energy $E_m{}^{CT}$ is given by the difference of the eigenvalues $\epsilon_J{}^D$ and $\epsilon_J{}^A$ and the interaction energy E_{int} between the molecular orbitals $\psi_J{}^D$ and $\psi_J{}^A$ in the complex.[16] Therefore, correlations

$$E_m{}^{CT} = (\epsilon_J{}^A - \epsilon_J{}^D) + 2E_{int} \quad (3)$$

between the CT absorption energies and the energy changes of the highest occupied donor molecular orbital(s) $\psi_J{}^D$ due to the electronic effects of the substituents are expected only if the following conditions are fulfilled.

(i) The energy gap between the first and second acceptor molecular orbital should be large, because a definite assignment of more than one CT absorption is possible only if excitations from the different donor orbitals take place into the same acceptor orbital. Tetracyanoethylene was chosen because the energy gap between the first and second unfilled orbital has been calculated to amount to 2 eV.[17] This powerful acceptor has the additional advantage that the CT absorptions are usually found far outside of the self-absorption of both donor and acceptor.

(ii) The intermolecular distance D–A should be approximately constant irrespective of electronic or steric substituent influences, otherwise the terms C_1 and C_2 (eq 1) as well as E_{int} (eq 3) will change. Effects of this kind can be excluded by measuring both the TCNE and I_2 complexes of benzene derivatives, which, according to ir investigations in solution,[18] X-ray analysis,[19] and theoretical considerations,[20] are of different structure.



(4)

(iii) Correct values for the CT excitation energies, *i.e.*, 0 → 0 transition energies of a certain complex configuration cannot be obtained from the broad CT bands. Nevertheless the constancy of the CT band I in 1- and 1,4-substituted benzene derivatives[21,22] indicates that the observed CT band maxima are a reasonable approximation for the excitation energies.

Owing to assumptions i–iii, charge-transfer studies seem to be somewhat unreliable. Therefore, the ionization energies IE of benzene derivatives have been determined by means of a mass spectrometer equipped with a Fox ion source. The resulting excellent correlation with the long-wavelength CT absorption maxima $\bar{\nu}_m{}^{CT}$ is shown in Figure 1.

The linear regression from Figure 1 justifies the approximations of eq 2. As according to Koopmans' theorem[23] the first ionization energies are equivalent to the energies of the highest occupied (SCF) molecular orbitals, eq 3 with $\epsilon_J{}^A$ and E_{int} assumed to be constants will serve as a basis for the following interpretations.

II. Monosilyl- and Monoalkylbenzenes. CT Absorptions of TCNE and I_2 Complexes. In the case of benzene the degeneracy of the highest occupied e_{1g} molecular orbitals ψ_{as} and ψ_s is generally removed by the electronic effects of substituents X. A qualitative MO scheme for tetracyanoethylene (TCNE) complexes of monosubstituted benzene derivatives is given in Figure 2. According to the MO diagram (Figure 2) in ψ_{as} the substitution center is situated in the nodal plane, so only

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Table I. CT Absorptions (cm^{-1}) of C_6H_5X–TCNE Complexes in CH_2Cl_2 Solution

Compd no.	Substituent X	Exptl CT band max		CT band I	CT band II
1	H	26,050		26,050	26,050
2	CH_3	24,650			(23,200)
3	SiH_3	26,000		26,000	
4	CH_2CH_3	24,250			
5	$C(CH_3)_3$	24,000			(22,650)
6	$CH_2C(CH_3)_3$	24,100			(22,800)
7	$Si(CH_3)_3$	24,650			(23,600)
8	$CH_2Si(CH_3)_3$	24,050	20,550	(24,400)	(20,200)
9	$CH_2CH_2Si(CH_3)_3$	23,900			(22,000)
10	CH_2SiCl_3	25,300			(23,000)
11	CH_2SiF_3	25,700			(23,500)
12	$CH(Si(CH_3)_3)_2$	24,700	19,600	24,700	19,600
13	$CH(Si(CH_3)_3)C_6H_5$	24,500	20,000 sh	24,500	(19,800)
14	$C(Si(CH_3)_3)_2C_6H_5$	25,300	17,650	25,300	17,650
15	$CH_2C(Si(CH_3)_3)_3$	24,250			(21,600)
16	$Si(CH_3)_2Si(CH_3)_3$	24,800		(25,000)	(20,400)
17	$(Si(CH_3)_3)_2C_6H_5$	25,000		25,000	(20,600)

ψ_s will be affected. Substituents X exerting a $+I$ effect raise the molecular orbital ψ_s giving rise to a second CT band II at longer wavelengths. The CT excitation energy II is increased by counteracting conjugative interactions $-M_x$ with empty atomic orbitals of the substituent X. Because the CT band of the TCNE–C_6H_6 complex has a half-band width $\Delta\tilde{\nu}_{1/2}$ = 5800 cm^{-1},[24] both the CT bands I and II of C_6H_5X–TCNE complexes will only be separated if the difference of the eigenvalues $\epsilon_s - \epsilon_{as}$ is large enough and if their molar extinctions are of comparable size. Otherwise the broad and/or extremely asymmetric CT absorption observed must be analyzed (*cf.* Experimental Section) to obtain the desired CT band maxima $\tilde{\nu}_m^{CTI}$ and $\tilde{\nu}_m^{CTII}$ (Figures 3 and 4). The experimental data for C_6H_5X–TCNE complexes are given in Table I and for C_6H_5X–I_2 complexes in Table II.

