d_π–p_π Interaction in Trimethylsilyl Substituted Naphthalenes. Part I. A Study using Polarography, and Charge Transfer and Ultraviolet Spectroscopy

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We have carried out experiments to determine the extent of d_π–p_π interaction in silylnaphthalenes by examining a series of $SiMe_3$ and CMe_3 substituted naphthalenes using the techniques of polarography, and charge transfer and u.v. spectroscopy. The results show (*a*) that an inductive effect is operating for the t-butylnaphthalenes, which raises the energies of the lowest unoccupied and of the two highest occupied levels relative to naphthalene and (*b*) that two opposing effects are operating for the trimethylsilylnaphthalenes, an inductive effect which tends to raise the energy levels, and an electron back donation effect from the aromatic π system to the vacant silicon $3d$ atomic orbitals which tends to lower the energy levels. This latter effect is the more important for the lowest unoccupied level and the former for the two highest occupied levels.

THERE has been much discussion concerning the d_π–p_π interaction in compounds containing silicon.[1] It has been found that silyl and alkyl groups have a different effect on the lowest unoccupied molecular orbital of π electron systems. Alkyl groups act as electron donors, whereas silyl groups, although having a stronger positive inductive effect, also involve a d_π–p_π effect, due to the unoccupied silicon $3d$ orbitals, and this more than compensates for their stronger inductive effect. E.s.r. and polarographic techniques have been used by Allred and Bush[2] for 1,4-$(SiMe_3)_2$-naphthalene and by Bock et al.[3] for 1,4-, 1,5-, and 2,6-$(SiMe_3)_2$-naphthalenes, and these authors have discussed their results in terms of this d_π–p_π interaction.

In this paper we describe experiments to determine the extent of d_π–p_π interaction in silylnaphthalenes by taking a series of $SiMe_3$ and CMe_3 substituted naphthalenes, examining them using the techniques of polarography, and charge transfer and u.v. spectroscopy, and comparing the results for the silylnaphthalenes with those for the corresponding t-butyl compounds.

EXPERIMENTAL

Materials.—Dimethoxyethane (DME) (B.D.H.) was allowed to stand over sodium wire for 2 h, refluxed over sodium for a further 24 h, and fractionally distilled, the fraction with b.p. 83—84 °C being collected. This was transferred to a high vacuum apparatus and further treated with Na–K alloy, over which it was stored. Dimethylformamide (DMF) (B.D.H.) was dried over anhydrous sodium carbonate and distilled from sodium hydride immediately before use. Tetra-n-butylammonium iodide (B.D.H.) was recrystallised twice from dry DMF. Methylene dichloride (B.D.H.) was fractionally distilled and the fraction with b.p. 39·5 °C was used to make up the solutions. Tetracyanoethylene (TCNE) (Koch–Light) was recrystal-

lised twice from chlorobenzene and dried[4] by first distilling off the low-boiling azeotrope of water and chlorobenzene.

Trimethylsilylnaphthalenes.—These were prepared by three different methods, (*a*) *in situ* Grignard, (*b*) Wurtz–Fittig, using sodium in toluene, and (*c*) butyl-lithium synthesis. In each case the starting compound was the corresponding bromonaphthalene. From this the metal-naphthalene compound was prepared which either reacted simultaneously with trimethylchlorosilane or reacted with it as a second step in the same reaction vessel. In either case the trimethylsilylnaphthalene was formed as the product. All reactions were carried out under dry nitrogen.

The following dibromonaphthalenes which could not be obtained commercially were prepared from readily available hydroxynaphthalenes using triphenylphosphorus dibromide, prepared according to Wiley et al.[5] Much improved yields of dibromonaphthalene were obtained by letting the temperature rise to 300 °C, which is considerably higher than that used by Wiley et al. (200 °C). This was consistent with the results of Schaefer and Higgins[6] for the preparation of 2-bromonaphthalene. 1,5-Dibromonaphthalene[7] had m.p. 130° (lit.,[8] 131°), 6-bromo-2-naphthol[9] had m.p. 128—129° (lit.,[10] 129—130°), 2,6-dibromonaphthalene had m.p. 160° (lit.,[11] 160°), and 2,7-dibromonaphthalene had m.p. 140° (lit.,[12] 140·5°). Each dibromide gave a correct elemental analysis and a single g.l.c. peak.

