Electronic supplementary information

Radical Anions of Hypervalent Silicon Compounds. 1-Substituted Silatranes

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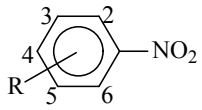


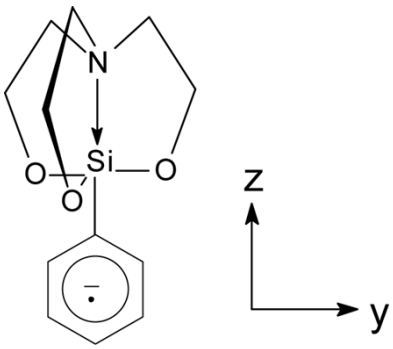
Table S1 Experimental EPR hyperfine coupling constants (in Gauss) of the radical anions of the *para*- (**2a**), *meta*- (**2b**), and *ortho*- (**2c**) isomers of nitrophenoxysilatrane in DMF and acetonitrile solutions

	R	Solvent	$a_N^{NO_2}$	$a_{H(2)}$	$a_{H(3)}$	$a_{H(4)}$	$a_{H(5)}$	$a_{H(6)}$
2a$^{-\bullet}$	*p*-OSi(OCH$_2$CH$_2$)$_3$N	DMF	11.10	3.40	1.15	-	1.15	3.40
		acetonitrile	11.80	3.30	1.10	-	1.10	3.30
2b$^{-\bullet}$	*m*-OSi(OCH$_2$CH$_2$)$_3$N	DMF	10.35	3.30	1.00	3.55	-	3.30
		acetonitrile	10.50	3.25	1.0	3.50	-	3.25
2c$^{-\bullet}$	*o*-OSi(OCH$_2$CH$_2$)$_3$N	DMF	13.70	3.50	0.90	3.50	0.60	-
		acetonitrile	14.00	3.40	0.90	3.40	0.60	-

Table S2 B3PW91/6-31+G(d,p)//B3PW91/6-31+G(d,p) Mulliken charges (*q*, e) in the neutral structure XSi(OCH$_2$CH$_2$)$_3$N (X = C$_6$H$_5$), **1**, in its radical anion **1**$^{-\bullet}$ and in complex **1**$^{-\bullet}\cdot$ K$^+$ in DME solution (C-PCM model)

	1	**1**$^{-\bullet}$	**1**$^{-\bullet}\cdot$ K$^+$
K	-	-	0.96
X[a]	-0.60	-1.26	-1.57
C1	-1.75	-1.55	-1.85
Si	1.65	1.38	1.57
N	-0.70	-0.38	-0.46
O1	-0.57	-0.60	-0.60
O2	-0.59	-0.62	-0.60
O3	-0.63	-0.64	-0.60

[a] The total charge on the phenyl ring.



The phenyl moiety is oriented in the yz-plane with the silatranyl group along the z-axis.

Table S3 Calculated isotropic g-factor and g-tensor components for the isolated $\mathbf{1}^{-\bullet}$ and complex $\mathbf{1}^{-\bullet}\cdot K^+$ in DME solution (C-PCM model)[a]