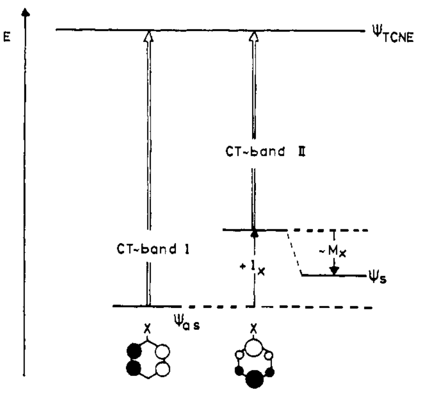

Figure 2. Qualitative MO scheme for the CT bands I and II of C_6H_5X–TCNE complexes showing positive inductive perturbation $+I_X$ and additional conjugative interaction $-M_X$ with unoccupied atomic orbitals of the substituent X.

Table II. CT Absorptions (cm^{-1}) of C_6H_5X–I_2 Complexes in CCl_4 Solution

Compd no.	Substituent X	Exptl CT band max	CT band I	CT band II
1	H	34,250	34,250	34,250
2	CH_3	33,100		
7	$Si(CH_3)_3$	33,100		
5	$C(CH_3)_3$	32,250		
9	$CH_2CH_2Si(CH_3)_3$	32,600		
8	$CH_2Si(CH_3)_3$	32,800	32,800	(29,700)
12	$CH(Si(CH_3)_3)_2$	29,000		29,000
14	$C(Si(CH_3)_3)_2C_6H_5$	27,600		27,600

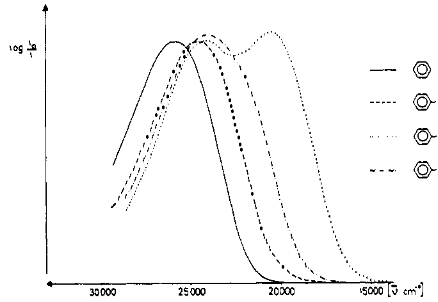

Figure 3. CT band shapes of C_6H_5X–TCNE complexes (X = H, $Si(CH_3)_3$, $CH_2Si(CH_3)_3$, $CH_2CH_2Si(CH_3)_3$) in CH_2Cl_2 solution.

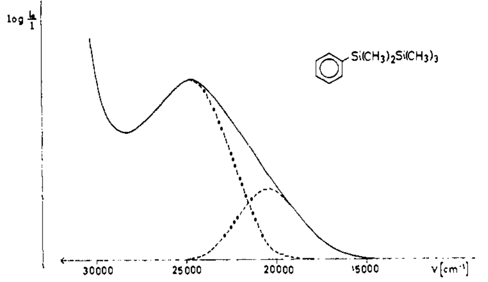

Figure 4. CT band analysis of the $C_6H_5Si(CH_3)_2Si(CH_3)_3$–TCNE complex absorption in CH_2Cl_2 solution.

The following discussions of the substituent effects are based on the TCNE complexes. The I_2 complexes are not as advantageous because the CT band I is often hidden by the ^1L_b benzene self-absorption and the CT band II is generally of lower intensity; these facts in most cases prevent a reliable band analysis. Nevertheless conformity of the observed CT band shifts of the corresponding TCNE and I_2 complexes (Tables I and II) clearly indicates that steric effects due to the different structure (4) of the former can be neglected. This is confirmed also by the excellent correlation of the CT band maxima $\tilde{\nu}_m{}^{CT}$ and the mass spectroscopically determined ionization energies *IE* of the donor molecules (Figure 1).

Alkyl Substituents. The electronic spectra of alkylbenzene–TCNE complexes show only one CT absorption maximum (Figure 3). This stems from the overlap of the CT bands I and II as can be deduced from the enlarged half-band widths ($\Delta\tilde{\nu}_{1/2}$ (C_6H_6–TCNE) = 5800 cm^{-1}, $\Delta\tilde{\nu}_{1/2}$ ($C_6H_5CH_3$–TCNE) = 6200 cm^{-1}, $\Delta\tilde{\nu}_{1/2}$ ($C_6H_5C(CH_3)_3$–TCNE) = 6750 cm^{-1}). The maxima of the CT bands II determined by band analysis are shifted about 3000 cm^{-1} to longer wavelengths. Both the values for the CT bands II as well as the observed absorption maxima (Table I) reveal a slightly increasing inductive effect $+I_x$ in the sequence of substituents $CH_3 < CH_2CH_3 < CH_2C(CH_3)_3 < C(CH_3)_3$ raising the molecular orbital ψ_s (Figure 2).