1-Trimethylsilylnaphthalene was prepared by '*in situ*' Grignard synthesis. The oil finally obtained was fractionally distilled under vacuum and the fraction with b.p. 108—110° at 2 mmHg was collected (lit.,[13] 118—119° at 3 mmHg). This still contained some 1-bromonaphthalene when analysed by g.l.c. and was purified further by dry column chromatography,[14] τ 1·85—2·70(m) and 9·57(s) (lit.,[15] τ 9·57). 1-Trimethylsilylnaphthalene became discoloured on prolonged contact with air and light, and so was distilled under high vacuum and stored in calibrated vessels (1 ml) in the dark. 2-Trimethylsilylnaphthalene was prepared using the method of Eaborn and Pande.[16] The fraction with b.p. 101—104° at 1 mmHg was collected

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(lit.,[13] 102—103° at 1 mmHg) and was further purified by dry column chromatography to give an oil, τ 2·00—2·65(m) and 9·65(s) (lit.,[13] τ 9·65). 1,4-Bis(trimethylsilyl)naphthalene was prepared using the Wurtz method. The fraction with b.p. 125—150° at 3 mmHg was collected. This solidifies on cooling and was recrystallised four times from methanol, m.p. 92° (lit., 89—90·5,[13] 91—92,[17] and 92—93° [18]), τ 1·90—2·70(m) and 9·57(s). 1,5-Bis(trimethylsilyl)naphthalene was prepared by the Wurtz method. The fraction with b.p. 115—160° at 2 mmHg was collected. This was an oil shown by g.l.c. to be a mixture of 1-trimethylsilyl- and 1,5-bis(trimethylsilyl)-naphthalenes in the ratio ca. 3 : 2. 1,5-Bis(trimethylsilyl)naphthalene was separated, purified by dry column chromatography, and recrystallised once from ethanol, m.p. 121°, τ 1·89—2·75(m) and 9·55(s) (Found: C, 70·55; H, 8·95. $C_{16}H_{24}Si_2$ requires C, 70·5; H, 8·85%). 2,6-Bis(trimethylsilyl)naphthalene was prepared using butyl-lithium, 2,6-dibromonaphthalene, and chlorotrimethylsilane. The final oil was separated, purified by dry column chromatography and the product recrystallised from aqueous ethanol, m.p. 74—75°, τ 2·15—2·60(m) and 9·67(s) (Found: C, 70·5; H, 8·85%). 2,7-Bis(trimethylsilyl)naphthalene was prepared using butyl-lithium in a similar way to the 2,6-compound, m.p. 84°, τ 2·03—2·51(m) and 9·68(s) (Found: C, 70·5; H, 8·85%). t-Butylnaphthalenes were kindly given by Dr. H. van Bekkum [19] (Technische Hogeschool, Delft, Holland). Each silyl compound gave a single g.l.c. peak.

Purity.—The purity of the compounds was checked on a Pye series 104 gas chromatograph with thermostatted oven. Nitrogen was the carrier gas with a silicone gum SE 30 column which separated mixtures of naphthalene, bromonaphthalenes, and trimethylsilylnaphthalenes and was thus a good measure of purity. In addition, dry column chromatography [14] was used when it was difficult to separate the product from its impurities. Activated alumina (Laporte and Fisons 100—200 mesh) deactivated with $4\frac{1}{2}\%$ v/v distilled water was employed. The size of the column was determined from Loev's graph [14] applying to a difficult separation. T.l.c. with the same alumina and light petroleum (b.p. 60—80°) as eluant was used to determine R_F values. The column was cut in 1 cm parts on either side of where the compound was expected to be according to the R_F value. The cuts were extracted with diethyl ether, the portions containing pure compound (as determined by g.l.c.) were combined, the ether was distilled off under reduced pressure, and the compound was recrystallised or distilled. N.m.r. spectra were recorded on a Perkin-Elmer 100 MHz spectrometer.

Polarography.—The Metrohm polarographic stand E 354 was used in conjunction with the Metrohm E 446 iR compensator and Polarecord E 261, using DMF as solvent and tetra-n-butylammonium iodide as supporting electrolyte. A rapid dropping attachment (E 354S) gave a controlled drop rate of ca. 0·16 s, which meant that a polarographic recording could be made in 1 min instead of the 10 min for a conventional polarograph. A 0·1M solution of tetra-n-butylammonium iodide was made up in DMF. Enough compound to give a ca. 10^{-3}M solution was dissolved in this and dry oxygen-free nitrogen was passed through for 15 min.

