The Obtrusive $(d\leftarrow n)\pi$-Interaction in Silyl Aryl Ethers

By H. BOCK* and H. ALT

(*Institute of Inorganic Chemistry, University of Munich, Meiserstr. 2, Munich 1*)

THE differing properties of analogous R_3Si- and R_3C-substituted compounds are usually discussed in terms of inductive polarization $+I_{SiR_3}$ being greater than $+I_{CR_3}$ and an additional electron-back donation into empty silicon 3*d*-orbitals. The so-called $(d\leftarrow p)\pi$-interactions have been shown both in the case of carbon π-electron systems[1] $(Si_d\leftarrow C_\pi)$ and in the case of adjacent heteroatoms X carrying free electron pairs[2] n $(Si_d\leftarrow n_x)$. Contrary to these results no $(d\leftarrow n)\pi$-interactions could be detected in trimethylsilyl-$[^{15}N]$anilines by means of ^{15}N–H coupling constants.[3] This finding may possibly be attributed to the fact that basic postulates used[3] breakdown.[4,5] Unambiguous information on $(d\leftarrow n)\pi$-interactions should be obtained whenever energy differences associated therewith, in the highest occupied molecular orbitals, are accessible for direct measurement.

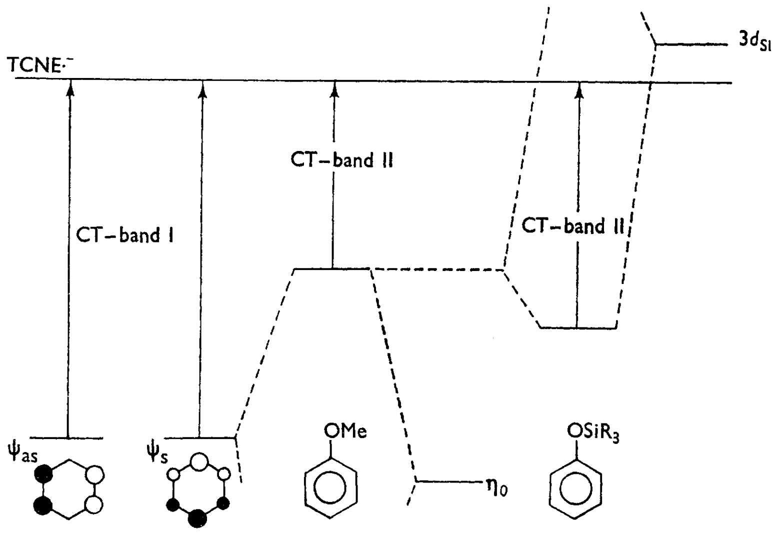


FIGURE 1. *Qualitative energy level diagram for the tetracyanoethylene charge-transfer complexes of alkoxy and siloxy-benzene.*

Accordingly we studied alkyl and silyl aryl ethers, since the π-bonding between the aromatic ring and the ether oxygen is quite adequate and—unlike the aniline derivatives—sensitive to twisting distortions. If the silicon 3*d*-orbitals and the aromatic π-system compete for the free electron pairs at the oxygen atom, then the highest occupied molecular orbitals in the silicon derivatives must be lowered relative to those in the alkyl aryl ethers. The resulting energy differences should be detectable by means of the charge-transfer maxima of suitable donator–acceptor complexes. For tetracyanoethylene (TCNE) adducts of alkoxy- and siloxy-benzenes, the following qualitative MO scheme (Figure 1) may be discussed.

The perturbation of the benzene π-system by an alkoxy-group removes the degeneracy of the e_{1g}-molecular orbitals. Whereas the asymmetric one $(c_{as,1} = c_{as,4} = 0)$ remains approximately constant the symmetric one (ψ_S) is strongly split, This gives rise to the observed long-wavelength charge-transfer absorption band II. Additional $(d\leftarrow n)\pi$-interaction in the siloxy-compound should lower the highest occupied molecular orbital ψ_4 and therefore increase the frequency of the absorption band II whereas the short-wavelength absorption band I should not be shifted noticeably. The recorded charge-transfer maxima of the complexes of mono- and 1,4-di-substituted alkoxy- and siloxy-benzenes confirm the foregoing predictions including the insensitiveness to twisting around the C–O(R) bond (*cf.*, tabulated values, R = isopropyl).