Silylalkyl Substituents. In contrast to the yellow alkylbenzene–TCNE complexes the introduction of a trimethylsilyl group in the β position to the benzene ring leads to red or violet complexes. In the CT spectra the two CT bands I and II are well separated (Figure 3) as is found for monosubstituted benzene derivatives only in the case of strong $+M_x$ substituents like OR or NR_2 groups.[13] The following details concerning compounds **8–15** (Table I) are to be pointed out.

(i) The trimethylsilylmethyl group lowers the CT excitation energy relative to the benzene–TCNE complex by about 5850 cm^{-1} = 0.73 eV. The donor strength of the $(CH_3)_3SiCH_2$ substituent therefore is about twice that of an alkyl group.

(ii) A second β-$Si(CH_3)_3$ group shifts the CT maximum II to even longer wavelengths both in toluene (**8** → **12**) and in diphenylmethane derivatives (**13** → **14**).

(iii) Replacement of CH_3 by Cl or F in the R_3SiCH_2 group causes a short-wavelength shift (**8** → **10** → **11**), the CT excitation energy being greater than in alkylbenzene–TCNE complexes. The CT bands I and II are no longer separated.

(iv) Silyl groups in γ positions to the benzene ring (**9**), *i.e.*, $R_3SiCH_2CH_2$ substituents only shift the CT band II by the same amount as alkyl substituents. Perturbation by three γ-silyl groups (**15**) still does not match the effect of one β-silyl group.

From iii and iv one concludes that the $(CH_3)_3SiCH_2$ substituent effect is mainly an inductive one. The extreme σ-donor strength is only exceeded by that of an $(CH_3)_3SnCH_2$ group. The blue $C_6H_5CH_2Sn(CH_3)_3$–TCNE complex shows its CT band II maximum at 17,800 cm^{-1}, at longer wavelengths as the naphthalene–TCNE complex![24]

Silyl Substituents. Considering the strong $+I_{CH_2SiR_3}$ effect and the usual inductive strengthening factor $I_\alpha/I_\beta \sim 1.7$[25] for substituents in α and β position to a π system, the TCNE complex of trimethylsilylbenzene might be expected to be blue with an CT absorption II around 16,000 cm^{-1}. Actually the complex is yellow and shows only one CT absorption maximum (Figure 3). The CT band II determined by band analysis is at even shorter wavelengths than in the *t*-butylbenzene–TCNE complex (Table I). This result is further confirmed be the ionization energy of trimethylsilylbenzene (Figure 2) as well as by the comparison of the half-band widths ($\Delta\tilde{\nu}_{1/2}$ ($C_6H_5Si(CH_3)_3$–TCNE) = 6050 cm^{-1}, $\Delta\tilde{\nu}_{1/2}$ ($C_6H_5C(CH_3)_3$–TCNE = 6750 cm^{-1}). From the small increase in energy of the benzene molecular orbital ψ_s it must be deduced that the strong inductive effect of an α-silyl substituent is almost cancelled out by a counteracting $Si \leftarrow C_\pi$ interaction of the benzene π system with unoccupied silicon atomic orbitals of π symmetry (Figure 2).

In the $C_6H_5SiH_3$–TCNE complex the $+I_{Si}$ effect is completely compensated by $Si \leftarrow C_\pi$ electron back-donation. The CT absorption ($\tilde{\nu}_m{}^{CT}$ = 26,000 cm^{-1}, $\Delta\tilde{\nu}_{1/2} \approx 6000$ cm^{-1}) cannot be distinguished from that of benzene itself.

Disilanyl Substituents. The electronic influence of SiR_2SiR_3 groups has been explained on the basis of uv[26] and esr data[27] of polysilanes by the assumption of "d_π–d_π" bonding. The delocalization of benzene π electrons on both silicon atoms of an attached disilanyl group should enhance the acceptor property relative to that of monosilyl groups. The energy of the CT band II, easily determined by analysis of the extremely asymmetric CT absorption (Figure 4), is about equal to that of the $C_6H_5CH_2SiR_3$–TCNE complex. This unexpected result, *i.e.*, disilanyl substituents exerting the same extreme σ-donor effect as trimethylsilylmethyl groups, was verified by the mass spectroscopically determined ionization energy of pentamethyldisilanylbenzene. The value (*IE* = 7.82 eV) is almost the same as for the trimethylsilylmethyl derivative (*IE* = 7.96 eV[12]) and relative to the one for benzene (*IE* = 9.20 eV[12]) lowered by about 1.4 eV. As the CT absorption of the $C_6H_5Si(CH_3)_2Si(CH_3)_3$–TCNE complex is due to a π electron excitation it has to be assumed that the benzene molecular orbital ψ_s is considerably raised (Figure 2). Although an enhancement of the π-acceptor function of the disilanyl group by "d_π–d_π" bonding cannot be excluded, effects of this kind are obviously overcompensated by the donor property of β-silyl groups. Further credit to this interpretation is given by the fact that $Si(CH_3)_2Si(CH_3)_3$ and $Si(CH_3)_2Si(CH_3)_2C_6H_5$ substituents influence the benzene π system similarly (Table I): interaction over the Si–Si bridge with the second phenyl ring owing to "d_π–d_π" delocalization should alter the CT absorption II considerably. Thus in the ground state of disilanylbenzene "d_π–d_π" bonding must be of minor importance.

