d_π–p_π Interaction in Trimethylsilyl-substituted Naphthalenes. Part II.[1] Electron Spin Resonance Studies

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Trimethylsilyl-substituted naphthalenes have been studied by the use of e.s.r. spectroscopy and theoretical calculations carried out on the results. Molecular orbital calculations of the effect of $SiMe_3$ and CMe_3 groups on the energy levels show, by comparison with the experimental results, that *d* orbital participation by the silicon atom is operating to give d_π–p_π conjugation.

THERE has been much discussion concerning the d_π–p_π interaction in compounds containing silicon.[2] E.s.r. and polarographic techniques have been used by Allred and Bush [3a] for 1,4-$(SiMe_3)_2$-naphthalene and by Gerson *et al.*[3b] for 1,4-, 1,5-, and 2,6-$(SiMe_3)_2$-naphthalenes. In Part I [1] we described a study of $SiMe_3$- and CMe_3-substituted naphthalenes using polarography and charge transfer and u.v. spectroscopy. The results showed that d_π–p_π conjugation operates in the case of the $SiMe_3$-naphthalenes. In the present paper we extend this study by e.s.r. examination of the radical anions of the same substituted naphthalenes.

EXPERIMENTAL

Materials.—These were prepared and purified as described in Part I.[1] Li, Na, K, and Rb were purified as described earlier.[4]

E.s.r. and U.v. Measurements.—Solutions of the various substituted naphthalenes in dimethoxyethane (DME) were allowed to come into contact with Li, Na, K, or Rb for a short time. On passing over the alkali-metal film the colourless solutions of the neutral naphthalenes became dark green and strongly paramagnetic. E.s.r. measurements were made on Varian V 4500 and Varian E3 spectrometers and the spectra measured over the temperature range 193—293 K using a Varian temperature controller (E257). The spectra were analysed and the splitting constants obtained by means of a computer programme. The radical concentration was determined by integrating the e.s.r. spectrum (using a specially written computer programme) using a standard solution of diphenylpicrylhydrazyl (DPPH) for calibration purposes. The visible and u.v. spectra of these solutions were then recorded on a Unicam SP 800 spectrometer over this temperature range (using a similar temperature control system). The alkali-metal concentration of the solutions was determined by flame photometry using an Evans Electroselenium Ltd. flame photometer.

Product analysis was carried out on the solutions after opening to air and evaporating the solvent.

RESULTS

E.s.r. Spectra.—A well resolved e.s.r. spectrum was obtained for each system after appropriate dilution. The splitting constants obtained are given in Table 1. The results for 1,4-, 1,5-, and 2,6-$(SiMe_3)_2$-naphthalenes are in good agreement with those obtained by Gerson *et al.*[3b] The radical-anion concentration was obtained by integrating a low resolution spectrum by computer and comparison of this with the integral of a standard solution of DPPH under comparable conditions.

TABLE 1

Results obtained from e.s.r. spectral data

Substituent	Splitting constants (G)									
	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_{Si}	$a_H^{CH_3}$
$SiMe_3$										
1		2·51	1·72	5·02	4·72	1·06	2·23	4·44	4·16	0·00
2	4·88		0·80	4·82	4·82	2·91	0·80	4·82	2·30	0·09
1,4		2·33	2·33		3·21	1·41	1·41	3·21	4·65	0·05
1,5		2·17	1·72	4·80		2·17	1·72	4·80	3·53	0·04
2,6	4·65		0·26	4·51	4·65		0·26	4·51	2·72	0·13
2,7	5·55		1·56	4·07	4·07	1·56		5·55	2·80	0·09
Unsubstituted	4·90	1·83	1·83	4·90	4·90	1·83	1·83	4·90		
CMe_3										
1		1·48	1·91	5·00	5·00	2·22	1·68	5·00		0·00
1,4		1·75	1·75		5·25	1·75	1·75	5·25		0·00
2,6	4·85		2·27	4·85	4·85		2·27	4·85		0·00
2,7	5·03		1·87	4·68	4·68	1·87		5·03		0·00

The spectra were identical for all gegenions, and there was no splitting due to the metals at any temperature. The only change in spectrum with change in temperature from 193 to 293 K was a change in resolution; no evidence of any disproportionation reaction was observed. Beer's law was obeyed for all the systems over a 5- to 10-fold change in concentration.

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[1] Part I, A. G. Evans, B. Jerome, and N. H. Rees, *J.C.S. Perkin II*, 1973, 447.

