We are interested here in purely inductive substituent effects, *i.e.*, the effect arising from polarity of the σ bonds linking a substituent to one atom in a benzene ring. Real substituents can, however, also exert conjugative effects and it would be difficult to disentangle these from concomitant inductive contributions; in order to study the latter in isolation, we therefore introduced a hypothetical substituent termed H*, the properties of which are identical with those of a hydrogen atom apart from one-center core attraction integral U_{ss}[4].

MINDO calculations were carried out for $C_6H_5H^*$ for various values of $U_{ss}(H^*)$; the response of the net charges on the hydrogen atoms is indicated in Figure 1. The signs of the changes in net charge correspond to those expected for a classical inductive effect, an increase in the electronegativity of H* (represented by a decrease in U_{ss}) leading to a decrease in net charge at all positions; this result is entirely different from that observed in nonconjugated systems.

The relative magnitudes of the changes in net charge at the *ortho*, *meta*, and *para* positions (2.0:1.1:1) are very close indeed to the ratios (2.0:1.15:1) predicted according to a simple classical model for the interaction, assuming the "inductive effect" to be propagated directly across space (*i.e.*, a field effect) rather than by successive polarization of bonds.[20] Indeed, the calculated charge densities suggest that the classical "inductive effect" is attenuated very rapidly, its effect being negligible after the carbon atom linked to H*. The change in electronegativity of this carbon atom does, however, lead to a polarization of the π electrons (π-inductive effect) and this in turn leads to an alternation of induced charge around the ring; thus an increase in electronegativity of H* leads to positive induced charges in the positions *ortho* and *para* to it but to negative ones in the *meta* positions, the charges being in the ratio 20:−4:1 (Figure 2). Note that this charge alternation is not transmitted to the adjacent hydrogen atoms. The alternation is due to a polarization of the π electrons in the ring, and there is apparently little transmission of this to the CH σ bonds. This again emphasizes the low efficiency with which classical inductive effects are propagated; polarization of the π bonds to a given carbon atom apparently has little effect on the other (σ) bonds formed by it.

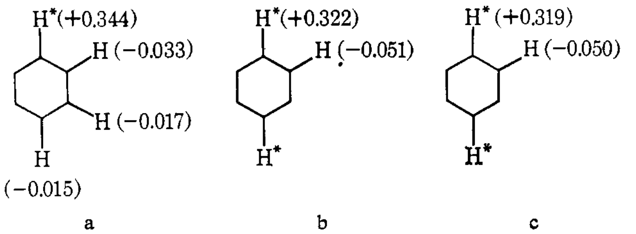

Figure 3. Changes in charge densities calculated by the MINDO method (U_{ss}(H) = −10.6 eV; U_{ss}(H*) = −13.6 eV) for (a) $C_6H_5H^*$ and (b) *p*-$C_6H_4H_2^*$; (c) shows charges calculated on the basis of additivity, using the results in a.

In the absence of interfering conjugative interactions, substituent effects in benzene are found to be additive. In order to see if the same would hold for the charge densities given by our MINDO calculations, we also studied the disubstituted benzenes $C_6H_4H^*_2$. The MINDO changes in net charge indeed agreed within 2% with those calculated on the basis of additivity, using the charges predicted for $C_6H_5H^*$; this result held for all three isomers of $C_6H_4H^*_2$ over the whole range of values for $U_{ss}(H^*)$. A typical example is shown in Figure 3.

This result would of course be expected if long-range "inductive effects" are in fact due to direct electrostatic interactions across space; deviations from additivity would be expected to occur only in cases where the polarizations are very large.

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(20) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, 84, 3548 (1962).

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d-Orbital Effects in Silicon-Substituted π-Electron Systems. XV.[1] The Color of Silyl Ketones

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Contribution from the Institute of Inorganic Chemistry of the University of Munich, Munich, Germany. *Received May 3, 1968*

Abstract: Relative to the colorless dialkyl ketones the n → π^* transition energies of the yellow monosilyl and the violet disilyl ketones are considerably lowered. To elucidate the influence of R_3Si groups on the carbonyl chromophore, vertical ionization energies, charge-transfer maxima, half-wave reduction potentials, and electronic transitions of alkyl and silyl derivatives of phenyl or naphthyl ketones have been measured and assembled in an approximate experimental MO scheme. The energy differences can be rationalized in terms of both strong inductive effects $+I_{Si} > +I_C$ on the oxygen lone pair n_O and additional electron back-donation Si ← C_π in the excited states, as well as in the ground state.

In 1957 Brook[2] synthesized triphenylsilyl phenyl ketone which in contrast to the analogous carbon compound is yellow. Since then, numerous yellow monosilyl and disilanyl derivatives[3–7] and one violet disilyl

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(1) Previous communication, H. Bock, H. Alt, and H. Seidl, *Angew. Chem.*, 80, 906 (1968); *Angew. Chem. Int. Ed. Engl.*, 7, 885 (1968).

(2) A. G. Brook, *J. Amer. Chem. Soc.*, 79, 4373 (1957).

(3) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *ibid.*, 82, 5102 (1960); A. G. Brook and J. R. Pierce, *Can. J. Chem.*, 42, 298 (1964).