III. Di-, Tri-, and Tetrasilyl- and -alkylbenzenes. CT Absorptions of TCNE and I_2 Complexes. The CT absorptions of monosilyl- and monoalkylbenzene–TCNE complexes have been interpreted on the basis of a qualitative MO model and furnish information on the different electronic effects of the individual substituents. In most cases however the CT maxima I and II which indicate the splitting of the e_{1g} benzene molecular orbitals ψ_{as} and ψ_s could only be determined by analysis of the broad and asymmetric CT absorptions. In certain polysubstituted benzene derivatives the energy difference $\epsilon_s - \epsilon_{as}$ should be enlarged by the combined substituent effects giving rise to well-sepa-

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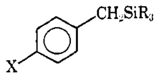
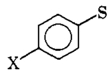
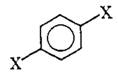
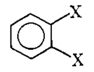
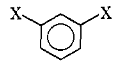
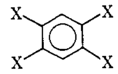
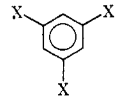
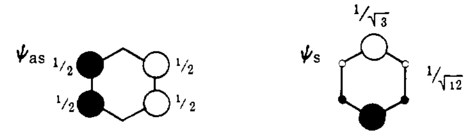
Table III. CT Absorptions (cm^{-1}) of TCNE Complexes of 1,4-, 1,2-, 1,3-, 1,2,4,5-, and 1,3,5-Silyl- and Alkylbenzenes in CH_2Cl_2 Solution

Compound	Compd no.	Substituent X	Exptl CT band max		CT band I	CT band II
	**18**	CH_3	23,650	18,550	23,650	18,550
	19	CR_3	23,700	18,000	23,700	18,000
	20	SiR_3	23,650	19,250	23,650	19,250
	**21**	CR_3	23,900			
	**22**	CH_3	24,100	21,750 sh	(24,250)	(29,800)
	23	CR_3	23,900		23,900	(19,700)
	24	SiR_3	23,900		(24,400)	(22,000)
	25	CH_2SiR_3	23,850	16,800	23,850	16,800
	**26**	CH_3	23,250			
	27	SiR_3	23,300			
	28	CH_2SiR_3	21,250		(18,700)	(22,400)
	**29**	CH_3	22,750			
	30	SiR_3	23,350			
	31	CH_2SiR_3	20,000–19,600		(18,200)	(21,900)
	**32**	CH_3	20,850		(18,500)	(21,600)
	33	SiR_3	21,000 sh		(20,800)	
	**34**	CH_3	21,700		21,700	21,700
	35	SiR_3	22,850		22,850	22,850
	36	CH_2SiR_3	18,500		18,500	18,500

rated bands. In addition different types of substitution should cause different perturbations of the benzene π system and thus confirm the MO interpretations. According to first-order perturbation the change in the HMO eigenvalues ϵ_J due to inductive effects is proportional to the squares of the HMO coefficients $c_{J\mu}$ at the substitution centers μ as well as the change in the Coulomb integral α.[28] With the HMO coefficients of the benzene e_{1g} molecular orbitals

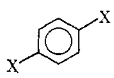
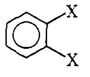
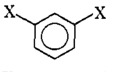
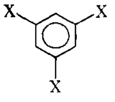
$$\Delta\epsilon_J = \sum_{\mu} c_{J\mu}^2 \Delta\alpha \qquad (5)$$



(6)

the following shifts of the CT bands I and II shown in Figure 5 are predicted. The experimental data for the TCNE complexes of polysubstituted benzenes are given in Table III, and for the corresponding I_2 complexes in Table IV.

Table IV. CT Absorptions (cm^{-1}) of I_2 Complexes of 1,4-, 1,2-, 1,3-, and 1,3,5-Silyl- and Alkylbenzenes in CCl_4 Solution

Compound	Compd no.	Substituent X	Exptl CT band max	CT band I	CT band II
	**22**	CH_3	32,900	32,900	(29,850)
	23	CR_3	32,250		
	24	SiR_3	32,250		
	25	CH_2SiR_3	26,400		26,400
	**26**	CH_3	31,650		
	27	SiR_3	32,700		
	**29**	CH_3	31,450		
	30	SiR_3	32,700		
	**34**	CH_3	30,100	30,100	30,100
	35	SiR_3	31,450	31,450	31,450
	36	CH_2SiR_3	27,950	27,950	27,950

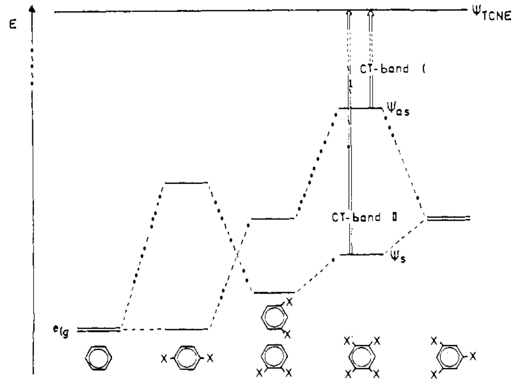


Figure 5. HMO scheme for the CT bands I and II of TCNE complexes of polysubstituted benzenes showing the positive inductive perturbation $+I_X$ of substituents X.