[2] (*a*) M. D. Curtis, R. K. Lee, and A. L. Allred, *J. Amer. Chem. Soc.*, 1967, **89**, 5150; (*b*) H. Bock and H. Seidl, *J. Organometallic Chem.*, 1968, **13**, 103; *J. Chem. Soc.* (*B*), 1968, 1158; (*c*) H. Bock, J. Alt, and H. Seidl, *J. Amer. Chem. Soc.*, 1969, **91**, 355; (*d*) H. Bock and H. Alt, *ibid.*, 1970, **92**, 1569; (*e*) C. J. Attridge, *Organometallic Chem. Rev.*, 1970, **5A**, 323.

[3] (*a*) A. L. Allred and L. W. Bush, *J. Amer. Chem. Soc.*, 1968, **90**, 3352; (*b*) F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv. Chim. Acta*, 1968, **57**, 707.

[4] A. G. Evans, J. C. Evans, P. J. Emes, C. L. James, and P. J. Pomery, *J. Chem. Soc.* (*B*), 1971, 1484.

Visible and U.v. Spectra.—The visible and u.v. spectra of the radical anions gave peaks which are listed in Table **2**; they were independent of both the nature of the gegenion and the temperature in the range 193—293 K.

TABLE 2

U.v. peaks in radical anion spectra

Substituents	λ_{max}/nm
1-SiMe$_3$	230, 284(s), 294, 320(s), 327, 370, 434(s), 810
2-SiMe$_3$	235, 297, 315, 321, 330, 378, 436
1,4-(SiMe$_3$)$_2$	229, 289, 296, 317, 327, 372, 434, 811
1,5-(SiMe$_3$)$_2$	234, 286(s), 296, 319, 327, 371, 438, 815
2,6-(SiMe$_3$)$_2$	236, 294, 304, 326, 336, 390, 450, 806
2,7-(SiMe$_3$)$_2$	235, 295, 305, 328(s), 339 392, 444, 805
1-CMe$_3$	226, 284(s), 295, 321, 327, 372, 435, 770
1,4-(CMe$_3$)$_2$	230, 287, 297, 301(s), 330, 375, 430(s), 760
2,6(CMe$_3$)$_2$	231, 287(s), 297, 320, 328, 370, 425(s), 785
2,7-(CMe$_3$)$_2$	229, 290(s), 296, 320, 328, 375, 430(s), 790

s = Shoulder.

Product Analysis.—Analysis of the system after opening it to the air, gave only the original compound, together with a small fraction of naphthalene.

DISCUSSION

Since no alkali-metal splitting was observed in any of the e.s.r. spectra of the radical anions, it is probable that the ion pairs are not in contact, but are either solvent separated or exist as free ions. This was confirmed by the fact that the u.v.–visible spectra of the radical anions were independent of the nature of the alkali metal. Since Beer's law was obeyed by all the radical anions in solution, the ions must be present either completely as solvent separated ion pairs or completely as free dissociated ions.

TABLE 3

Spin densities calculated for 1-Me$_3$Si-naphthalene

	ρ exp	ρ calc Hückel	 McLachlan $\lambda = 1·00$	 McLachlan $\lambda = 0·40$
Si*Me*$_3$		0·064	0·063	0·063
1		0·171	0·203	0·184
2	0·096	0·076	0·061	0·070
3	0·066	0·062	0·037	0·052
4	0·192	0·180	0·224	0·197
5	0·180	0·163	0·200	0·178
6	0·041	0·060	0·038	0·051
7	0·089	0·066	0·049	0·059
8	0·169	0·159	0·192	0·172
8a		0·000	−0·035	−0·014
4a		0·000	−0·032	−0·013

Decreasing the temperature slightly sharpened the lines in the e.s.r. spectrum but had little effect on the radical-anion concentration, showing that no disproportionation equilibrium was present for any of the alkali metals. This was also confirmed by the u.v.–visible spectra of the radical anions which remain unchanged on reducing the temperature from **293** to **193** K. That Beer's law was obeyed also shows that no dimerisation or cleavage equilibrium was present in these systems.

