

CONFORMATION OF ACYLOXYTRIMETHYLSILANES
AND ACYLOXY(*p*-FLUOROPHENYL)DIMETHYLSILANES*

A. V. VARLAMOV^a, Z. PAPOUŠKOVÁ^b, J. POLA^b, P. TRŠKA^c and V. CHVALOVSKÝ^b

^a P. Lumumba University, Moscow, USSR

^b Institute of Chemical Process Fundamentals,

Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát 2 and

^c Institute of Chemical Technology, 166 28 Prague 6

Received August 4th, 1976

The dipole moments of the compounds $\text{RC(O)OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ with $\text{R} = \text{H}, \text{CH}_3, \text{ClCH}_2$ have been determined in benzene, and are discussed together with those for the compounds $\text{RC(O)OSi}(\text{CH}_3)_3$ with the same groups R in terms of the conformation heterogeneity. The ^{19}F -NMR spectra of the former compounds revealed $\text{RC(O)OSi}(\text{CH}_3)_2$ groups to have electron withdrawing effect and free rotation about $\text{C(O)}\text{—O}(\text{Si})$ bond.

With the esters $\text{RC(O)OR}'$ having isotropic R group the only possible internal rotation — rotation about $\text{C(O)}\text{—O}$ bond may result in equilibrium $I \rightleftharpoons II$. This equilibrium is mostly shifted to the left, and significant amounts of a high energy conformer II were reported only for bulky substituents R' like $(\text{CH}_3)_3\text{C}$, $(\text{C}_2\text{H}_5)_3\text{C}$, and $(\text{C}_6\text{H}_5)_3\text{C}$, destabilizing conformer I due to their repulsion with the carbonyl group¹⁻³. In our previous work⁴ we dealt with acyloxytrimethylsilanes $\text{RC(O)OSi}(\text{CH}_3)_3$, IR spectral study of those has revealed the existence of solely one conformer in solution. (This finding is surprising with regard to a large steric effect of the trimethylsilyl group, that was recently estimated⁵ to be even greater than steric effect of the *t*-butyl group.) It has become worthwhile to determine which conformer it is, and to answer this question in this work we present the study of the dipole moment of the acyloxytrimethylsilanes $\text{RC(O)OSi}(\text{CH}_3)_3$ with $\text{R} = \text{H}, \text{CH}_3$ and ClCH_2 . The same study of the acyloxy(*p*-fluorophenyl)dimethylsilanes $\text{RC(O)OSi}(\text{CH}_3)_2$ with the same R groups was carried out to examine the effect of the substitution in a silyl group on the conformation equilibrium. Being familiar with the observed response of the ^{19}F chemical shift to conformational heterogeneity of the fluorophenyl formamides⁶ we also attempted to examine the latter problem by ^{19}F -NMR spectroscopy.

* Part CXLIX in the series Organosilicon Compounds; Part CXLVIII: This Journal 42, 484 (1977).

EXPERIMENTAL

Materials

Acyloxy(p-fluorophenyl)dimethylsilanes $\text{RC(O)OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ with $\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{Cl}$ were prepared by treatment of an appropriate acid with *p*-fluorophenyldimethylchlorosilane in the presence of stoichiometric amounts of triethylamine in dry diethyl ether, and were obtained by rectification. Their purity was checked by gas-chromatography and their identity was confirmed by $^1\text{H-NMR}$ spectroscopy and elemental analysis. $\text{RC(O)OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ ($\text{R}, \text{yield} (\%), \text{b.p. } (^\circ\text{C/Torr}), n_{\text{D}}^{20}$): $\text{H}, 22, 82-83/9, 1.4770; \text{CH}_3, 75, 85-87/9, 1.4723; \text{ClCH}_2, 64, 118-119/9, 1.4915$. The preparation of acyloxytrimethylsilanes $\text{RC(O)OSi}(\text{CH}_3)_3$ with $\text{R} = \text{H}, \text{CH}_3, \text{ClCH}_2$ was described elsewhere⁷.

(*p*-Fluorophenyl)dimethylsilanol and bis(*p*-fluorophenyl)dimethyldisiloxane, both the products of hydrolysis of the compounds $\text{RC(O)OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ were prepared for the $^{19}\text{F-NMR}$ measurement to avoid an erroneous interpretation of $^{19}\text{F-NMR}$ spectra of the $\text{RC(O)OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ compounds. (*p*-Fluorophenyl)dimethylsilanol was prepared by hydrolysis of (*p*-fluorophenyl)dimethylchlorosilane with 26% aqueous solution of ammonia in diethyl ether performed at 0°C and obtained in 31% yield as a fraction with b.p. $94^\circ\text{C}/9 \text{ Torr}$. Bis(*p*-fluorophenyl)dimethyldisiloxane was prepared by hydrolysis of (*p*-fluorophenyl)dimethylchlorosilane (50% yield, b.p. $146-148^\circ\text{C}/11 \text{ Torr}, n_{\text{D}}^{20} 1.4939$).