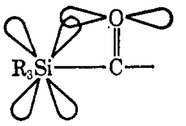
ketone[8] have been prepared. Comparison of their electronic absorption maxima,[9] their C=O stretching frequencies[3,5] and their pK_{BH^+} values[10] with those of the corresponding carbon analogs reveals characteristic changes (*cf.* Table I).

Table I. n → π* and π → π* Absorption Maxima,[9] C=O Stretching Frequencies,[3,5] and pK_{BH^+} Values[10] of Representative R_3C- and R_3Si-Substituted Ketones

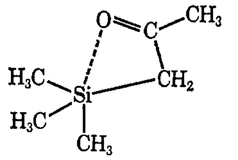
$R^1R^2C{=}O$ R^1	R^2	$\nu_m^{n\rightarrow\pi^*}$, cm^{-1} ($\epsilon_m^{n\rightarrow\pi^*}$)	$\nu_m^{\pi\rightarrow\pi^*}$, cm^{-1} ($\epsilon_m^{\pi\rightarrow\pi^*}$)	$\nu_{C=O}$, cm^{-1}	pK_{BH^+}
CH_3	$C(CH_3)_3$	34,800 (23)	53,800 (1,100)	1718	
	$Si(CH_3)_3$	26,900 (126)	51,200 (4,200)	1645	
C_6H_5	$C(C_6H_5)_3$	30,000 (195)	39,800 (10,200)	1690	−8.37
	$Si(C_6H_5)_3$	23,500 (295)	38,900 (16,200)	1618	−7.78

To explain the differing properties of alkyl and silyl ketones, especially the long-wavelength shift of the n → π* transition, several contradictory suggestions have been put forward.

A. d–n interactions between oxygen lone pairs and vacant silicon 3d orbitals (a),[3] as have been confirmed in the case of siloxanes[11] or silyl aryl ethers[12] with silicon and oxygen adjacent to another, have been proposed. The suggestion of a "superchromophore involving the silicon and carbonyl group"[3] served also as a basis to interpret some spectroscopic data of β-silyl ketones[13] (b).



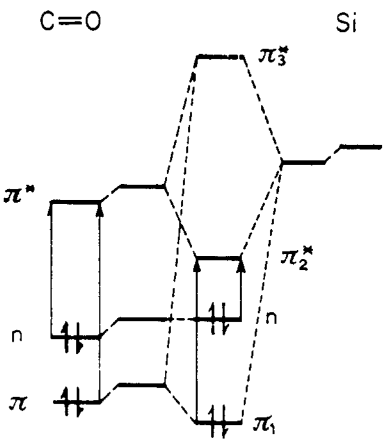
a



b

B. d–π* splitting as the main effect besides smaller d–π interaction, as well as an inductive raising of the n level "located on the more remote oxygen atom,"[14] has been proposed.

C. Stabilization of the (n → π*) excited state of the keto group relative to its ground state being due to "simultaneous operation of σ-donor and π-acceptor effects of the triorganosilyl group"[15] is the third proposal.



D. "The inductive effect of the (group IV) metal rather than d_π–p_π-bonding" has been proposed to be the primary cause of the long-wavelength shift of the n → π* transition.[6] Very recently Agolini, Klemenko, Csizmadia, and Yates[9] published the results of simple and extended Hückel molecular orbital calculations with or without d-orbital parameters in the latter. The conclusion drawn was "that it is the σ-donor property of silicon which is primarily responsible for the observed spectral shifts, and that any possible p_π–d_π interactions are of minor importance." [9]

In order to distinguish between interpretations A–D by means of an approximate experimental MO scheme the following quantities were measured: vertical ionization energies of the oxygen lone pairs, n_O; charge transfer transitions of suitable donor–acceptor complexes for ground-state interactions on the highest occupied π molecular orbitals; half-wave reduction potentials to gain some information on the relative energies of the lowest unoccupied molecular orbitals. The over-all effect of alkyl and silyl substituents shows up in the electronic transitions which represent only the differences of individual changes in ground and excited states.

Experimental Section

Vertical ionization energies were determined using a Krupp MAT CH 4 mass spectrometer equipped with a Fox ion source.[16] On repeating each measurement four times the individual values deviated by at most ±0.03 eV. The electronic spectra were recorded in Merck Uvasol *n*-hexane, dichloromethane, or methanol with a Cary N 14 spectrophotometer in the range 10000–50000 cm^{-1}. Half-wave reduction potentials were measured with the friendly permission of Professor E. Heilbronner at the Eidgenössische Technische Hochschule, Zürich, using a Metrohm Polarecord E 261 R. The measurements were performed in 0.1 *m* DMF solutions of tetra-*n*-butylammonium iodide at 22.5° with the Hg pool as the reference anode.

Of the phenyl and naphthyl ketones listed in Table II, compounds I, VII, and VIII were Fluka analytically pure grade; literature procedures were used to prepare the derivatives II,[17] III,[18] IV,[3] and V.[2]

***p*-(Trimethylsilyl)phenyl trimethylsilyl ketone** was synthesized by the route shown in eq 1. *p*-Bromobenzyl bromide (15 g, 60 mmol) was slowly dropped into 150 mg-atoms of magnesium (3.65 g) and 150 mmol of trimethylchlorosilane (16.3 g) in 100 ml of THF. After 24-hr refluxing the mixture was hydrolyzed with 2 *N* HCl. On the addition of 150 ml of ether two phases separated, of which the upper layer was fractionally distilled and the fraction boiling at 110–125° (20 mm) was purified by gas chromatography on a 6-m SE 30 column. The *p*-(trimethylsilyl)benzyltrimethylsilane[19] was heated with an excess of N-bromosuccinimide and a trace of dibenzoyl peroxide in CCl_4 for 2 hr. After filtration, an excess of

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(4) A. G. Brook, R. Kivisikk, and G. E. le Grow, *Can. J. Chem.*, **43**, 1175 (1965).