Again the conformity of the observed CT band shifts of the corresponding TCNE and I_2 complexes (Tables III and IV) indicates that steric effects can be neglected. Ionization energies of representative derivatives determined mass spectroscopically also fit into the correlation $\tilde{\nu}_m{}^{CT}$ (cm^{-1}) = 21,490 + 5264*IE* (eV) (Figure 1). The following discussions are based on the CT absorptions of the TCNE complexes.

1,4-Disubstituted Benzenes. The sequence of the substituent donor strengths $(CH_3)_3Si < CH_3 < C(CH_3)_3 < CH_2Si(CH_3)_3$ had to be derived in the case of monosubstituted benzenes by band analysis, comparison of the CT half-band widths, and correlation with the ionization energies. More reliable information is obtained from the TCNE complexes of *para*-substituted trimethylsilylmethylbenzenes $XC_6H_4CH_2Si(CH_3)_3$ because even for X = H the CT bands I and II are sepa-

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[28] E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendung," Verlag Chemie, 1968, p 134.

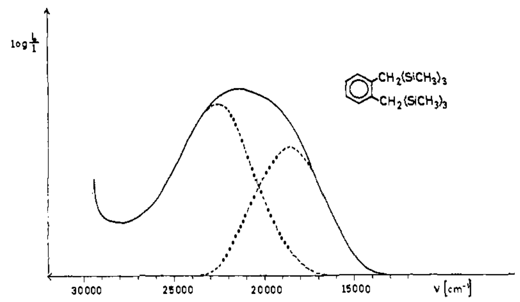


Figure 6. CT band analysis for the 1,2-bis(trimethylsilylmethyl)-benzene–TCNE complex.

rated (Figure 3). The observed CT maxima (Table III) confirm again that only the molecular orbital ψ_s is significantly raised (*cf.* Figure 5). Furthermore, the extreme σ-donor property of the $(CH_3)_3SiCH_2$ group is verified as well as the small perturbation by the $Si(CH_3)_3$ group, indicating a strong counteracting $Si \leftarrow C_\pi$ back-donation.

The different CT band II shifts produced by $(CH_3)_3Si$ groups in positions α and β to the benzene π system are further illustrated by the CT data (Table III) of 1,4-disubstituted benzene derivatives XC_6H_4X, whose CT maxima II are found between 22,000 (X = $Si(CH_3)_3$) and 16,800 cm^{-1} (X = $CH_2Si(CH_3)_3$). The values of the *t*-butyl and trimethylsilyl compounds **23** and **24** must again be determined by band analysis. The bulky substituents favor a certain complex conformation which reduces the intensity of the CT band II.[21] As with all other compounds for which ionization energies have been determined by mass spectroscopy the value for 1,4-bis(trimethylsilyl)benzene ($IE = 8.25$ eV) fits into the correlation $\tilde{\nu}_m^{CT}/IE$ (Figure 1). The same is valid for the ionization energy ($IE = 7.25$ eV) of bis-(trimethylsilylmethyl)benzene. The difference ΔIE = 1 eV again removes any doubt concerning the interpretation given.

1,2-, 1,3-, and 1,2,4,5-Substituted Benzenes. According to the HMO model (Figure 5) the perturbation of ψ_{as} is greater than that of ψ_s and the CT bands I and II invert their sequence. Furthermore for the *ortho* and *meta* derivatives only small energy differences $\epsilon_s - \epsilon_{as}$ are to be expected. These predictions are in agreement with the experimental data (Table III). In contrast to the well-separated CT bands I and II of most 1,4-disubstituted benzene–TCNE complexes, in the CT spectra of all 1,2 and 1,3 derivatives only a single maximum is found, even with $(CH_3)_3SiCH_2$ substituents (Figure 6). Band analysis yields two maxima at 22,400 and 18,700 cm^{-1} indicating that both CT bands I and II are shifted to longer wavelengths as predicted by the HMO model. This finding is further verified by the mass spectroscopically determined ionization energy ($IE = 7.74$ eV) being in satisfactory agreement with the value ($IE = 7.64$ eV) calculated from the correlation of Figure 1. The CT absorptions of all other 1,2 and 1,3 derivatives can be interpreted the same way. Although unambiguous band analyses are not possible for the silyl- and alkylbenzene–TCNE complexes, the substituent effects are reflected by the observed maxima which correspond approximately to the center of gravity of the CT bands I and II. Further confirmation of the HMO predictions (Figure 5) is given by the CT absorptions of 1,2,4,5-tetrasubstituted benzenes: their maxima are shifted to longer wavelengths than those of 1,2 and 1,3 derivatives and their half-band widths (*e.g.*, durene (**32**), $\Delta\tilde{\nu}^{1/2}$ = 6900 cm^{-1}) are increased, indicating stronger ψ_{as}/ψ_s splitting. Finally, comparison of the analyzed CT maxima I and II (Table III, **32** and **33**) again reveals the sequence of donor strength $CH_3 > Si(CH_3)_3$.