	Method	Basis set	g_{xx}	g_{yy}	g_{zz}	g_{iso}
$\mathbf{1}^{-\bullet}$	TPSSh	IGLOIII	2.0018	2.0026	2.0032	2.0025
	B3LYP	IGLOIII	2.0018	2.0027	2.0033	2.0026
	PBE0	IGLOIII	2.0018	2.0026	2.0033	2.0026
	B3LYP	EPRIII	2.0018	2.0027	2.0032	2.0026
	B3LYP	TZVP	2.0018	2.0026	2.0033	2.0026
	B3LYP	N07D	2.0018	2.0026	2.0031	2.0025
	TPSSh	**IGLOIII**	**2.0018**	**2.0026**	**2.0033**	**2.0026**
	B3LYP	**IGLOIII**	**2.0018**	**2.0026**	**2.0034**	**2.0026**
	PBE0	**IGLOIII**	**2.0018**	**2.0026**	**2.0034**	**2.0026**
	B3LYP	**EPRIII**	**2.0019**	**2.0026**	**2.0033**	**2.0026**
	B3LYP	**TZVP**	**2.0018**	**2.0026**	**2.0034**	**2.0026**
	B3LYP	**aug-CCPVTZ**	**2.0019**	**2.0025**	**2.0033**	**2.0026**
	B3LYP	**N07D**	**2.0019**	**2.0026**	**2.0032**	**2.0026**
$\mathbf{1}^{-\bullet}\cdot K^+$	TPSSh	IGLOIII	2.0011	2.0024	2.0034	2.0023
	B3LYP	IGLOIII	2.0011	2.0025	2.0034	2.0023
	PBE0	IGLOIII	2.0013	2.0024	2.0035	2.0024
	B3LYP	EPRIII	2.0011	2.0025	2.0035	2.0024
	B3LYP	TZVP	2.0015	2.0024	2.0034	2.0024
	B3LYP	N07D	2.0014	2.0024	2.0033	2.0024
	TPSSh	**IGLOIII**	**2.0013**	**2.0018**	**2.0036**	**2.0022**
	B3LYP	**IGLOIII**	**2.0013**	**2.0018**	**2.0037**	**2.0023**
	PBE0	**IGLOIII**	**2.0014**	**2.0017**	**2.0037**	**2.0023**
	B3LYP	**EPRIII**	**2.0013**	**2.0018**	**2.0037**	**2.0023**
	B3LYP	**TZVP**	**2.0017**	**2.0019**	**2.0035**	**2.0024**
	B3LYP	**N07D**	**2.0017**	**2.0018**	**2.0035**	**2.0023**

[a] UB3PW91/6-31+G(d,p) and UMP2/6-31+G(d,p) (in bold) geometry optimization, C-PCM solvation model.

Table S4 Experimental and calculated HFC constants a_H and the MAE parameter (in Gauss) for the radical anion of phenysilatrane in DME solution[a]

Optimization method	HFCC method	HFCC basis	$a_{H(2,6)}$	$a_{H(3,5)}$	$a_{H(4)}$	MAE
	Experiment		2.62	0.85	8.38	
UB3PW91	UB3PW91	6-31+G(d,p)	-3.88	-0.43	-11.67	1.33
	UPBE0	N07D	-3.45	-0.24	-10.41	0.98
	UB3LYP	N07D	-3.49	-0.55	-10.74	0.94
	UB3LYP	6-311++G(2d,2p)	-3.20	-0.44	-9.98	0.72
	UB3LYP	EPR3/IGLOIII	-3.35	-0.48	-10.33	0.83
			-3.38	*-0.44*	*-10.54*	*0.90*
	UB3LYP	IGLOIII	-3.09	-0.46	-9.42	0.55
			-3.11	*-0.42*	*-9.60*	*0.61*
	UTPSSh	IGLOIII	-3.28	-0.59	-9.02	0.50
			-3.24	*-0.57*	*-9.04*	*0.50*
	UB2PLYP	IGLOIII	-2.65	-1.49	-9.56	0.50
			-4.58	*0.85*	*-14.54*	*2.02*
	UPBE0	IGLOIII	-3.49	-0.25	-10.48	1.01
			-3.47	*-0.22*	*-10.55*	*1.03*
	UB3PW91	IGLOIII	-3.37	-0.40	-10.04	0.82
UMP2	UPBE0	N07D	-1.83	-1.26	-4.80	1.20
	UB3LYP	N07D	-1.85	-1.51	-4.74	1.30
	UB3LYP	EPR3/IGLOIII	-1.73	-1.40	-3.64	1.52
	UB3LYP	IGLOIII	-1.70	-1.31	-3.86	1.46
	UTPSSh	IGLOIII	-1.86	-1.35	-3.31	1.52
	UB2PLYP	IGLOIII	-2.01	-1.68	-4.16	1.42
	UB3PW91	IGLOIII	-1.92	-1.35	-4.62	1.23
	UPBE0	IGLOIII	-1.92	-1.27	-4.99	1.13

[a] UB3PW91/6-31+G(d,p) and UMP2/6-31+G(d,p) geometry optimization, C-PCM and COSMO (italics) solvation models. The calculated values a_H for ortho-protons and a_H for meta-protons are averaged over the degenerate by energy states A and B (see Fig. 5).