Measurements

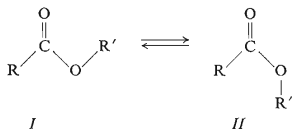
The dipole moments were determined on the bases of dielectric constants and refractive indices of solution of the acyloxysilanes in benzene over a concentration range from 10^{-2} to 10^{-3}M . The dielectric constants were determined by the resonance method at a frequency of 0.05 MHz. The refractive indices were measured by Zeiss immersion refractometer. All the measurements were carried out at 25°C . The dipole moments were calculated from the experimental data according to the procedure of Smith⁸.

The $^{19}\text{F-NMR}$ spectra were recorded with Varian XL-100 spectrometer (94.1 MHz) with ^1H -noise decoupling using solutions of the compounds in CDCl_3 or C_6D_6 and fluorobenzene as internal standard. The spectra were recorded at different temperatures from 37°C to 70°C in benzene and from -25°C to 60°C in CDCl_3 .

RESULTS AND DISCUSSION

The experimental and calculated dipole moments of acyloxytrimethylsilanes and acyloxy(*p*-fluorophenyl)dimethylsilanes are shown in Table I. Dipole moments were calculated by vector addition of the individual group moments as determined for $\text{C-H}, \text{C=O}, \text{C-O}$ and $(\text{CH}_3)_3\text{Si-O}$ groups in papers^{11,12}. From the same works were taken also the values for $\text{SiOC}, \text{OCO},$ and HCO bond angles. The value of the dipole moment for $(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2\text{Si-O}$ group 0.46 D was calculated from the dipole moment of *p*-fluorophenyltrimethylsilane¹³. From the Table I it is apparent, that the values of the dipole moments of the compounds $\text{RC(O)OSi}(\text{CH}_3)_3$ are close to those calculated for conformer *I* with $\text{R}' = \text{Si}(\text{CH}_3)_3$. The existence of only one conformer for these compounds was also inferred from their IR spectra⁴ without distinguishing which conformer it is. The dipole moment values enable us

to discern between conformer *I* and *II* in favour of the former. The dominant majority of conformer *I* in solution can be, with regard to a great volume of $(\text{CH}_3)_3\text{Si}$ group⁵, likely attributed to its stabilization by the $(p-d)\sigma \text{C}=\text{O} \rightarrow \text{Si}$ interaction. As it follows from Table I, the dipole moments for the compounds $\text{RC}(\text{O})\text{OSi} \cdot (\text{p-FC}_6\text{H}_4)(\text{CH}_3)_2$ are compatible with the significant occurrence of the conformer *II* ($\text{R}' = (\text{p-FC}_6\text{H}_4)(\text{CH}_3)_2\text{Si}$). The shift in conformation equilibrium $I \rightleftharpoons II$ changing $(\text{CH}_3)_3\text{Si}$ group for $(\text{p-FC}_6\text{H}_4)(\text{CH}_3)_2\text{Si}$ group is evidently a consequence of the enhancement of a steric effect of a silyl group.



We now report the dipole moments of the compounds $\text{ClCH}_2\text{C}(\text{O})\text{OSiR}(\text{CH}_3)_3$ with $\text{R} = \text{CH}_3$ and $\text{p-FC}_6\text{H}_4$ in relation to the additional conformation equilibrium associated with internal rotation of the $\text{CH}_2-\text{C}(\text{O})$ bond. The calculated dipole moments for all the conformers of the above compounds illustrated in Scheme 1 together with the determined dipole moments are shown in Table II. Presuming the conformer *I* is very significantly favoured with the acyloxytrimethylsilanes, one would expect conformation equilibrium $A \rightleftharpoons B$ with $\text{ClCH}_2\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$ compound. As a matter of fact this equilibrium was recently detected by the IR spectra⁴. From the comparison of the determined dipole moments of $\text{ClCH}_2\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$ compound with those calculated for all the conformers *A - D*, it turns out that the experimental value closely fits that of conformer *B*. The dipole moment of ClCH_2-

TABLE I

Determined and Calculated Dipole Moments in Debye Units, D, of Some $\text{RC}(\text{O})\text{OSi}(\text{CH}_3)_3$ and $\text{RC}(\text{O})\text{OSi}(\text{p-FC}_6\text{H}_4)(\text{CH}_3)_2$ Compounds