The three electrode system was used, in preference to a straightforward reduction against the silver–silver chloride reference electrode (using saturated KCl as electrolyte) because of the low conductivity of the solvent. Readings were repeated in triplicate and the mean value of the half-wave reduction potentials used. The values were consistent to $\pm 0·01$ V.

Charge Transfer Measurements.—A charge transfer complex was formed between the substituted naphthalene and tetracyanoethylene (TCNE) in methylene dichloride as solvent, using a 10^{-2}M solution of TCNE in which a range of different concentrations of the naphthalene (ca. 0·1—0·2M) was made up. The absorption spectra of the solutions were recorded at 325—700 nm on an SP 800 spectrophotometer fitted with a thermostatted cell holder. The instrument was modified with the scale expansion accessory and an auxiliary recorder (SP 22) so that the absorption peaks could be magnified. From these spectra a graph was drawn [20] and the extinction coefficient found by extrapolation for each λ_{max} of the complex.

U.v. Measurements.—These measurements were carried out for ethanol solutions. A Pye–Unicam SP 800 was used for all spectra. The machine scanned the u.v. and visible regions from 200 to 850 nm in pre-selected stages.

RESULTS

Polarography.—The solutions of the substituted naphthalenes were investigated polarographically and the half-wave reduction potentials, $E_{\frac{1}{2}}$, as measured against the Ag–AgCl reference electrode, are given in Table 1. So as to allow

TABLE 1

Polarographic data for substituted naphthalenes

Substituents	$-E_{\frac{1}{2}}$/V (Ag–AgCl)	$-E_{\frac{1}{2}}$/V (Hg pool)	$\Delta E_{\frac{1}{2}}$/V	$\Delta E_{\frac{1}{2}}$/cm⁻¹
2,7-$(CMe_3)_2$	2·72	2·09	0·11	886
2,6-$(CMe_3)_2$	2·70	2·07	0·09	725
1,4-$(CMe_3)_2$	2·67	2·05	0·07	564
1-CMe_3	2·64	2·03	0·05	403
None	2·58	1·98	0	0
2-$SiMe_3$	2·57	1·97	−0·01	−81
1-$SiMe_3$	2·52	1·93	−0·05	−403
2,7-$(SiMe_3)_2$	2·47	1·90	−0·08	−645
2,6-$(SiMe_3)_2$	2·44	1·87	−0·11	−886
1,5-$(SiMe_3)_2$	2·39	1·84	−0·14	−1130
1,4-$(SiMe_3)_2$	2·38	1·83	−0·15	−1210

easier comparison with other workers' results, these values have been converted to a mercury pool reference, using a proportionality factor of 0·768 derived from the $E_{\frac{1}{2}}$ value for naphthalene against each reference.

The theoretical value of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ is 55·4 mV [21] for a one electron reduction. The mean value obtained for the substituted naphthalene was 56 mV. Because of this agreement, together with the fact that the polarographic reduction of aromatic hydrocarbons is reversible,[22] and that silyl and t-butyl substituted diphenyls are reversibly reduced,[2] we conclude that the reductions in our experiments follow the normal mechanism for aromatic hydrocarbons in the absence of a proton donor, and have related the half-wave reduction potential to the lowest unoccupied energy level of the substituted naphthalene.

Charge Transfer Complexes.—The charge transfer spectrum

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TABLE 2

Charge transfer spectral data for complexes of TCNE–substituted naphthalenes

Absorption

Substituent	Band 1 $\Delta E_m \rightarrow$				Band 2 $\Delta E_{m-1} \rightarrow$			
	$\lambda_{max.}/nm$	$\bar{\nu}_{max.}/cm^{-1}$	$\Delta\bar{\nu}/cm^{-1}$	$\varepsilon/l\ mol^{-1}\ cm^{-1}$	$\lambda_{max.}/nm$	$\bar{\nu}_{max.}/cm^{-1}$	$\Delta\bar{\nu}/cm^{-1}$	$\varepsilon/l\ mol^{-1}\ cm^{-1}$
None	550	18,200	0	1200	430	23,300	0	1100
1-Me₃Si	571	17,500	700	1220	436	23,000	300	1120
2-Me₃Si	562	17,800	400	400	442	22,600	700	233
1,4-(Me₃Si)₂	588	17,000	1200	81	446	22,400	900	89
1,5-(Me₃Si)₂	586	17,100	1100	200	440	22,800	500	187
2,6-(Me₃Si)₂	590	17,000	1200	488	463	21,600	1700	417
2,7-(Me₃Si)₂	588	17,000	1200	323	460	21,800	1500	334
1-Me₃C	592	16,900	1300	715	438	22,800	500	370
1,4-(Me₃C)₂	626	16,000	2200	47	445	22,500	800	53
2,6-(Me₃C)₂	620	16,100	2100	572	487	20,500	2800	633
2,7-(Me₃C)₂	610	16,400	1800	625	501	20,000	3300	556