Table S5 UB3PW91/6-31+G(d,p) Mulliken charges (q, e) in the isomers of the neutral structures $XSi(OCH_2CH_2)_3N$ (X = $NO_2C_6H_4O$), **2**, and their radical anions, **2**$^{-\bullet}$, as well as their difference (Δq, e) in acetonitrile solution (C-PCM model)

	q	q	Δq	q	q	Δq	q	q	Δq
	2a	**2a**$^{-\bullet}$	**2a**$^{-\bullet}$**-2a**	**2b**	**2b**$^{-\bullet}$	**2b**$^{-\bullet}$**-2b**	**2c**	**2c**$^{-\bullet}$ [a]	**2c**$^{-\bullet}$**-2c**
NO_2Ph	-0.30	-1.21	-0.91	-0.25	-1.27	-1.01	-0.22	-1.22	-0.99
								-1.01	*-0.78*
X[b]	-0.81	-1.76	-0.95	-0.78	-1.80	-1.02	-0.71	-1.71	-1.00
								-1.62	*-0.91*
O	-0.50	-0.55	-0.05	-0.53	-0.53	-0.01	-0.49	-0.49	0.00
								-0.61	*-0.12*
Si	2.20	2.19	-0.01	2.20	2.25	0.05	2.16	2.12	-0.03
								2.09	*-0.07*
N	-0.94	-0.89	0.05	-0.91	-0.89	0.03	-0.95	-0.90	0.06
								-0.35	*0.60*
O11	-0.68	-0.69	-0.01	-0.69	-0.69	0.00	-0.71	-0.68	0.03
								-0.81	*-0.10*
O12	-0.70	-0.71	-0.01	-0.69	-0.71	-0.02	-0.71	-0.71	0.00
								-0.57	*0.15*
O13	-0.69	-0.70	-0.01	-0.72	-0.71	0.01	-0.72	-0.70	0.02
								-0.77	*-0.06*

[a] The charge values are given in normal type for **2c**$^{-\bullet}$(Si←N) isomer and in italics for **2c**$^{-\bullet}$(Si←O) isomer. [b] The total charge over the $NO_2C_6H_4O$ fragment.

Table S6 Experimental and calculated hyperfine coupling constants as well as the MAE parameter (in Gauss) for the *para*-isomer of $[NO_2C_6H_4OSi(OCH_2CH_2)_3N]^{-\bullet}$ in acetonitrile solution. Geometry optimization was carried out at the UB3PW91/6-31+G(d,p) and UMP2/6-31+G(d,p) (in bold) levels of theory (C-PCM and COSMO (in italics) solvation models)