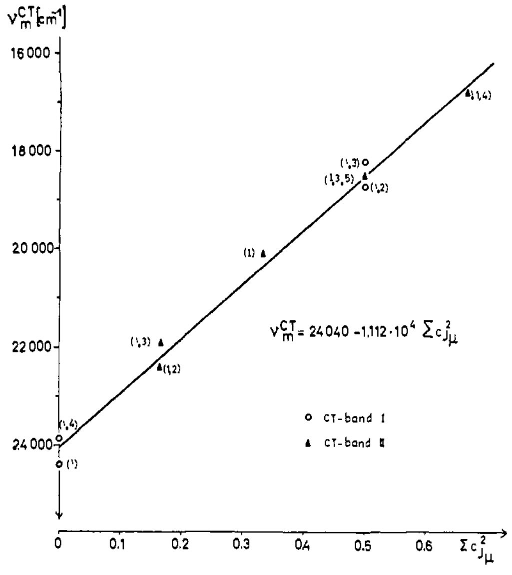


Figure 7. Correlation between the CT band maxima of trimethylsilylmethylbenzene–TCNE complexes and the $\sum_{\mu} c_{J,\mu}^2$ values for the different substitution types. In the figure the $\sum$ value should be $\sum_{\mu}$.

1,3,5-Trisubstituted Benzenes. Owing to D_{3h} symmetry on 1,3,5 substitution, the highest occupied benzene molecular orbitals—although both ψ_{as} and ψ_s are raised—remain degenerate (Figure 5). As expected compounds **34**, **35**, and **36** give rise only to a single CT band with a half-band width comparable with that of the benzene–TCNE complex. Therefore the CT maxima observed can be taken as clear-cut evidence for the increasing perturbation of the benzene π system in the sequence of substituents $(CH_3)_3Si < H_3C < (CH_3)_3SiCH_2$.

Correlation of CT Data within an HMO Model. As pointed out before an inductive perturbation of the e_{1g} benzene molecular orbitals should be proportional to $\sum_{\mu} c_{J\mu}^2$ (eq 5). Therefore a linear correlation is expected with the CT absorption maxima I and II of benzene derivatives inductively perturbed at different substitution centers μ. This is shown for the $(CH_3)_3SiCH_2$ compounds in Figure 7.

The inductive parameter $\Delta\alpha$ (eq 5) calculated from the slope of the line is about 11,000 cm^{-1}. The linear regression obtained favors the assumption of a predominant inductive effect of the $(CH_3)_3SiCH_2$ substituent, although a parallel hyperconjugative effect in the ground state cannot be excluded. For $(CH_3)_3Si$ substituents besides the inductive effect the conjugative $Si \leftarrow C_\pi$ electron back-donation must be taken into account. According to second-order perturbation theory in the HMO model a second term has to be considered, which

$$\Delta\epsilon_J = \sum_{\mu} c_{J\mu}{}^2 \frac{\beta_{c_\mu}{}^2{}_{Si}}{\epsilon_J - \epsilon_{Si}} \tag{7}$$

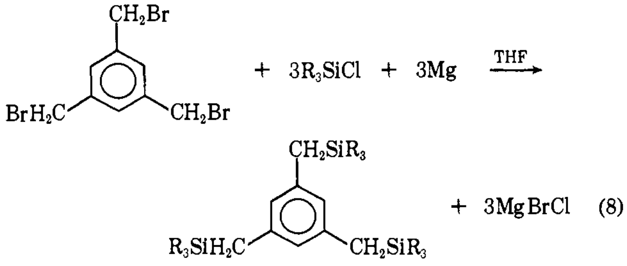
(for $\epsilon_{Si} > \epsilon_J$) will lower the highest occupied benzene molecular orbitals in the case of nonzero HMO coefficients $c_{J\mu}$. As shown by the long-wavelength shift of trimethylsilylbenzene–TCNE complex absorption relative to benzene itself the $+I_{Si}$ effect exceeds the $Si \leftarrow C_\pi$ back-donation in the ground state. The overall effect (eq 5 and 7) of trimethylsilyl groups expected for the different substituted benzenes $1 < 1,2 \sim 1,3 \sim 1,3,5 < 1,4 < 1,2,4,5$ is in agreement with the observed shifts of the long-wavelength CT maxima.

Experimental Section

Compounds **6**,[29] **7**,[30] **8**,[31] **13**,[32] **14**,[32] **21**,[33] **23**,[34] and **27**[35] have been prepared according to literature procedures. The derivatives **9** and **30** were synthesized by Wurtz reaction of the corresponding bromo- (**9**) or chloro-substituted aromatic compounds (**30**) with chlorotrimethylsilane–sodium in boiling toluene with 70–90% yield.

General Procedure. The halogen compound was added dropwise to 20% excess sodium suspension and chlorotrimethylsilane under nitrogen and with vigorous stirring. After the exothermic reaction started moderate reflux was maintained by controlling the dropping rate. Subsequently the mixture was refluxed for 3–5 hr. Excess sodium and the blue sodium halides were separated by filtration. Chlorotrimethylsilane and the solvent were distilled off and the product was fractionated.