(5) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davies, *J. Amer. Chem. Soc.*, **89**, 431 (1967); E. J. Corey, D. Seebach, and R. Freedman, *ibid.*, **89**, 434 (1967).

(6) G. J. D. Peddle, *J. Organometal. Chem.*, **5**, 486 (1966).

(7) A. G. Brook, D. G. Anderson, J. M. Duff, P. F. Jones, and D. M. McRae, *J. Amer. Chem. Soc.*, **90**, 1076 (1968).

(8) A. G. Brook and G. J. D. Peddle, *J. Organometal. Chem.*, **5**, 106 (1966).

(9) F. Agolini, S. Klemenko, J. G. Csizmadia, and K. Yates, *Spectrochim. Acta*, **24A**, 169 (1968).

(10) *Cf.* for example, K. Yates and F. Agolini, *Can. J. Chem.*, **44**, 2229 (1966).

(11) R. West, L. S. Whatley, and K. J. Lake, *J. Amer. Chem. Soc.*, **83**, 761 (1961).

(12) H. Bock and H. Alt, *Chem. Commun.*, 1299 (1967); *J. Organometal. Chem.*, **13**, 103 (1968).

(13) W. K. Musker and R. W. Ashby, *J. Org. Chem.*, **31**, 4237 (1966); W. K. Musker and G. L. Larsen, *J. Organometal. Chem.*, **6**, 627 (1966).

(14) D. F. Harnish and R. West, *Inorg. Chem.*, **2**, 1082 (1963); R. West, *J. Organometal. Chem.*, **3**, 314 (1965).

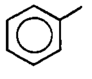
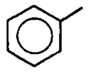
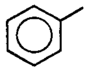
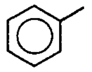
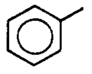
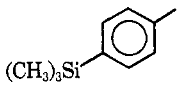
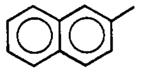
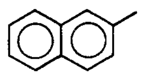
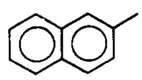
(15) L. E. Orgel, "Volatile Silicon Compounds," E. A. V. Ebsworth, Ed., Pergamon Press, New York, N. Y., 1963, p 81.

(16) R. I. Reed, "Ion Production by Electron Impact," Academic Press, New York, N. Y., 1962.

(17) J. U. Nef, *Justus Liebigs Ann. Chem.*, **310**, 318 (1900).

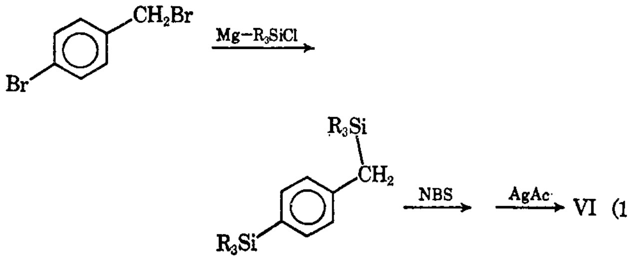
(18) C. Paal, *Chem. Ber.*, **17**, 911 (1884).

Table II. Analytical Data for Phenyl and Naphthyl Ketone Derivatives

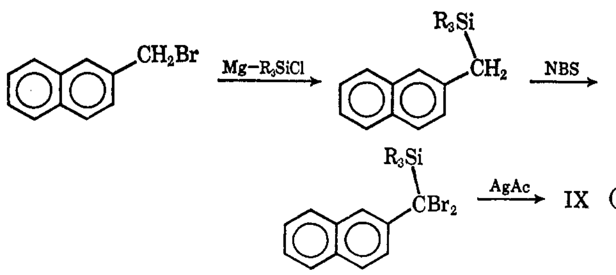
Compd	$R^1R^2C{=}O$		Bp (mm) or Mp, °C	Calcd, %		Found, %	
	R^1	R^2		C	H	C	H
I		CH_3	201 (720)	79.97	6.71	80.03	6.62
II		$C(CH_3)_3$	110 (18)	81.44	8.70	81.51	8.70
III		$C(C_6H_5)_3$	182	89.92	5.78	89.41	5.89
IV		$Si(CH_3)_3$	61 (1)	67.36	7.92	67.67	8.08
V		$Si(C_6H_5)_3$	103	82.37	5.53	81.87	5.50
VI		$Si(CH_3)_3$	82 (0.1)	62.33	8.85	62.22	8.62
VII		H	60	84.59	5.16	84.66	5.30
VIII		CH_3	56	84.68	5.92	84.94	7.87
IX		$Si(CH_3)_3$	113 (0.1)	73.63	7.06	74.06	6.97

silver acetate in acetone-ethanol-water was added to the solution, and the mixture was stirred for 24 hr at room temperature. The evaporation and ether extraction of the residue was followed by fractional distillation which yielded 55% VI.