HFCC method	a_N ^{NO2}	$a_{H(2)}$	$a_{H(3)}$	$a_{H(5)}$	$a_{H(6)}$	**MAE**
Experiment	11.80	3.30	1.10	1.10	3.30	0.00
C-PCM TPSSh/IGLOIII	8.24	-3.46	1.20	1.20	-3.46	0.81
C-PCM PBE0/IGLOIII	8.16	-4.05	1.80	1.80	-4.05	1.30
C-PCM B3PW91/IGLOIII	6.96	-3.79	1.53	1.53	-3.79	1.33
C-PCM B3LYP/IGLOIII	7.74	-3.46	1.33	1.33	-3.46	0.97
C-PCM B3LYP/EPRIII[a]	8.02	-3.78	1.47	1.47	-3.78	1.09
C-PCM B3LYP/6-311++G(2d,2p)	7.40	-3.64	1.40	1.40	-3.64	1.13
C-PCM B2PLYP/IGLOIII	-8.05	-1.62	-0.68	-0.68	-1.62	1.59
C-PCM B3LYP/N07D(5D)	12.06	-3.96	1.52	1.52	-3.96	0.48
COSMO TPSSh/IGLOIII	*8.61*	*-3.43*	*1.19*	*1.19*	*-3.43*	*0.72*
COSMO B3LYP/IGLOIII	*8.31*	*-3.50*	*1.35*	*1.35*	*-3.50*	*0.88*
COSMO B3LYP/EPRIII[a]	*8.56*	*-3.83*	*1.49*	*1.49*	*-3.83*	*1.02*
COSMO B2PLYP/IGLOIII	*16.91*	*-6.97*	*4.51*	*4.51*	*-6.97*	*3.85*
C-PCM TPSSh/IGLOIII	**15.94**	**-2.19**	**0.81**	**0.81**	**-2.19**	**1.39**
C-PCM B3LYP/IGLOIII	**15.75**	**-2.20**	**0.85**	**0.85**	**-2.20**	**1.33**
C-PCM B3LYP/EPRIII[a]	**15.99**	**-2.41**	**0.94**	**0.94**	**-2.41**	**1.26**
C-PCM B3LYP/6-311++G(2d,2p)	**15.16**	**-2.33**	**0.90**	**0.90**	**-2.33**	**1.14**
C-PCM B3LYP/N07D (6D)	**17.57**	**-2.53**	**0.97**	**0.97**	**-2.53**	**1.51**
C-PCM PBE0/IGLOIII	**16.23**	**-2.57**	**1.14**	**1.14**	**-2.57**	**1.19**
C-PCM B3PW91/IGLOIII	**14.84**	**-2.42**	**0.99**	**0.99**	**-2.42**	**1.01**
C-PCM B2PLYP/IGLOIII	**16.86**	**-0.31**	**-1.10**	**-1.10**	**-0.31**	**2.21**

[a] The IGLOIII basis set was used for Si in HFCC calculations.

Table S7 Experimental and calculated hyperfine coupling constants as well as the MAE parameter (in Gauss) for the *ortho*-isomers **2c⁻•**(Si←N) and **2c⁻•**(Si←O) of $[NO_2C_6H_4OSi(OCH_2CH_2)_3N]^{-\bullet}$ in acetonitrile solution. Geometry optimization was carried out at the UB3PW91/6-31+G(d,p) and UMP2/6-31+G(d,p) (in bold) levels of theory (C-PCM and COSMO (in italics) solvation models)