For the preparation of **12**, **18**, **20**, **24**, **25**, **33**, and **35** as well as the hitherto unknown compounds **28**, **31**, and **36** the "*in situ* Grignard"[32] reaction proved useful. The benzene derivatives **12** and **31** were prepared from the corresponding chloro compounds and compounds **18**, **20**, **24**, **25**, **28**, **33**, **35**, and **36** from the corresponding bromo compounds, *e.g.*



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General Procedure. The halogen compound was added dropwise under nitrogen to 50–100% excess of magnesium and chlorotrimethylsilane in dry tetrahydrofuran. After the usually spontaneous exothermic reaction slowed down the mixture was refluxed for 2–3 days and hydrolyzed cautiously with dilute hydrochloric acid. The ether extract was dried and after distilling off the solvent the product was fractionated or recrystallized from ethanol (**25**, **33**) or methanol (**24**).

p-*t*-Butyltrimethylbenzylsilane (**19**) can be obtained in 10% yield starting with *p*-bromo-*t*-butylbenzene by 3 days heating of the lithium organic compound with iodomethyltrimethylsilane in tetrahydrofuran. After hydrolysis with diluted hydrochloric acid, ether extraction, and drying, a fraction of bp 120° (12 mm) was distilled and further purified by gas chromatography.

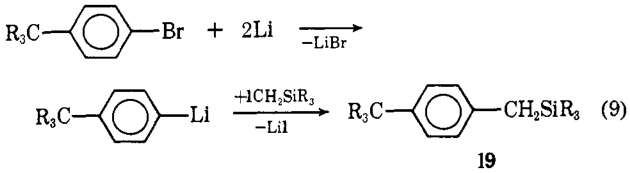

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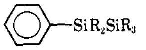
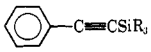
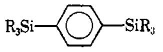
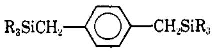
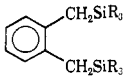
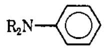
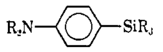
Table V. Analytical Data of the Silyl- and Alkylbenzenes

Compd no.	Mp or bp (Torr), °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
6	75 (16)	89.12	10.88	89.26	10.93
7	170 (730)	72.92	9.39	72.79	9.30
8	76 (13)	73.09	9.81	73.15	9.70
9	96 (15)	74.08	10.17	74.01	10.20
12	60 (1)	66.02	10.23	66.10	10.23
13	75	79.87	8.38	80.01	8.54
14	103	73.00	9.03	73.24	9.10
18	95 (15)	74.08	10.17	74.26	10.16
19	120 (12)	76.30	10.98	76.48	10.99
20	16	66.02	10.23	66.37	10.22
21	78.5	75.66	10.74	75.66	10.62
23	76	88.35	11.65	88.15	11.76
24	97	64.78	9.97	64.74	9.94
25	62	67.12	10.46	67.26	10.60
26	119 (13)	64.78	9.97	65.33	9.93
27	121 (12)	67.12	10.46	67.09	10.59
30	112 (21)	64.78	9.97	65.28	9.87
31	70 (5×10^{-3})	67.12	10.46	67.08	10.14
35	27	61.14	10.27	61.40	10.26
36	35–36	64.20	10.77	64.60	10.63
33	171	58.94	10.47	59.28	10.37

Table VI. Ionization Energies of Benzene Derivatives Determined by Mass Spectrometry

Compd (R = CH_3)	*IE*, eV
	7.82
	8.16
	8.25
	7.25
	7.74
	6.76
	6.73

Compounds **10** and **11** were kindly given to us by Professor V. Chvalovsky, Prague; the disilanylbenzenes **16** and **17** were provided by Professor M. Kumada, Kyoto. The preparation of compound **15** was described in an earlier investigation.[12] All volatile benzene derivatives were purified by gas chromatography using a Varian Aerograph A700 equipped with a 6-m silicon column SE 30. Analytical data of the benzene derivatives synthesized are given in Table V.

Charge-Transfer Spectra. The solutions of the TCNE complexes were prepared by mixing the components dissolved in methylene dichloride (Merck Uvasol). Their electronic spectra were recorded at 20° using a Cary N14 spectrometer. Varying the concentrations of the components had no influence on the CT band position. The band maxima presented in Tables I and III were measured with an excess of the aromatic donors.

With the concentrations chosen neither the donor nor the acceptor showed noticeable self-absorptions in the region $\bar{\nu} < 25{,}000\ cm^{-1}$. Tetracyanoethylene was purified by sublimation.

The spectra of iodine complexes were recorded in CCl_4 solutions. To obtain CT band maxima which differed little from the ^1L_b bands of the donors, in the sample and in the reference cells donor solutions of equal concentrations were used. Then iodine was added to the sample cell solution until the CT band showed sufficient extinction.

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[29] E. Berliner and R. Berliner, *J. Amer. Chem. Soc.*, **71**, 1195 (1949).

[30] K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

[31] H. Gilman and F. J. Marshall, *J. Amer. Chem. Soc.*, **71**, 2066 (1949).

