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SOME ELECTRONIC EFFECTS OF THE SILATRANE GROUP

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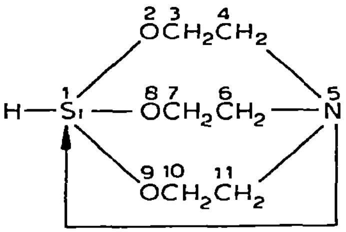
Summary

The electronic effects of the silatrane group have been studied by examination of the ^{19}F NMR spectra of 1-(*m*- and 1-(*p*-$FC_6H_4CH_2$)silatrane and the charge transfer spectra of the TCNE complexes of 1-phenyl- and 1-benzylsilatrane. Along with a quite large electron-releasing inductive effect, the CH_2silatrane group has a substantial electron-releasing hyperconjugative effect, though this is somewhat smaller than that of the CH_2SiMe_3 group.

Introduction

Following pioneering studies by Frye and his colleagues, [1], Voronkov and his co-workers have carried out an extensive series of investigations of derivatives of 2,8,9-trioxa-5-aza-1-silabicyclo[3,3,3]-undecane (I) which, for convenience, they call 'silatrane' [2,3].



(I)

In connection with other studies we have had reason to examine the electronic effects of the silatrane system on the organic group in 1-organosilatranes, and the results are described below.

Results and discussion

^{19}F *NMR spectra*

In spite of some doubts about the theoretical basis of the method, and demonstration of its deficiencies in some special cases (see, e.g., ref. 5, and the literature cited in ref. 6), the ^{19}F chemical shifts, δ_m^F and δ_p^F, of *m*- and *p*-XC_6H_4F compounds, respectively, relative to that of fluorobenzene can provide a useful empirical guide to the inductive and resonance effects of the X groups [4]. We were especially interested to see how effectively the CH_2—silatrane bond could release electrons hyperconjugatively, and in the absence of other suitable probes into the electronic effects of the 1-silatrane group, we examined the ^{19}F NMR spectra of *m*- and *p*-$FC_6H_4CH_2Si(OMe)_3$ and 1-(*m* and 1-(*p*-FC_6H_4-CH_2)silatrane in deuteriochloroform. The observed chemical shifts and the values of the inductive, σ_I, and resonance, σ_R^0, constants of the substituents derived by use of eqns. 1 and 2 [4] are shown in Table 1, which also lists data for some other substituents for comparison.

$$\delta_m^F = 7.1\ \sigma_I + 0.60 \tag{1}$$

$$\delta_m^F = -29.5\ \sigma_R^0 + \delta_m^F \tag{2}$$

The most striking feature of the results is the large positive shift produced by the *p*-CH_2silatrane group, indicating a large overall release of electrons to the *para*-position by this group, falling midway between that by the *p*-CH_2SiMe_3 and *p*-OMe groups. The derived values of σ_I and σ_R^0 indicate that while the inductive effect of the $CH_2Si(OMe)_3$ group is little different from that of the CH_3 group, that of the CH_2silatrane group is much larger. The resonance electron release by the latter group is also large, and similar to that of the CH_2SiMe_3 group. More detailed discussion is not justified at present in view of the uncertainty in the σ_I, and thus the σ_R^0, values for compounds of the types under consideration [6].

It is relevant to note that the overall electron supply to the *para*-position by a silatrane group directly attached to the aromatic ring, as indicated by the

TABLE 1

^{19}F CHEMICAL SHIFTS, δ^F FOR XC_6H_4F COMPOUNDS RELATIVE TO FLUOROBENZENE

X	δ^F	σ_I	σ^0_R	Ref.
p-CH_2silatrane[a]	9.32		—0.21	This work
p-$CH_2Si(OMe)_3$[b]	6.51[c]		—0.175	This work
p-CH_2SiMe_3	7.06[d]		—0.20	6
p-Silatrane	2.43			7
p-$SiMe_3$	-0.60			7
p-CH_3	5.34[d]		—0.14	6
p-OMe	11.50[d]		—0.45	11
p-Silatrane	2.43			7
m-CH_2silatrane[b]	3.15	—0.36		This work
m-$CH_2Si(OMe)_3$[b]	1.34[c]	—0.10		This work
m-CH_2SiMe_3[c]	1.14[d]	—0.08		6
m-CH_3	1.23[d]	—0.09		6

[a] 5% solution in $CDCl_3$. [b] 10% solution in $CDCl_3$. [c] A virtually identical value was obtained for a solution in MeOH. [d] In CCl_4.

δ_p^F value for 1-(p-FC_6H_4)silatrane, is markedly larger than that by the $SiMe_3$ group [7].