was obtained for each substituted naphthalene. The change of optical density at the two $\lambda_{max.}$ values with change in concentration of substituted naphthalene, [B], was determined. The corresponding values of y [equation (1) where l is the path length and O.D. the optical density]

$$y = l[\text{TCNE}]/\text{O.D.} \qquad (1)$$

were plotted against $1/[B]$ and gave straight lines (e.g. Figure 1 shows the plot for 2-SiMe₃-naphthalene). The

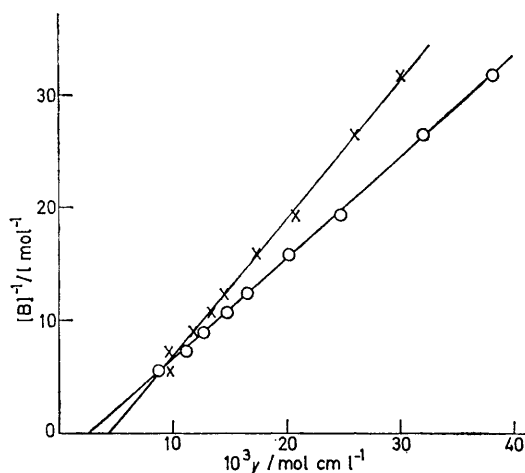FIGURE 1 Plot to determine extinction coefficients for 2-tri-methylsilylnaphthalene–TCNE complex. ○, $\lambda_{max.}$ 562 nm; ×, $\lambda_{max.}$ 442 nm

TABLE 3

U.v. absorption for substituted naphthalenes

Substituent	β⁺ Band λ/nm	p Band λ/nm	$\bar{\nu}/cm^{-1}$	$\Delta\bar{\nu}/cm^{-1}$	α Band λ/nm
None	222	275	36,360	0	310
1,SiMe₃	225	282	35,460	−900	314
2-SiMe₃	228	278	35,970	−390	311
1,4-(SiMe₃)₂	227	287	34,840	−1520	315
1,5-(SiMe₃)₂	229	288	34,720	−1640	316
2,6-(SiMe₃)₂	235	281	35,590	−770	311
2,7-(SiMe₃)₂	234	280	35,710	−650	310
1,CMe₃	227	281	35,590	−770	313
1,4-(CMe₃)₂	228	285	35,090	−1270	315
2,6-(CMe₃)₂	228	273	36,630	+270	306
2,7-(CMe₃)₂	225	274	36,500	+140	305

intercepts of these lines correspond to the reciprocals of the extinction coefficients. The ε values determined in this way are given in Table 2.

U.v. Spectra.—The u.v. spectra consist of a very intense band at *ca.* 220 nm, a medium intensity band at *ca.* 275 nm, and a low intensity band at *ca.* 300 nm. These are the β⁺, p, and α bands respectively. Table 3 gives the $\lambda_{max.}$ values for the three bands for each substituted naphthalene.

DISCUSSION

In this work naphthalenes substituted by t-butyl and trimethylsilyl groups have been examined using the techniques of polarography, and charge transfer and u.v. spectra. These experimental observations are concerned with the electronic levels of the molecules (Figure 2). Polarography is concerned with E_{m+1}, charge transfer spectra with E_m and E_{m-1}, u.v. spectra with $\Delta E_{m,m+1}$.