[32] R. L. Merker and M. J. Scott, *ibid.*, **85**, 2243 (1963).

[33] C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

[34] H. Meyer and K. Bernhauser, *Monatsh. Chem.*, **53/54**, 727 (1929).

[35] C. Eaborn, K. L. Jaura, and D. R. M. Walton, *J. Chem. Soc.*, 1198 (1964).

For trimethylsilylbenzene as a representative example the 1:1 stoichiometry of the CT complexes was demonstrated by a Benesi–Hildebrand[36] plot of the concentration dependence of the CT extinction: the equilibrium constant K of the 1:1 complex I_2–trimethylsilylbenzene amounts to 0.287 l./mole, the molar extinction ϵ_m is 9800 l./mole cm. The corresponding values for the TCNE–trimethylsilylbenzene complex are $K = 0.275$ l./mole and $\epsilon_m = 2850$ l./mole cm.

The CT band analysis was based on CT band contours observed in CT spectra in which CT bands I and II were well separated. The CT band shapes fulfill reasonably eq 10 given by Briegleb and Czekalla[37] in which the wave number $\tilde{\nu}_l$ corresponds to the longer wavelength absorption, $\tilde{\nu}_h$ to the shorter wavelength absorption with $\epsilon = \epsilon_m/2$, and $\tilde{\nu}_h$ to the CT band maximum.

$$\frac{\tilde{\nu}_h - \tilde{\nu}_l}{2(\tilde{\nu}_m - \tilde{\nu}_l)} \approx 1.2 \qquad (10)$$

Ionization Energies. Ionization potentials were determined using a Krupp Mat CH4 mass spectrometer equipped with a Fox ion source.[38] The values obtained in addition to the ionization energies of monosubstituted benzene derivatives published in ref 12 are given in Table VI. They were also used for calculating the regression $IE/\tilde{\nu}_m^{CT}$ (Figure 1).

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[36] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

[37] G. Briegleb and J. Czekalla, *Z. Phys. Chem.*, **24**, 37 (1960).

[38] R. I. Reed, "Mass Spectroscopy," Academic Press, London, 1965.

Concerning the Reactivity of Amines toward Carbonium Ions Derived from Ortho Esters[1]

K. Koehler and E. H. Cordes[2]

Contribution No. 1766 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401. *Received August 7, 1969*

Abstract: First-order rate constants for decomposition of a series of *para*-substituted methyl orthobenzoates in aqueous solutions of semicarbazide, methoxyamine, and hydroxylamine are independent of amine concentration under conditions in which substantial fractions of the ortho esters yield amine adducts as products. Analysis of product composition as a function of amine concentration indicates that products are derived from the partitioning of the carbonium ion derived from ortho ester between amine, generating an amine adduct as product, and water, generating the carboxylic ester as product. Relative rate constants for attack of amine and water on such carbonium ions are correlated by a single straight line in a Brønsted plot with a slope of 0.4. This slope is independent, within experimental error, of the nature of the polar substituent in the parent ortho ester. The mode of partitioning of the tetrahedral intermediate generated from the addition of methoxyamine to the carbonium ion derived from methyl orthobenzoate does not depend on the concentration of an acetate buffer.

Reaction of amines with ortho esters appears to be a rather general process. Both early and recent developments relevant to such reactions have been reviewed.[3,4] Largely as a result of the efforts of Roberts and his associates, it is clear that reaction of simple amines with ortho esters may generate either imidates or amidines depending on substrate structure, the ratio of reactants, and the presence or absence of acid catalysts.[5–7] Reactions of more complicated amines yield a variety of products including heterocycles.[4]

In addition to their synthetic value, the reaction of amines with ortho esters has, in one case, provided evidence relevant to the mechanism of hydrolysis of the latter species. Fullington and Cordes observed that rate constants for decomposition of methyl orthobenzoate in aqueous solutions of semicarbazide and hydroxylamine are independent of amine concentration even though substantial amounts of amine-derived reaction products were formed.[8] This finding corroborated earlier suggestions, based on a variety of experimental approaches, that ortho esters hydrolyze by a pathway not involving the participation of solvent as a nucleophilic reagent in the transition state.[9]

In this investigation, we have extended our earlier studies to examine both the influence of basicity on rate constants for reaction of amines with ortho ester derived carbonium ions and the influence of carbonium ion stability on their selectivity to nucleophilic attack by amines.

Experimental Section

Materials. Methyl ortho-*p*-hydroxybenzoate, methyl ortho-*p*-methoxybenzoate, methyl ortho-*p*-methylbenzoate, methyl orthobenzoate, methyl ortho-*p*-chlorobenzoate, and methyl ortho-*p*-nitrobenzoate were prepared and purified as described elsewhere.[10] Organic amines were recrystallized or redistilled before use with the following exceptions: hydrazine, 97% (anhydrous), which was obtained from Matheson Coleman and Bell, and 2,2,2-trifluoroethylamine hydrochloride, which was obtained from Pennisular Chemresearch Co., were used without further purification. Sub-

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[1] Supported by Grant No. 08232 from the National Institutes of Health.

[2] Career Development Awardee of the National Institutes of Health.

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