For the tetracyanoethylene complexes of 1- and

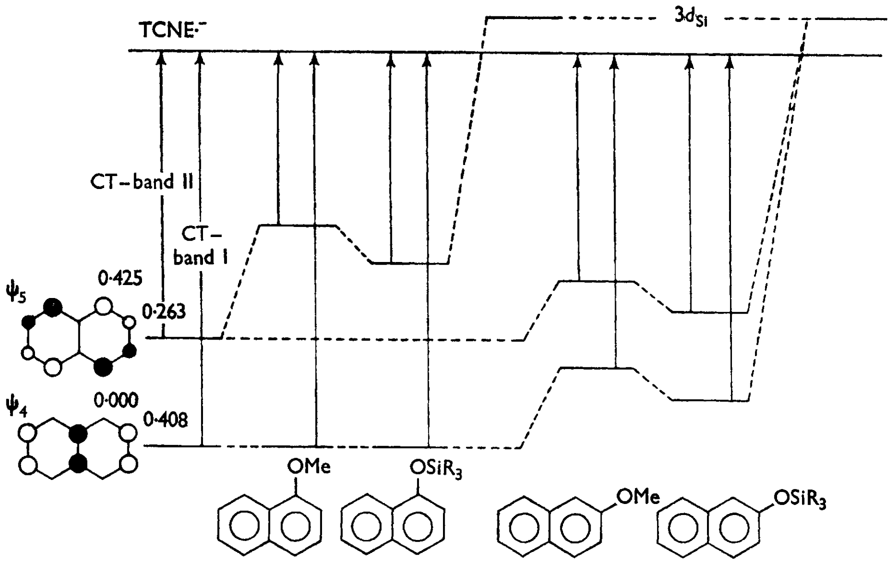
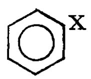
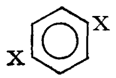
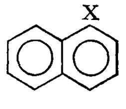
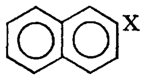


FIGURE 2. *Qualitative energy level diagrams for the tetracyanoethylene charge-transfer complexes of* 1- *and* 2-*alkoxy- and -siloxy-naphthalenes.*

TABLE

Charge-transfer maxima of the tetracyanoethylene complexes at 20° *in dichloromethane*

		CT-band I [cm.$^{-1}$]	CT-band II [cm.$^{-1}$]
	X=H	26050	—
	OMe	26050	19700
	OCHMe$_2$	25650	19400
	OSiMe$_3$	[25500]sh	21400
	OMe	26200	15800
	OSiMe$_3$	26300	18000
	H	23300	18200
	OMe	23450	15150
	OSiMe$_3$	23400	15850
	OMe	20700	16400
	OSiMe$_3$	21050	17000

2-substituted naphthalene derivatives one would deduce the following qualitative MO schemes (Figure 2). Again the tabulated data agree with the predictions of the simple one-electron model used: substitution in 1-position must leave the CT-band I unchanged ($c_{41} = 0$) and shift the CT-band II in the R$_3$SiO-compound to higher frequencies. For substitution in 2-position ($c_{42} = 0{\cdot}408$; $c_{52} = 0{\cdot}263$) blue-shifts are to be expected both for CT-bands I and II. Furthermore one would conclude from the coefficients of the molecular orbital ψ_5 ($c_{51} = 0{\cdot}425$; $c_{52} = 0{\cdot}263$) that first-order perturbations and therefore substituent effects in the 1-position should outweigh those in the 2-position as is clearly shown by the reverse behaviour of the CT-bands I and II.

The higher transition energies of the tetracyanoethylene complexes of trimethyl aryl ethers compared to those of the corresponding alkyl derivatives are just the reverse of what is observed for the substituent groups $-CH_2\cdot SiR_3$ and $-CH_2\cdot CR_3$ at the same position of the same aromatic system; for instance:

	ν_m^{CT}[PhOR,TCNE]	ν_m^{CT}[Ph·CH_2R,TCNE]
R = $SiMe_3$	21400 cm.$^{-1}$	20600 cm.$^{-1}$
Me	19700	24250
CMe_3	—	24100

Considering the insulating properties of the tetrahedral carbon atoms for π-bonding, the main influence of $-CH_2\cdot SiR_3$ groups must be as an $+I_{SiR_3}$-effect. According to the observed charge-transfer maxima for $OSiR_3$-substituted aromatic systems in this case the inductive polarization must be exceeded by an additional electron-back donation. Since the HMO-π-electron-density at the oxygen atoms corresponds almost to that of a lone-pair, the experimental results prove an $(d\leftarrow n)\pi$-interaction in silyl aryl ethers.

(*Received, October* 16*th*, 1967; *Com.* **1113**.)

---

[1] Previous papers on "*d*-Orbital effects in silicon-substituted π-electron systems", H. Alt, H. Bock, F. Gerson, J. Heinzer, and H. Seidl, *Angew. Chem.*, 1967, **79**, 932, 933, 934, and in the press; *Internat. Ed.*, 1967, **6**, 941, 941, 942, and in the press, and references given therein.

[2] S. Bell and A. D. Walsh, *Trans. Faraday Soc.*, 1966, **62**, 3005, and the summary by H. Bürger, *Fortschr. Chem. Forsch.*, 1967, **9**, 1.

[3] E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1966, **88**, 722.

[4] E. A. V. Ebsworth, *Chem. Comm.*, 1966, 530; E. W. Randall and J. J. Zuckerman, *Chem. Comm.*, 1966, 732.

[5] P. G. Perkins, *Chem. Comm.*, 1967, 268.