Trimethylsilyl β-naphthyl ketone VII was prepared as shown in eq 2. The procedure described before applied to 85 mmol of



(1)



(2)

β-bromomethylnaphthalene (19 g) yielded 75% β-trimethylsilylmethylnaphthalene, mp 61° (*Anal.* Calcd for $C_{14}H_{18}Si$: C, 78.45; H, 8.46; mol wt, 214.34. Found: C, 78.54; H, 8.46). Bromination as above yielded 80% of the dibromo derivative, mp 92° (*Anal.* Calcd for $C_{14}H_{16}Br_2Si$: C, 45.30; H, 4.35; mol wt, 372.21. Found: C, 45.60; H, 4.50) which was hydrolyzed with the same silver acetate mixture and yielded 60% IX.

Results and Discussion

Vertical Ionization Energies of Phenyl Ketone Derivatives. The vertical ionization energies of the phenyl ketone derivatives I, II, and IV were obtained with reasonably good precision by the retarding potential difference method,[20] as is shown by their well-resolved ion current-appearance potential plots (Figure 1).

The ionization potentials determined by this method correspond—in contrast to the "adiabatic" ionization energies from electronic spectra—to a "vertical" excitation in the Franck-Condon scheme. Nevertheless, for benzene derivatives the values from both methods of measurements are in excellent agreement[21] indicating that the vertical excitation in the case of cyclic π-electron systems corresponds to a $0 \rightarrow 0$ transition. Ionization of simple ketone derivatives occurs from the oxygen lone pair, n_O, which—as is shown by the long-wavelength $n \rightarrow \pi^*$ transitions—represents the highest occupied ketone orbital. The vertical and adiabatic ionization energies of acetone (IE_v = 9.89 eV;[22] IE_a = 9.70 eV[23]) suggest that the values from both methods for ketones are still comparable.

In accordance with Koopman's theorem, first ionization potentials are generally correlated to the highest

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(19) Physical data agree with those reported by C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

(20) R. E. Fox, W. M. Hickam, T. Kjeldaas, and D. J. Grove, *Phys. Rev.*, **84**, 859 (1951).

(21) H. Bock and H. Seidl, *Chem. Ber.*, **101**, 2815 (1968).

(22) K. Higasi, J. Omura, and A. Baba, *Nature*, **178**, 652 (1956).

(23) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. van Nostrand, Inc., Princeton, N. J., 1966, p 658.

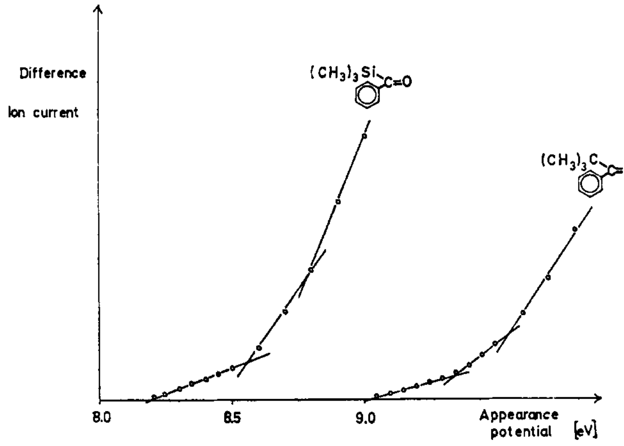

Figure 1. Ion current–appearance potential plots for *t*-butyl and trimethylsilyl phenyl ketones.

occupied SCF molecular energy level.[24] On the assumptions included, the vertical ionization potentials (Figure 2) represent the relative energies of the highest occupied molecular orbitals of the benzene and benzoyl compounds.

The electronic spectra of benzoyl derivatives in the range 28,000–45,000 cm^{-1} generally exhibit three distinct absorptions (*i.e.*, the weak n → π* transition $\bar{\nu}_m \sim 30{,}000$ cm^{-1} ($\epsilon_m \sim 100$), the symmetry-forbidden ^1L_b band $\bar{\nu}_m \sim 35{,}000$ cm^{-1} ($\epsilon_m < 1000$), and the allowed ^1L_a absorption with intramolecular charge transfer $\bar{\nu}_m = 40{,}000$ cm^{-1} ($\epsilon_m \sim 10{,}000$)).[25] The long-wavelength transition confirms that the highest occupied phenyl ketone orbital is still represented by an oxygen lone pair, n_O. Alkyl substitution will raise the n_O level as expected. A much stronger positive inductive effect is exerted by the trimethylsilyl group, lowering the ionization potential to 8.20 eV. The foregoing observations are in complete agreement with measurements on numerous alkyl- and silyl-substituted linear and cyclic π-electron systems[21,26] Trimethylsilyl groups in a β position to a chromophore, *i.e.*, insulated by a tetrahedral carbon atom, always cause the greatest decrease in the ionization potentials, *e.g.*, in the R_3SiCH_2-substituted benzene down to 7.96 eV (Figure 2). The oxygen lone pairs orthogonal to the π system of silyl ketones—also in the β position to the R_3Si group—are influenced in the same way. In the silyl ketones, $R'R_3SiC{=}O$ the R_3Si groups—raising the n_O level of the oxygen lone pairs in the β position—are also in an α position to the carbonyl π system. According to the strengthening factor for inductive effects of substituents in the α and β positions to a chromophore, $I_\alpha/I_\beta \sim 1.6$,[27] the ionization energy of trimethylsilyl benzene should be smaller than the ionization energy of trimethylsilylmethyl benzene. As one can deduce from the ionization potentials of benzene derivatives (Figure 2, $IE_{C_6H_5SiR_3} > IE_{C_6H_5CR_3} > IE_{C_6H_5CH_2SiR_3}$), the inductive effect of α-silyl substituents is obviously counteracted by Si ← C_π electron back-donation. Therefore—as is the case for other π-electron systems[21,26]—the highest occupied π-molecular orbital of the carbonyl chromophore in silyl ketones should also be lowered relative to the one in the corresponding alkyl derivatives.