Charge transfer spectra

The frequencies of the charge-transfer maxima of $XC_6H_5 \cdot$ TCNE (TCNE = tetracyanoethylene) complexes give an indication of the ability of the group X to release electrons to the ring, and eqn. 3 can be used to give approximate values of σ^+-constants [8].

$$\nu = (9300\sigma^+ + 26200) \pm 500 \text{ cm}^{-1} \qquad (3)$$

We have determined the positions of the maxima for some 1-phenyl-and 1-benzyl-silatranes and for $PhCH_2Si(OMe)_3$ [$PhSi(OMe)_3$ did not give a clear maximum], and the results are shown in Table 2 along with those previously reported for some other relevant compounds. The most striking feature is that the electron-release from the CH_2silatrane group is rather similar to that from the CH_2SiMe_3 group. The derived σ_p^+ value for the CH_2silatrane group is correspondingly large, and this is to be associated with the marked hyperconjugative electron-release from the CH_2—Si bond. However, the charge transfer method gives a σ^+ value for the CH_2SiMe_3 group (viz. 0.66) rather higher than the true value (viz. —0.54 [9]), and we suggest an approximate σ_p^+ value of —0.48 for the CH_2silatrane group. The detailed indications of the ^{19}F shifts and charge transfer spectra are not wholly in accord, in that if the CH_2silatrane group really does have a markedly larger electron-releasing inductive effect than the CH_2SiMe_3 group, but a similar electron-releasing resonance effect, as suggested by the ^{19}F shifts, then the σ_p^+ value for the former should be significantly larger than that for the latter group.

The other features of the results are as follows:

(*a*). The electron-release by the $CH_2Si(OMe)_3$ group is significantly smaller than that by the CH_3 group.

TABLE 2

CHARGE TRANSFER MAXIMA FOR COMPLEXES BETWEEN XC_6H_5 COMPOUNDS AND TETRACYANOETHYLENE IN DICHLOROMETHANE AT 21°

X	Molar concn. of XC_6H_5 and of TCNE	λ max (nm)	ν max (cm^{-1})	σ_p^+ by eqn. 3	σ_p^+
CH_2silatrane	0.025	478	20920	—0.58	—0.48[a]
$CH_2Si(OMe)_3$	0.05	405.5	24660	—0.17	—0.25[b]
Silatrane	0.017	417.5	23950	—0.24	—0.35[b]
3,7,10-Me_3silatrane	0.005	424	23600	—0.27	—0.40[b]
CH_2SiMe_3		486[c]	20580	—0.66[c]	—0.54[d]
$SiMe_3$	0.05	405	24690	—0.16	—0.24[b]
CH_3		412	24270	—0.21	—0.31[b]

[a] See discussion. [b] The value of σ_p^+ derived from Me from eqn. 3 is substantially lower than the usual value of —0.31. For the substituents X having effects similar to those of the Me group, the σ_p^+ values in this column have been 'normalized' by multiplying the values in the preceeding column by 0.31/0.21. [c] From ref. 8. [d] From ref. 9.

(*b*). The electron-release by the silatrane group directly attached to the benzene ring (in 1-phenylsilatrane) is much larger than that by the $SiMe_3$ group (in $PhSiMe_3$), which is consistent with the evidence from the δ_p^F values above. Indeed, the silatrane group in these circumstances seems to release electrons more strongly than the Me group.

(*c*). The electron-release by the 3,7,10-trimethylsilatrane group directly attached to the benzene ring is, as expected, greater than that of the silatrane group itself. The difference is quite large, and it is possible that the electron-release by the additional methyl groups leads to an increase in the amount of π-bonding in the Si—O linkage, so that the overall influence is significantly greater than that expected for operation of inductive effects alone.

Experimental

Preparations of 1-organosilatranes (cf. ref. [1])

Usually, a stirred mixture of the appropriate organotrimethoxysilane (0.1 mol) and triethanolamine (0.1 mol) was heated, for the time specified in Table 3, by means of an oil bath maintained at the temperature indicated in the same table, the formed methanol being removed continuously through a short fractionating column. The solid residue was recrystallized from chloroform. Tri-isopropanolamine was used analogously in the preparation of 1-phenyl-3,7,10-trimethylsilatrane. Yields, m.p.'s, and analyses are shown in Table 3.

Spectroscopic measurements

(*a*). The ^{19}F chemical shifts were measured in deuteriochloroform at ca. 21° with Cl_3CF as internal standard. The δ^F values in Table 1 are derived by assuming a chemical shift of 113.15 ppm for fluorobenzene relative to Cl_3CF.

(*b*). The charge transfer spectra were measured with dichloromethane solutions at ca. 21°. The spectral range 200-600 nm was scanned with an SP 800 spectrophotometer, and the position of the longest wave length maximum then confirmed with an SP 500 spectrophotometer.

TABLE 3

PREPARATIONS OF SUBSTITUTED SILATRANES

Substituent(s)	Temp. (°C); Time (h)	Yield (%)	M.p. (°C)	Found (Calcd.) (%) C	H	N
$1\text{-}C_6H_5\text{-}3,7,10\text{-}Me_3$	140; 2	87	134-135[a]			
$1\text{-}C_6H_5CH_2$	130; 2	65	256-257	58.7 (58.8)	7.2 (7.2)	5.4 (5.3)
1-*m*-$FC_6H_4CH_2$	80; 1	50	210.5-211	55.2 (55.1)	6.6 (6.4)	4.9 (4.9)
1-*p*-$FC_6H_4CH_2$	110; 5	62	225	55.1 (55.1)	6.3 (6.4)	4.8 (4.9)

[a] Lit. [2], m.p. 133-134°.

Acknowledgements

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