Polarography.—If the only effect of the substituent on the $m + 1$ energy level were that due to the inductive effect, its energy would be raised in all cases, and since $+I_{SiMe_3} > +I_{CMe_3}$,[1d] this increase in energy would be greater for SiMe₃ substituted naphthalenes than for the corresponding CMe₃ substituted compounds. This is not observed experimentally (Table 1, Figure 3). It is seen that, although the $m + 1$ energy levels are raised by CMe₃ substitution, they are lowered by SiMe₃ substitution. In the case of the silylnaphthalenes, therefore, there must be some factor which opposes the
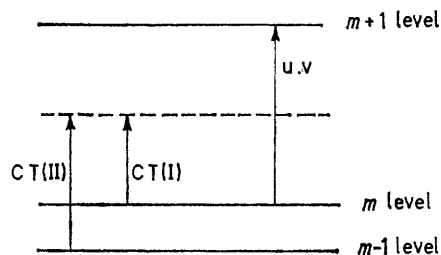

FIGURE 2 Electronic levels of the molecules

inductive effect and which lowers the energy level below that of unsubstituted naphthalene. This factor is the electron back donation from the π system to a vacant silicon 3d orbital and the results show that this effect is more important than the inductive effect of SiMe₃ for the lowest unoccupied ($m + 1$) molecular orbital.

It is seen that 1-SiMe₃ has a greater effect than 2-SiMe₃, and 1,4-(SiMe₃)₂ and 1,5-(SiMe₃)₂ a greater effect than 2,6-(SiMe₃)₂ and 2,7-(SiMe₃)₂ as one would expect from the electron distribution in the lowest unfilled $m + 1$ orbital of naphthalene (Figure 4). In
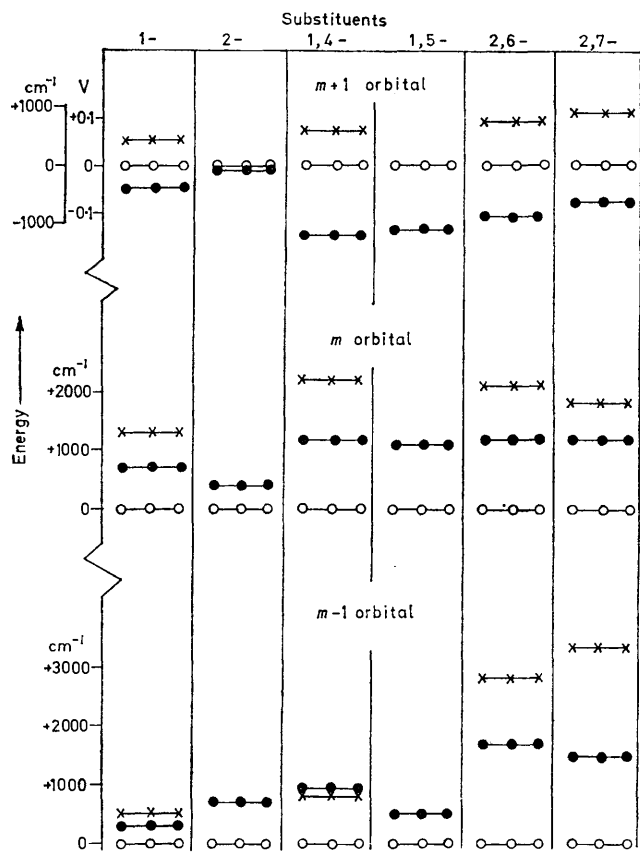

FIGURE 3 Energy levels of $m - 1$, m, and $m + 1$ molecular orbitals from data obtained from polarography and charge transfer experiments on substituted naphthalenes. O—O—O, Unsubstituted naphthalenes; ×—×—×, CMe₃-naphthalenes; ●—●—●, SiMe₃-naphthalenes
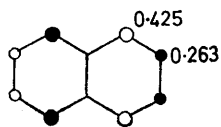
FIGURE 4 Lowest unfilled $m + 1$ orbital of naphthalene. O, Positive coefficient; ●, negative coefficient in the eigenfunction. The size of the circle represents the size of the coefficient and the number is the actual coefficient

addition, disubstitution has a greater effect than mono-substitution [comparison of 1,4-(CMe₃)₂ with 1-CMe₃; 1,4-(SiMe₃)₂ and 1,5-(SiMe₃)₂ with 1-SiMe₃; and 2,6-(SiMe₃)₂ and 2,7-(SiMe₃)₂ with 2-SiMe₃]. On the other hand, the fact that 2,6-(CMe₃)₂ and 2,7-(CMe₃)₂ substituents have a greater effect than 1,4-(CMe₃)₂ would not be expected from the electron distribution of this orbital.