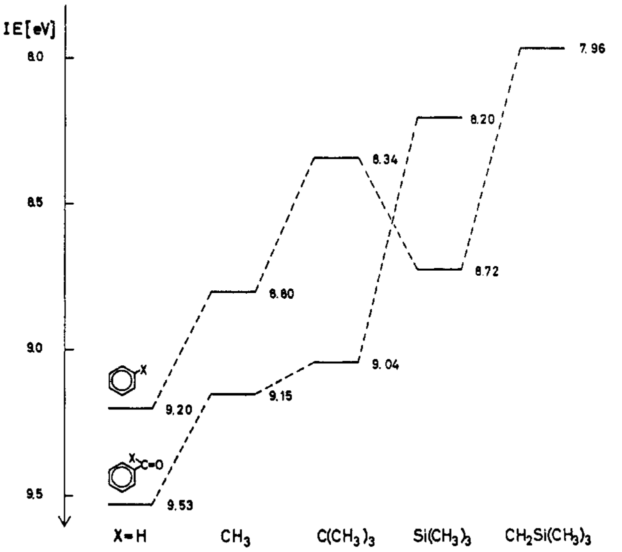

Figure 2. Vertical ionization energies *IE* (eV) of benzene and benzoyl compounds (X = H, CH_3, $Si(CH_3)_3$, $C(CH_3)_3$).

By mass spectrometry only the first ionization potential was exactly measured (Figure 1). The reverse order of the values for *t*-butyl- and trimethylsilyl-substituted benzenes and phenyl ketones (Figure 2) furnishes additional proof that the excitation in the latter should occur from the oxygen lone pair, n_O, which will only reflect inductive substituent effects.[22] To determine the second ionization potential of ketone derivatives, *i.e.*, the relative energies of their highest occupied π molecular orbitals, other methods have to be used.

Charge Transfer Maxima of TCNE–Naphthalene Ketone Complexes. According to the Mulliken theory of charge-transfer complexes D–A, the absorption ν_m^{CT} (D–A) is linearly proportional to the adiabatic ionization energy of the donor IE_D if the following conditions are fulfilled: identical acceptor A in complexes of comparable type, *i.e.*, comparable equilibrium distances and complex configuration. This very efficient method to determine relative ionization energies for similar compounds[12] can not be applied to phenyl ketone derivatives because their TCNE complexes exhibit an absorption in the same region where both the donor (n → π*) and acceptor (π → π*) absorb. Furthermore, the removal of the degeneracy of the e_{1g} benzene molecular orbitals by the COR group might be too small to observe two separated CT bands.

β-Naphthyl ketones have been chosen and prepared for the following reasons. Their highest occupied molecular orbitals are not degenerate, and their higher energy levels permit CT transition outside the self-absorption range. Twisting around the naphthalene carbonyl bond in the α position due to nonbonding interactions with the *peri* hydrogen is avoided by substitution in the β position.

The long-wavelength charge-transfer maxima (Figure 3) strongly depend on the donor properties of the sub-

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(24) (a) *Cf.* L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, p 152; (b) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1967, p 188.

(25) J. Dehler and F. Dörr, *Tetrahedron Lett.*, 2155 (1965).

(26) H. Bock and H. Seidl, *Angew. Chem.*, **79,** 1106 (1967); *Angew. Chem. Int. Ed., Engl.*, **6,** 1085 (1967); *J. Organometal. Chem.*, **13,** 87 (1968); *J. Amer. Chem. Soc.*, **90,** 5694 (1968); *J. Chem. Soc., B*, 1158 (1968).

(27) O. Exner and J. Jonas, *Collect. Czech. Chem. Commun.*, **27,** 2296 (1962).

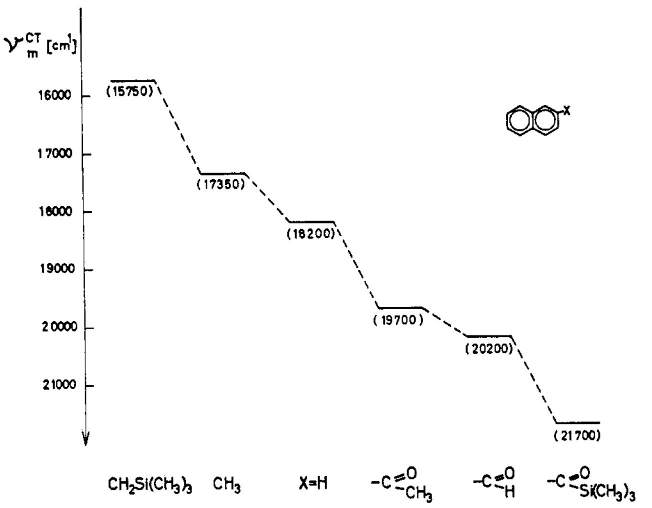


Figure 3. Charge-transfer maxima of some β-naphthalene derivative–TCNE complexes.