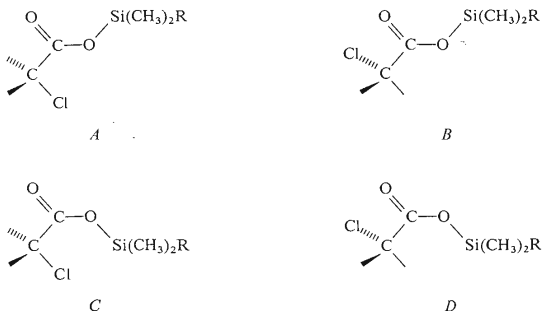
R	$\text{R}' = \text{Si}(\text{CH}_3)_3^{a,b}$	$\text{R}' = \text{Si}(\text{p-FC}_6\text{H}_4)(\text{CH}_3)_2^a$
H	2.05 (1.63, 3.33)	2.15 (2.76, 1.92)
CH_3	1.85 ^c (1.63, 3.33)	2.10 (2.76, 1.92)

^a In parentheses, the first value relates to conformer *I*, the second one to conformer *II*. The rotation about O—Si bond was considered to be free in $\text{RC}(\text{O})\text{OSi}(\text{p-FC}_6\text{H}_4)(\text{CH}_3)_2$ compounds.

^b Ref.⁹. ^c In agreement with ref.¹⁰.

—C(O)Si(CH₃)₃ compound 2-78 D is thus in very good agreement with equilibrium $A \rightleftharpoons B$ being shifted in favour of conformer *B*.

The comparison of the determined and the calculated dipole moments of ClCH₂.C(O)OSi(*p*-FC₆H₄)(CH₃)₂ compound (Table II) favours the conformers *B* or *D* and justifies thus statement, that conformational phenomena for this compound can be described as equilibrium $B \rightleftharpoons D$. However assuming the finding, that *p*-FC₆H₄(CH₃)₂Si group dislikes a proximity of the carbonyl group, equilibrium $C \rightleftharpoons D$ and its dominant shift to the side of the conformer *D* explains internal rotation of this compound better.



SCHEME 1

The relatively high sensitivity of the ¹⁹F-NMR shielding to intramolecular changes¹⁴ and recently reported response of the ¹⁹F chemical shift to conformation heterogeneity of the fluorophenyl formamides⁶ led us to examine also ¹⁹F-NMR spectra of the compounds RC(O)OSi(*p*-FC₆H₄)(CH₃)₂. The ¹⁹F-NMR signals of the above compounds were found not to be splitted and their values are shown in Table III.* The estimation of the polar effect of RC(O)OSi(CH₃)₂ groups (R = H, CH₃, ClCH₂) was carried out on the ground of papers^{17,18} and it shows these groups to have rather strong electron withdrawing effect (Table III).

The unanswered question still remained if the occurrence of the only ¹⁹F-NMR signal in spectra of the RC(O)OSi(*p*-FC₆H₄)(CH₃)₂ compounds might be caused by the presence of one conformer or by the occurrence of both *I* and *II* conformers

* In fact, almost negligible peaks with δF 1.52 and 1.78 p.p.m. were also found in spectra and ascribed to *p*-fluorophenyldimethylsilanol and bis(*p*-fluorophenyldimethyl)disiloxane respectively.

with unhindered rotation about C(O)—O(Si) bond. In the following consideration we have used the presumption of limited mutual interference of fluorine and R groups in *para*-substituted benzenes (despite that we are aware of its limited correctness). The dipole moments of the compounds *p*-FC₆H₄R with R = (CH₃)₂N, NH₂, OH, OCH₃, OC₆H₅, CH₃ and Cl (ref.¹⁹) and those of the compounds of the same type measured in this work (R, μ(D): OCH₃, 2.15; H, 1.45; Cl, 0.30; Br, 0.45) linearly correlate with Hammett σ_p constants of group R. Having used this correlation, σ_p constants of RC(O)OSi(CH₃)₂ groups where R = H, CH₃ in conformers *I* and *II* of acyloxysilanes RC(O)OSi(*p*-FC₆H₄)(CH₃)₂ were acquired from the dipole moments calculated for both *I* and *II* conformers of the RC(O)OSi(*p*-FC₆H₄)(CH₃)₂ compounds (Table I), and the difference between them was found about 0.4. As-

TABLE II

Calculated Dipole Moments in Debye Units, D, of ClCH₂C(O)OSi(CH₃)₂R Compounds

Conformer	R = CH ₃ ^{a,b}	R = <i>p</i> -FC ₆ H ₄ ^{a,c}
<i>A</i>	0.17–0.65	1.58–1.55
<i>B</i>	2.70–3.20	3.03–3.40
<i>C</i>	1.90–1.68	0.88–1.17
<i>D</i>	4.00–4.42	2.45–2.90

^a The values of m_{C-Cl} 1.55 D (ref.¹⁵) and 2.05 D (ref.¹⁶) were used in the calculation and the calculated dipole moments (reported in table) follow this order; ^b experimental value 2.78 D; ^c experimental value 2.71 D.