CMe₃ Substitution raises the $m + 1$ energy level of naphthalene by 0·05, 0·07, 0·09, and 0·11 V in the case of 1-CMe₃, 1,4-(CMe₃)₂, 2,6-(CMe₃)₂, and 2,7-(CMe₃)₂ respectively (Table 1, Figure 3). If we assume that

$+I_{\text{SiMe}_3} = +I_{\text{CMe}_3}$, we may obtain the following lower limits for the effect of the $d_\pi-p_\pi$ bonding of SiMe₃ in lowering the $m + 1$ energy levels, 0·10, 0·22, 0·20, and 0·19 V for 1-SiMe₃, 1,4-(SiMe₃)₂, 2,6-(SiMe₃)₂, and 2,7-(SiMe₃)₂ respectively, showing that the effect of back donation to Si is at least twice the $+I$ effect of CMe₃ (Figures 3 and 5). Here again we see that 1,4-(SiMe₃)₂ has a greater effect than 2,6-(SiMe₃)₂ and 2,7-(SiMe₃)₂, in greater effect than 2,6-(SiMe₃)₂ and 2,7-(SiMe₃)₂, in keeping with the electron distribution in the $m + 1$ level, and that disubstitution has a greater effect than monosubstitution [the effect of 1,4-(SiMe₃)₂ is approximately double that of 1-SiMe₃].

Charge Transfer Spectra.—Table 2 shows that for most charge transfer complexes the extinction coefficients are in the same range (200—700 l mol⁻¹ cm⁻¹), and for these cases it is reasonable to assume that the intermolecular distances are approximately constant. There are three exceptions to this, the complexes of 1-SiMe₃-naphthalene, 1,4-(SiMe₃)₂-naphthalene, and 1,4-(CMe₃)₂-naphthalene. The first of these has a relatively large extinction coefficient [1220 (Band 1) and 1120 (Band 2)] which are approximately the same as those of unsubstituted naphthalene [1200 (Band 1) and 1100 (Band 2)]. The other two have very small extinction coefficients, 81 and 89 for 1,4-(SiMe₃)₂ and 47 and 53 for 1,4-(CMe₃)₂, showing that when these bulky groups are substituted on the same ring the TCNE molecule cannot approach as closely, as demonstrated by Merryfield and Phillips [20] in the case of hexamethyl- and hexaethyl-benzene complexes. In such cases the coulombic interaction (which
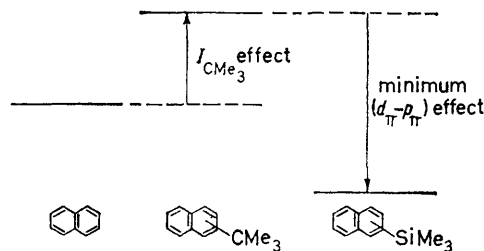

FIGURE 5 Changes in the $m + 1$ energy level

acts in the direction of lowering the energy of the complex) would be smaller than normal, resulting in a higher v̄ than would otherwise be obtained, and so the m and $m - 1$ energy levels as depicted in Figure 3 may be too low for 1,4-(CMe₃)₂, somewhat too low for 1,4-(SiMe₃)₂, and slightly too low for the remainder, with the exception of 1-SiMe₃-naphthalene.

Looking at the general pattern of results from charge transfer spectra (Table 2, Figure 3) we see that SiMe₃ and CMe₃ substituents all raise the energy level of the m and $m - 1$ molecular orbitals causing red shifts in the charge transfer spectra. This is to be expected since both groups exercise $+I$ inductive effect. Since the inductive effect of SiMe₃ is greater than that of CMe₃ [1d] one would have expected this raising of the energy level to be more pronounced for SiMe₃ than for CMe₃. The results, however, show in every case (except for 1,4-

substitution in the $m - 1$ level) that the reverse is true, and again this is due to electron back donation to a vacant silicon $3d$ atomic orbital *via* p_π–d_π bonding, which opposes the positive inductive effect of $SiMe_3$.

In this respect the results agree with those of polarography for the $m + 1$ level. There is this difference, however, that whereas the effect of electron back donation on the energy of the $m + 1$ level was found to exceed that of the $+I_{SiMe_3}$ effect, resulting in a net lowering of the energy, charge transfer experiments show that the $SiMe_3$ group raises the energy of the m and $m - 1$ levels with respect to naphthalene, and hence for these levels the effect of d_π–p_π back donation is not as pronounced as for the $m + 1$ level.

Assuming that coulombic interaction in the charge transfer complex is not changed on replacing CMe_3 by $SiMe_3$, a minimum value for the effect of back donation on the m and $m - 1$ levels can be obtained (Figure 6) by taking the inductive effect of $SiMe_3$ as equal to that of CMe_3 (as in the section on polarography).