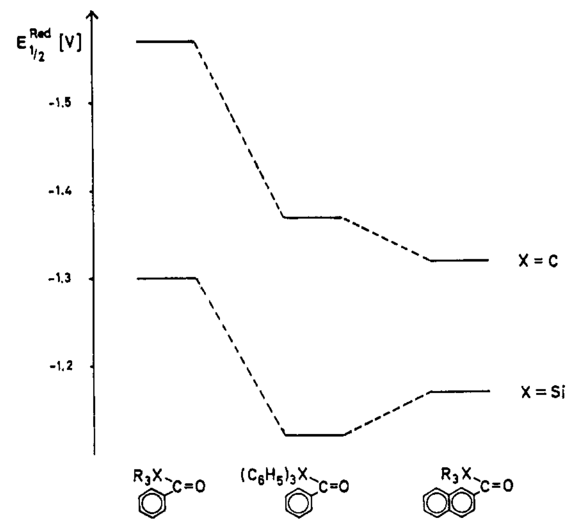


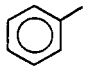
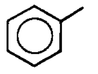
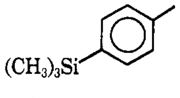
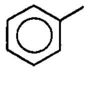
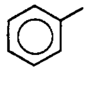
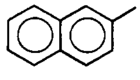
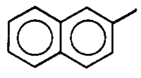
Figure 4. Half-wave reduction potentials $E_{1/2}^{red}$ (V) of alkyl- and silyl-substituted aromatic ketones.

stituents ($+I_{CH_2SiR_3} > +I_{CH_3} > +I_H$). The acceptor function of the carbonyl group is modified by the individual substituents. The value for naphthyl silyl ketone clearly indicates that—despite the larger $+I_{SiR_3}$ effect ($\nu_m^{CT}(CH_3) > \nu_m^{CT}(CH_2SiR_3)$)—the energy of the highest occupied molecular orbital is considerably lowered in the silyl derivative. This finding has to be explained by an additional strong silicon acceptor function Si $\leftarrow$ C_π of π-symmetry—presumably of 3d type—in the ground state. Analogous measurements on the CT complexes of more than 60 aromatic compounds confirm the ground-state interactions in silicon-substituted π-electron systems.[12,28] In most cases the $+I_{SiR_3}$ effect is not overcompensated by the electron back-donation Si $\leftarrow$ C_π, but only cancelled out to a certain extent. This is shown also by the vertical ionization energies of the benzene derivatives (Figure 2).

That the above TCNE complexes are of the π type is proved for naphthalene by X-ray analysis[29] and confirmed for the other compounds by the consistency of the results as well as by the agreement with MO calculations.[12,28] The possibility of n_O complexes for the ketone derivatives is excluded by the fact that the second charge-transfer bands of VII and VIII are observed at about 24,400 cm^{-1}, originating from the next lower occupied-molecular orbital of the naphthalene π system.

Half-Wave Reduction Potentials. Information on excited-state interactions, *i.e.*, on substituent effects in higher spectroscopic states, are difficult to obtain. Nevertheless, the relative energies of the lowest unoccupied molecular orbitals can be correlated with the half-wave reduction potentials of reversible redox reactions.[30] The polarographic reduction of aromatic carbonyl compounds in aqueous solution of high pH values is assigned to a one-electron insertion yielding the corresponding ketyl radical.[31] Because acylsilanes are sensitive to nucleophilic attack, DMF was used as an aprotic solvent. The polarographic data (Table III) fulfill the criterion of Tomes[32] that the difference $E_{3/4} - E_{1/4}$ for reversible one-electron redox equilibria at 22.5° should be about 56 mV. The number of inserted electrons, n, was evaluated from $E/\log [i/(i_d - i)]$ plots and confirms in all cases a reversible one-electron process, which also follows from alternating current polarograms.

Table III. Polarographic Data on the Reversible One-Electron Reduction of Phenyl and Naphthyl Ketone Derivatives

	$R^1R^2C{=}O$		$E_{1/2}^{red}$,	$E_{3/4}$ −	
Compd	R^1	R^2	V	$E_{1/4}$, mV	n
II		$C(CH_3)_3$	−1.575	61	0.86
IV		$Si(CH_3)_3$	−1.30	63	1.03
VI		$Si(CH_3)_3$	−1.24	58	0.95
III		$C(C_6H_5)_3$	−1.375	64	0.91
V		$Si(C_6H_5)_3$	−1.125	60	0.92
VIII		CH_3	−1.32	62	0.97
IX		$Si(CH_3)_3$	−1.17	59	1.04

The half-wave reduction potentials (Figure 4) show clearcut evidence that the lowest antibonding molecular orbital is shifted further downward in the silyl derivatives (X = Si). Due to better energy matching with vacant (3d ?) silicon orbitals the $+I_{SiR_3}$ effect is far overcompensated. Considerable electron delocaliza-

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(28) H. Bock and H. Alt, *Angew. Chem.*, **79**, 934 (1967); *Angew. Chem. Int. Ed. Engl.*, **6**, 943 (1967); H. Bock and H. Alt, *J. Amer. Chem. Soc.*, in press.