TABLE III

The ¹⁹F-NMR Chemical Shifts, δ(F) of the Compounds RC(O)OSi(*p*-FC₆H₄)(CH₃)₂ and Calculated σ_p Constants of RC(O)OSi(CH₃)₂ Groups

The symbol δ(F) is used for ¹⁹F-NMR shifts given in ppm units relative to fluorobenzene as internal standard, positive values δ(F) refer to upfield shift; the conditions of the measurement were identical with those used by Taft¹⁷.

R	δ(F) in CDCl ₃		δ(F) in C ₆ D ₆		σ_p
	20°C	-25°C	70°C	37°C	
H	3.66	3.76	3.28	3.28	0.23
CH ₃	3.08	3.21	2.81	2.83	0.26
ClCH ₂	3.89	3.95	3.55	3.60	0.21

suming further the linear correlation between the ^{19}F -NMR chemical shift and σ_p values for *para*-fluorosubstituted benzenes¹⁷, the above, a relatively great, difference in σ_p values yields a difference in ^{19}F -NMR shifts between conformers *I* and *II* of $\text{RC}(\text{O})\text{OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ compounds being several ppm units. Based on our temperature measurement of the ^{19}F -NMR spectra of the above acyloxysilanes — ^{19}F -NMR signal does not split when going from 70°C to -25°C — and in connection with the comparison of the determined and calculated dipole moments for these compounds (Table I), we suppose rather conformational equilibrium $I \rightleftharpoons II$, that is shifted significantly neither to conformer *I* nor *II*. Chemical shift $\delta(\text{F})$ for all the $\text{RC}(\text{O})\text{OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ compounds is not affected by the temperature changes in C_6D_6 , but it increases in CDCl_3 with the decrease of the temperature. This phenomena can be ascribed to the interaction between the carbonyl oxygen of acyloxysilanes and deuterium of the deuteriochloroform, that becomes more significant at lower temperature. Relatively free rotation about $\text{C}(\text{O})\text{—O}(\text{Si})$ bond with $\text{RC}(\text{O})\text{OSi}(p\text{-FC}_6\text{H}_4)(\text{CH}_3)_2$ compounds thus deteriorates distinguishing of conformers *I* and *II*, but differs these compounds from acyloxytrimethylsilanes, that have equilibrium $I \rightleftharpoons II$ shifted dominantly to the left.

REFERENCES

- Oki M., Nakanishi H.: Bull. Chem. Soc. Jap. 43, 2558 (1970).
- Morgan K. J., Unwin N.: J. Chem. Soc. (B) 1968, 880.
- George W. O., Hassid D. V., Maddams W. F.: J. Chem. Soc., Perkin 2, 1973, 952.
- Pola J., Jakoubková M., Papoušková Z., Chvalovský V.: This Journal, in press.
- Charton M.: J. Amer. Chem. Soc. 97, 1552 (1975).
- Arnold Z., Krchňák V., Trška P.: Tetrahedron Lett. 1975, 347.
- Pola J., El Attar A., Chvalovský V.: This Journal 41, 1772 (1976).
- Smith J. W.: Trans. Faraday Soc. 46, 394 (1950).
- Jakoubková M., Papoušková Z.: The Abstract of the Fourth International Symposium on Organosilicon Chemistry, Moscow 1975, Vol. 1, Part 1, p. 87.
- Cumper C. W. N., Melnikoff A., Vogel A. J.: J. Chem. Soc. (A) 1966, 323.
- Bock E., Iwacha D., Hutton H., Queen A.: Can. J. Chem. 46, 1645 (1968).
- Ulbricht K., Vaisarová V., Bažant V., Chvalovský V.: J. Organometal. Chem. 13, 343 (1968).
- Roberts J. D., McElhill E. A., Armstrong R.: J. Amer. Chem. Soc. 71, 2923 (1949).
- Tribble M. T., Traynham J. G. in the book: *Advances in Linear Free Energy Relationships* (N. B. Chapman, J. Shorter, Eds). Plenum Press, New York 1972.
- Smith J. W.: *Electric Dipole Moments*. Butterworths, London 1955.
- Volkenshtein M. V.: *Struktura a fyzikální vlastnosti molekul*, p. 266. Published by Nakladatelství ČSAV, Prague 1962.
- Taft R. W., Price E., Fox I. R., Lewis I. C., Andersen K. K., Davis G. T.: J. Amer. Chem. Soc. 85, 3146 (1963).
- Jaffé H. H.: Chem. Rev. 53, 191 (1953).
- Leonard N. J., Sutton L. E.: J. Amer. Chem. Soc. 70, 1564 (1948).

Translated by the author (J. P.).