From the results (Figure 3) it is seen that [with the exception of the $m - 1$ level for the $1,4$-$(SiMe_3)_2$-naphthalene] the effect on the m and $m - 1$ level of this back donation to Si is at least half the $+I$ effect of CMe_3.
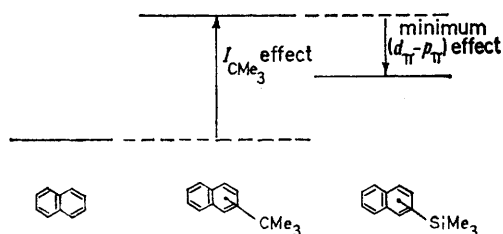

FIGURE 6 Changes in the m and $m - 1$ energy levels

The fact that the $1,4$-substituted naphthalenes are exceptional may be connected with the low extinction coefficients of their TCNE complexes (Table 2). As mentioned above, the coulombic interaction in these complexes will be smaller than normal, and as a result the m and $m - 1$ energy levels given in Figure 3 may be too low for $1,4$-$(CMe_3)_2$- and somewhat too low for $1,4$-$(SiMe_3)_2$-naphthalenes. Since the extinction coefficients for $1,4$-$(CMe_3)_2$ (47 and 53) are about half those of $1,4$-$(SiMe_3)_2$ (81 and 89), allowance for this steric effect would raise the $1,4$-$(CMe_3)_2$ levels by a greater amount than the $1,4$-$(SiMe_3)_2$ levels and could bring the $1,4$-$(CMe_3)_2$ level above that for $1,4$-$(SiMe_3)_2$ in the $m - 1$ orbital.

If we compare the effect of α-substitution with that of β-substitution we find that the effect of 1-, 1,4-, and 1,5-substitution is greater for the m level (Band 1) than for the $m - 1$ level (Band 2); on the other hand the effect of 2-, 2,6-, and 2,7-substitution is greater for the $m - 1$ level (Band 2) than for the m level (Band 1). This is to be expected from the electron distribution in the m and $m - 1$ levels (Figure 7). Again, as one would expect, disubstitution has a greater effect than monosubstitution; 1,4- and 1,5-substituents have a greater effect than 1-substituents for CMe_3 and $SiMe_3$, and 2,6-

and 2,7-substituents a greater effect than 2-substituents for $SiMe_3$.

U.v. Spectra.—The p bands are associated with the transitions from the m to the $m + 1$ level. Since we are here dealing with *changes* in energy levels due to substitution, it is possible that the effect of substituents on the u.v. spectra should agree with the changes of the m and $m + 1$ levels which we have detected by charge transfer and polarography respectively, even though the solvents are different for the three techniques (EtOH for
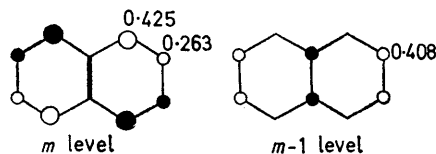

FIGURE 7 Electron distribution in the m and $m - 1$ levels. $\bigcirc$, Positive coefficient; $\bullet$, negative coefficient in the eigenfunction. The size of the circle represents the size of the coefficient and the number is the actual coefficient

u.v., CH_2Cl_2 for charge transfer, and DMF for polarography). The results (Figure 8) show that there is a fair agreement, except for 2,6- and 2,7-substituted naphthalenes.

(a) $SiMe_3$ *Substituted naphthalenes.* From polarography and charge transfer spectra we found that the introduction of silyl groups into naphthalene lowers the $m + 1$ levels and raises the m levels. Thus we would expect the effect of silyl substitution to reduce $\Delta E_{m,m+1}$ and so reduce the value of $\bar{\nu}$ below that of naphthalene and this is found to be the case (see Figure 8).

Silyl substitution lowers the $m + 1$ level to a greater extent for 1-substitution than for 2-substitution and raises the m level more for 1-substitution than for 2-substitution. Thus we would expect $\Delta E_{m,m+1}$ to be smaller for 1-substituents than for 2-substituents and $\bar{\nu}_1$ to be less than $\bar{\nu}_2$ which is seen to be the case. Running parallel to this we have that $\bar{\nu}_{1,4}$ and $\bar{\nu}_{1,5}$ are less than $\bar{\nu}_{2,6}$ and $\bar{\nu}_{2,7}$. Disubstitution has a greater effect than monosubstitution, *e.g.* $\bar{\nu}_{1,4}$ and $\bar{\nu}_{1,5}$ are less than $\bar{\nu}_1$; $\bar{\nu}_{2,6}$ and $\bar{\nu}_{2,7}$ are less than $\bar{\nu}_2$.