TABLE 4

Eigenvalues for substituted naphthalene radical anions

	Unsubstituted	1-Me$_3$Si	2-Me$_3$Si	1,4-(Me$_3$Si)$_2$	1,5-(Me$_3$Si)$_2$	2,6-(Me$_3$Si)$_2$	2,7-(Me$_3$Si)$_2$
ψ_6	−0·618	−0·598	−0·610	−0·579	−0·581	−0·601	−0·602
ψ_5	0·618	0·603	0·612	0·588	0·589	0·606	0·607

This evidence, together with the fact that product analysis gave only the original compound, together with a small fraction of naphthalene, means that we are dealing with systems which contain only the species (substituted naphthalene)$\cdot$ M$^+$ in the form of solvent-separated ion pairs or of free ions.

Analysis of Spectra.—SiMe$_3$-*Substituted naphthalenes.* Table 3 gives an example of the values of ρ_{exp} calculated for 1-Me$_3$Si-naphthalene from the splitting constants using a *Q* value of −26·1, which gave the best overall fit. This value lies within the accepted range of −22·5 to −30 and agrees favourably with −26·7 for unsubstituted naphthalene. The theoretical treatment of these systems was carried out by considering SiMe$_3$ as a group X involving a vacant *p* orbital. Parameters covering a wide range of values were used: h_x from −1·00 to −1·60 in increments of 0·1; k_{c-x} from +0·35 to +0·60 in increments of 0·05; and δ from 0·00 to 0·15 in increments of 0·05. Two values were used for the McLachlan correction: λ 1·00, as used originally, and λ 0·40 as used by Gerson *et al.*[3b] The range of values for *h*, *k*, and δ include those used by Curtis *et al.*[2a] and by Gerson *et al.*[3b]

There were several sets of h_x, k_{c-x}, and δ which gave a good fit between ρ_{exp} and ρ_{calc}. From these sets we chose that one which gave the best fit with the results in Part I (*i.e.* polarography and charge transfer and u.v. spectra). These values are $h_x = -1·50$, $k_{c-x} = +0·55$, $\delta = 0·15$ (for α and β substituents). (Gerson *et al.*[3b] used the values $h = -1·50$, $k = +0·55$, $\delta = 0·00$.) Table 3 gives the ρ_{calc} values obtained using these parameters. The eigenvalues for the lowest unoccupied level, ψ_6, and for the highest occupied level, ψ_5, found using these parameters are given in Table 4 for all the SiMe$_3$-substituted naphthalenes.

CMe$_3$-*Substituted naphthalenes.* Table 5 gives an example of the values of ρ_{exp} calculated for 1-CMe$_3$-naphthalene from the splitting constants using a *Q* value of −26·1. The model used for the theoretical treatment of the CMe$_3$-substituted naphthalenes was to consider the CMe$_3$ group as X, having a *p* orbital containing two electrons which were contributed to the overall π system.[5] The parameters were varied, h_x from 1·40 to 1·60 in increments of 0·10 and k_{c-x} from 0·45 to 0·60 in increments of 0·05; for δ the following values were used: 0·00, 0·02, and 0·05. There are several sets of h_x, k_{c-x}, and δ values which give a good fit between ρ_{exp} and ρ_{calc}. From these sets we chose that one which gave the best fit with the results in Part I. These values are

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TABLE 5

Spin densities calculated for 1-CMe_3-naphthalene

	ρ_{exp}	ρ_{calc} Huckel	ρ_{calc} McLachlan $\lambda = 1{\cdot}00$	ρ_{calc} McLachlan $\lambda = 0{\cdot}40$
CMe_3		0·010	0·007	0·009
1		0·177	0·217	0·193
2	0·057	0·060	0·036	0·051
3	0·073	0·070	0·052	0·063
4	0·192	0·170	0·207	0·185
5	0·192	0·185	0·225	0·201
6	0·085	0·072	0·052	0·064
7	0·064	0·067	0·044	0·058
8	0·192	0·188	0·231	0·205
8a		0·000	−0·035	−0·014
4a		0·000	−0·036	−0·014