(29) R. M. Williams and S. C. Wallwork, *Acta Cryst.*, **22**, 899 (1967).

(30) *Cf.* ref 24b, p 177.

(31) R. W. Schmid and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1453 (1954).

(32) J. Tomes, *Collect. Czech. Chem. Commun.*, **9**, 12 (1937).

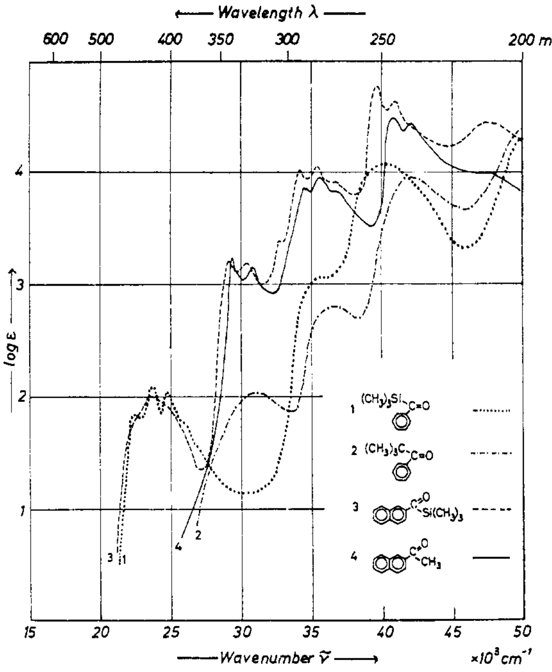
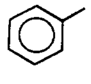
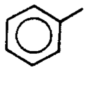
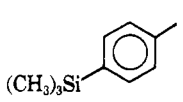
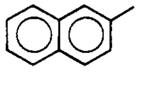
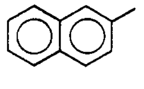


Figure 5. Electronic spectra of the alkyl and silyl aromatic ketones II, IV, VIII, and IX in *n*-hexane.

Table IV. Absorption Maxima and Molar Extinctions of the Alkyl and Silyl Aryl Ketones II, IV, VI, VIII, and IX in *n*-Hexane

Compd	$R^1R^2C{=}O$ R^1	R^2	ν_m, cm^{-1} (ϵ_m) $n \rightarrow \pi^{*a}$	$\pi \rightarrow \pi^*$
II		$C(CH_3)_3$	31,250 (103)	36,500 (660) 42,000 (8,800) 50,300 (25,400)
IV		$Si(CH_3)_3$	23,650 (119)	35,400 (1,140) 40,000 (11,300) 50,000 (19,450)
VI		$Si(CH_3)_3$	23,400 (110)	35,100 (2500) sh 38,750 (18,500)
VIII		CH_3		29,400 (1,620) 30,800 (1,400) 34,400 (7,000) 35,700 (8,950) 40,800 (30,400) 42,100 (26,350)
IX		$Si(CH_3)_3$	23,450 (102)	29,900 (1,570) 30,300 (1,530) 34,250 (10,400) 35,350 (11,250) 39,700 (55,800) 41,000 (43,000) 47,600 (27,300)

[a] Most intense peak.

tion Si ← C_π in radical anions of silicon-substituted π-electron systems can be shown from the ^{29}Si coupling constants in their esr spectra.[33] The same conclusion is drawn by Jones and West[34] from the esr spectra of the radical anions of silyl ketones. From the spin population in the benzaldehyde radical anion,[35] one deduces that the interaction with acceptor substituents should be strongest at the carbonyl carbon and less in the *p*-phenyl position. This expectation is met by the half-wave reduction potential of the *p*-silylphenyl silyl ketone VI differing by only 0.07 V from that of the phenyl derivative.

The differences between the half-wave reduction potentials of acetophenone ($E_{1/2}^{\text{red}} = -1.52$ V) and the corresponding *t*-butyl compound II ($E_{1/2}^{\text{red}} = -1.57$ V) might be attributed to the smaller inductive effect $+I_{\text{CH}_3} < +I_{\text{C(CH}_3)_3}$. The differences between the trimethyl and triphenyl ketone derivatives (II/III and IV/V) could be interpreted on the same basis, *i.e.*, sp^3 carbon atoms exerting stronger positive inductive effects than sp^2-hybridized ones.