(b) CMe_3 *Substituted naphthalenes.* Polarography and charge transfer spectra show that CMe_3 substitution raises the energy levels of both the $m + 1$ and the m molecular orbitals. Since the m levels are raised by the greater amount it is to be expected that $\Delta E_{m,m+1}$ and hence $\bar{\nu}$ will be less than for naphthalene. The results show that, as expected, $\bar{\nu}_1$ is less than $\bar{\nu}$ for naphthalene and that disubstitution has more effect than monosubstitution, $\bar{\nu}_{1,4}$ being less than $\bar{\nu}_1$ (Figure 8). On the other hand, although $\bar{\nu}_{2,6}$ and $\bar{\nu}_{2,7}$ are greater than $\bar{\nu}_{1,4}$ in agreement with the results of polarography and charge transfer spectra, their values are in fact greater than for unsubstituted naphthalenes, which is in disagreement with what we would expect from the charge transfer and polarography results (Figure 8).

Correlation of the Data obtained from the Three Experimental Methods.—The combined data of polarography, and charge transfer and u.v. spectroscopy show that (a)

an inductive effect is operating for the t-butylnaphtha-lenes which raises the energy levels relative to naphtha-lene, and (b) two opposing effects are operating for the trimethylsilylnaphthalenes, an inductive effect which tends to raise the energy levels and a back donation

to the fact that the $3d$ orbital energy is much more nearly matched to the excited state of the $2p_\pi$ orbital than to its ground state, thus making interaction of the orbitals more probable in the lowest anti-bonding state than in the two highest bonding states. This conclusion
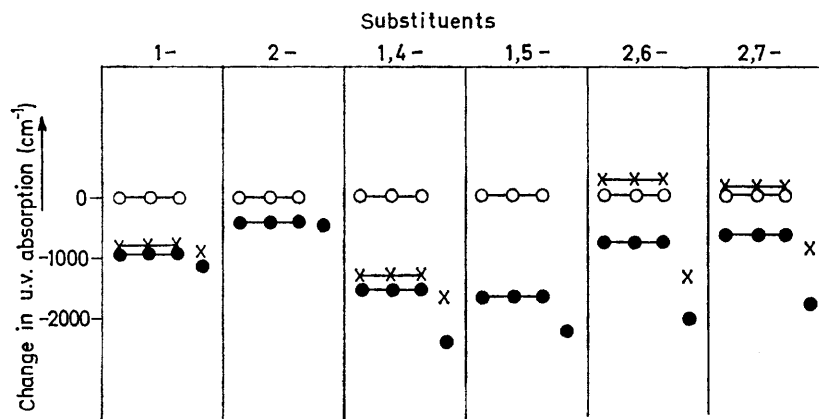

FIGURE 8   Change in u.v. absorption [p band $(m \longrightarrow m + 1)$] with change in substituent.   O—O—O, Unsubstituted naphthalene;
×—×—×, CMe_3-naphthalenes; ●—●—●, $SiMe_3$-naphthalenes.   Change in u.v. absorption expected from polarographic and
charge transfer results.   ×, CMe_3-naphthalenes; ●, $SiMe_3$-naphthalenes

effect which tends to lower the energy levels, the latter effect being the more important for the lowest un-occupied level, $m + 1$, and the former for the two highest occupied levels, m and $m - 1$. These results can be explained by the electron back donation from the aromatic π system to a vacant silicon $3d$ atomic orbital.

In the excited $m + 1$ state the back donation effect is greater than the inductive effect of CMe_3 (at least double) whereas in the two bonding orbitals, m and $m - 1$, the back donation effect appears to be at least half the inductive effect of CMe_3. This is possibly due

has been reached by several workers [23,24] on a purely theoretical basis in considering the interaction of Si $3d$ orbitals with the $2p_\pi$ system.

[23] H. Bock and H. Siedl, J. Amer. Chem. Soc., 1968, 90, 5694.
[24] J. Nagy and J. Ressy, J. Organometallic Chem., 1970, 22, 573.