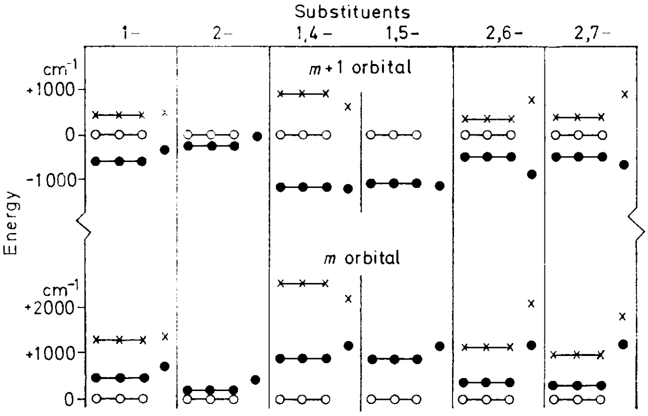
$h_x = 1{\cdot}5$, $k_{c-x} = 0{\cdot}50$, and $\delta = 0{\cdot}02$. Table 5 gives the ρ_{calc} values obtained using these parameters. Since it is assumed that each CMe_3 group contributes two electrons to the system, the highest occupied level for monosubstituents will be ψ_6, and the lowest unoccupied level will be ψ_7; with two substituents the corresponding levels will be ψ_7 and ψ_8. The eigenvalues for these levels are given in Table 6.

TABLE 6

Eigenvalues for substituted naphthalene radical anions

	Unsubstituted	1-Me_3C		1,4-$(Me_3C)_2$	2,6-$(Me_3C)_2$	2,7-$(Me_3C)_2$
ψ_7	−0·618	−0·634	ψ_8	−0·648	−0·629	−0·630
ψ_6	0·618	0·574	ψ_7	0·530	0·578	0·584

The experimental odd electron densities, and hence the hyperfine splitting constants, were assigned to the positions in the naphthalene ring according to the order of magnitude from the calculations. This order was hardly affected by changing the parameters *h*, *k*, and δ in the calculations, and was thus assumed to give a true indication of the electron density distribution around the ring system.



Energy levels of m and $m + 1$ molecular orbitals from e.s.r. data [the value of β used is 36,360/1236 cm^{-1} (calculated from the $m \longrightarrow m + 1$ u.v. absorption of naphthalene)]: ○–○–○, unsubstituted naphthalenes; X–X–X, CMe_3-naphthalenes; and ●–●–●, $SiMe_3$-naphthalenes. Energy levels obtained from the results of polarography ($m + 1$) and charge transfer (m) results:[1] ×, CMe_3-naphthalenes; and ●, $SiMe_3$-naphthalenes

Effect of Substituents.—If the inductive effect were the only factor involved, the eigenvalues (for the substituted naphthalenes) would lie higher in energy than for unsubstituted naphthalene. Furthermore, since $+I_{Me_3Si} > +I_{Me_3C}$ [2d] the energy levels for the Me_3Si-naphthalenes should lie higher than those for the corresponding naphthalenes. In the Figure we show the positions of the energy levels $m + 1$ (lowest unfilled) and m (highest filled), for the different substituted naphthalenes as calculated from e.s.r. data. It is seen that the energy levels for $SiMe_3$-naphthalenes lie at a lower level than those for the corresponding CMe_3-naphthalenes. Not only this, but in the case of the $m + 1$ level, the $SiMe_3$-naphthalenes actually lie lower in energy than does unsubstituted naphthalene. This shows that an electron-delocalising effect is acting in opposition to the positive inductive effect of $SiMe_3$, and we attribute this to the vacant *d* orbitals on silicon which enable d_π–p_π interaction to occur. This interaction is clearly more effective for the $m + 1$ level than for the m level. The Figure includes the corresponding energy levels obtained from polarography and charge transfer experiments;[1] it is seen that the agreement is good for the $m + 1$ level and less good for the m level.

Further support for this d_π–p_π interaction is given by the ^{29}Si splittings and the methyl proton splittings observed in the $SiMe_3$-naphthalenes (Table 1). No methyl proton splitting was observed for any of the CMe_3-naphthalenes. For methyl proton splitting to occur, some of the odd electron density must be distributed on to the methyl carbon atoms. It therefore needs to be transmitted through the silicon atom *via* the *d* orbitals. No methyl proton splitting is observed, however, for 1-$SiMe_3$-substituted naphthalene. Here the bulky $SiMe_3$ group is directly opposite the *peri*-hydrogen atom so that steric effects are possibly involved.[3b] Similarly in the 1,4- and 1,5-$(SiMe_3)_2$-naphthalenes the methyl proton splittings are hardly discernible, and this we attribute to the same effect. No methyl proton splitting was observed for any of the CMe_3-substituted naphthalenes, showing, as one would expect, that no odd electron density was being transmitted *via* the carbon atom to the methyl groups.

We thank Dow Corning, Barry, for a studentship (to B. J.) and for their interest and help in this work, and Dr. H. van Bekkum for his gift of the CMe_3-naphthalenes.

[3/1380 *Received, 2nd July,* 1973]