Electronic Transitions. The missing link to connect the foregoing substituent influences on the inner molecular orbitals of the alkyl and silyl ketones are their electronic transitions (Figure 5, Tables I and IV). The electronic spectra of alkyl and silyl phenyl ketones have been discussed in detail by Agolini, Klemenko, Csizmadia, and Yates[9] including the vibrational fine structure of the n → π* absorption bands. Therefore only the following remarks will be added here. The differences in n → π* transition energies between the monosilyl ketones and the corresponding alkyl derivatives amount to about 1 eV, independent of any other substituent attached to the silyl carbonyl chromophore. Nevertheless, a methyl group (Table I) or an aromatic π system like phenyl, *p*-silylphenyl, or naphthyl (Table IV) will determine the position of the n → π* absorption maximum. Thus, besides the essential inductive rise of the n_O level, additional conjugative excited-state interactions have to be taken into account. Looking at the π → π* transitions (^1L_a-type bands) of the phenyl ketones II and IV—which, according to PPP calculations, seem to be almost pure $\psi_1 \rightarrow \psi_{-1}$ excitations[36]—the relatively small shift of about 0.25 eV suggests similar ground-state interactions too. The corresponding long axis polarized transitions of the naphthyl ketones VII and IX show an even smaller difference. The substituent influences on the n_O, π, and π* levels have been confirmed separately by the vertical ionization energies, charge-transfer excitations and half-wave reduction potentials discussed above.

The over-all view developed is supported by additional experimental data. β-Silyl ketones with the silyl group in the γ position to the oxygen lone pair no longer show significant long-wavelength n → π* shifts[4] (Table V). In 2,5-disubstituted quinones[37] the silyl group is also in γ position to the oxygen lone pair but in α position to the π system. As expected the π* level ($E_{1/2}^{\text{red}}$), but also the π level ($\Delta\nu_m^{\pi\rightarrow\pi^*} = 0$) is lowered. The small long-wavelength shift of the n → π* absorption band thus can be interpreted as being mainly due to excited-state interactions.

Approximate Experimental MO Schemes for *t*-Butyl and Trimethylsilyl Phenyl Ketone. The collected energy values can be combined to approximate experimental MO schemes on several assumptions. The energy

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(33) F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv. Chim. Acta*, **51**, 707 (1968).

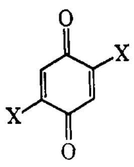
(34) R. West, private communication; *Cf.* Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract M-146.

(35) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

(36) J. Kroner, private communication.

(37) H. Bock and H. Alt, *Angew. Chem.*, **79**, 932 (1967); *Angew. Chem. Int. Ed. Engl.*, **6**, 941 (1967).

Table V

Compd	X	n → π*, cm^{-1}	π → π*, cm^{-1}	$E_{1/2}^{red}$, V
	$C(CH_3)_3$	21,900	39,200	−0.15
	$Si((CH_3)_3$	19,900	39,200	+0.04

values obtained always represent differences between the initial and the final state of the molecule. As the energy levels of different molecules may be altered in different ways on the same type of excitation, the differences in ionization energies will represent the differences of the ground-state energies only in a crude approximation. The energies of exited states also depend on the type of excitation and only in a simple one-electron MO model can the same π* level be used in the description of n → π* as well as π → π* transitions. Furthermore this lowest unoccupied molecular orbital can only be used with reservation for the description of the open-shell radical anions, although the differences in free energies between such a radical anion and the neutral molecule yields a reasonable linear correlation with the molecular orbital energy. σ states are completely ignored.

Nevertheless a comparison of the approximate experimental MO schemes for the two similar phenyl ketone derivatives (Figure 6) provide quite useful information regarding the relative substituent effects in these molecules. Starting with the oxygen lone pair, n_O, its energy is considerably increased by the positive inductive effect of the silyl group in the β position, which is consistent with the enhanced basicity of the silyl phenyl ketones (Table I). The π level remains almost constant relative to the one of the *t*-butyl standard. In view of the strong $+I_{SiR_3}$ effect this suggests a counteracting Si ← C_π electron withdrawal which also would explain the unexpected lone-wavelength shift of the C=O stretching frequencies (Table I) by a lowering of the force constants. Due to better energy matching the interaction between vacant silicon orbitals of π symmetry and the π system should be even stronger in the excited states, the $+I_{SiR_3}$ effect being overcompensated by electron back-donation. This interpretation is confirmed by the observed bathochromic shift of the π → π* transition and the comparison of the polarographic data.

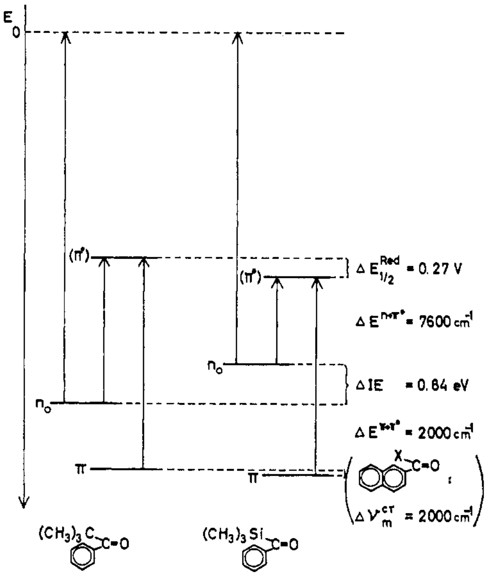


Figure 6. Approximate experimental MO schemes for *t*-butyl and trimethylsilyl phenyl ketone.

The yellow color of trimethylsilyl phenyl ketone is therefore due to strong inductive raising of the oxygen n_O level as well as to considerable excited-state interaction Si ← π^*_{CO} as deduced from the experimentally established approximate MO scheme.

Acknowledgments. The investigations have been financially supported by the Deutsche Forschungsgemeinschaft and the Stiftung Volkswagenwerk.