Molecule	HFCC method	a_N^{NO2}	$a_{H(2)}$	$a_{H(3)}$	$a_{H(4)}$	$a_{H(5)}$	**MAE**
	Experiment	14.00	3.40	0.90	3.40	0.60	0.00
2c⁻•(Si←N)	C-PCM TPSSh/IGLOIII	7.74	-3.79	1.25	-3.79	0.71	1.50
	C-PCM B3LYP/IGLOIII	7.35	-3.69	1.38	-3.69	0.89	1.60
	C-PCM B3LYP/N07D	11.48	-4.18	1.57	-4.18	1.02	1.03
	COSMO TPSSh/IGLOIII	*7.90*	*-3.81*	*1.21*	*-3.81*	*0.66*	*1.46*
	COSMO B3LYP/IGLOIII	*7.70*	*-3.79*	*1.38*	*-3.79*	*0.87*	*1.56*
	C-PCM TPSSh/IGLOIII	**27.97**	**-0.33**	**1.59**	**-0.33**	**-0.13**	**4.25**
	C-PCM B3LYP/IGLOIII	**27.49**	**-0.36**	**1.31**	**-0.36**	**-0.09**	**4.10**
	C-PCM B3LYP/N07D	**29.13**	**-0.36**	**1.29**	**-0.36**	**-0.08**	**4.43**
	C-PCM B3LYP/EPRIII[a]	**27.61**	**-0.38**	**1.38**	**-0.38**	**-0.09**	**4.13**
	C-PCM B3LYP/6-311++G(2d,2p)	**26.35**	**-0.36**	**1.25**	**-0.36**	**-0.08**	**3.86**
	C-PCM PBE0/IGLOIII	**27.82**	**-0.38**	**1.32**	**-0.38**	**-0.10**	**4.16**
	C-PCM B3PW91/IGLOIII	**26.56**	**-0.37**	**1.32**	**-0.37**	**-0.10**	**3.91**
	C-PCM B2PLYP/IGLOIII	**28.93**	**-0.34**	**1.23**	**-0.34**	**-0.17**	**4.36**
2c⁻•(Si←O)	C-PCM TPSSh/IGLOIII	10.30	-3.34	1.16	-3.34	0.75	0.85
	C-PCM B3LYP/IGLOIII	9.61	-3.25	1.23	-3.25	0.89	1.06
	C-PCM B3LYP/N07D	14.07	-3.70	1.40	-3.70	1.03	0.32
	COSMO TPSSh/IGLOIII	*10.57*	*-3.28*	*1.14*	*-3.28*	*0.75*	*0.81*
	COSMO B3LYP/IGLOIII	*10.16*	*-3.27*	*1.25*	*-3.27*	*0.92*	*0.96*
	C-PCM TPSSh/IGLOIII	**23.89**	**-1.38**	**1.01**	**-1.38**	**0.18**	**2.89**
	C-PCM B3LYP/IGLOIII	**23.94**	**-1.37**	**0.92**	**-1.37**	**0.24**	**2.88**
	C-PCM B3LYP/N07D	**25.47**	**-1.54**	**0.96**	**-1.54**	**0.30**	**3.11**
	C-PCM B3LYP/EPRIII[a]	**23.99**	**-1.50**	**0.98**	**-1.50**	**0.27**	**2.84**
	C-PCM B3LYP/6-311++G(2d,2p)	**22.90**	**-1.44**	**0.91**	**-1.44**	**0.27**	**2.63**
	C-PCM PBE0/IGLOIII	**24.26**	**-1.58**	**1.06**	**-1.58**	**0.38**	**2.86**
	C-PCM B3PW91/IGLOIII	**23.04**	**-1.50**	**0.99**	**-1.50**	**0.30**	**2.65**
	C-PCM B2PLYP/IGLOIII	**25.87**	**-0.36**	**-0.19**	**-0.36**	**-0.83**	**3.78**

[a] The IGLOIII basis set was used for Si in HFCC calculations.

Table S8 Experimental and calculated[a] g-values for the radical anions of nitrophenoxysilatrane in acetonitrile solution

	method	g_{iso}
2a$^{-\bullet}$	Exp.	2.0054
	UTPSSh/IGLOIII//UB3PW91	2.0049
	UPBE0/IGLOIII//UB3PW91	2.0051
	UPBE0/TZVP//UB3PW91	2.0051
	UB3LYP/IGLOIII//UB3PW91	2.0051
	UB3LYP/EPRIII//UB3PW91	2.0051
	UB3LYP/TZVP//UB3PW91	2.0052
	UB3LYP/N07D//UB3PW91	2.0048
	UTPSSh/IGLOIII//UMP2	2.0052
	UPBE0/IGLOIII//UMP2	2.0054
	UB3LYP/IGLOIII//UMP2	2.0054
	UB3LYP/EPRIII//UMP2	2.0053
	UB3LYP/TZVP//UMP2	2.0054
	UB3LYP/N07D//UMP2	2.0050
2b$^{-\bullet}$	Exp.	2.0063
	UTPSSh/IGLOIII//UB3PW91	2.0048
	UB3LYP/IGLOIII//UB3PW91	2.0050
	UB3LYP/TZVP//UB3PW91	2.0051
	UB3LYP/N07D//UB3PW91	2.0047
	UTPSSh/IGLOIII	2.0050
	UB3LYP/IGLOIII	2.0052
	UB3LYP/TZVP	2.0053
	UB3LYP/N07D	2.0049
2c$^{-\bullet}$	Exp.	2.0068
2c$^{-\bullet}$(Si←N)	UTPSSh/IGLOIII//UB3PW91	2.0049
	UB3LYP/IGLOIII//UB3PW91	2.0052
	UB3LYP/TZVP//UB3PW91	2.0052
	UB3LYP/N07D//UB3PW91	2.0049
	UTPSSh/IGLOIII//UMP2	2.0059
	UB3LYP/IGLOIII//UMP2	2.0062
	UB3LYP/TZVP//UMP2	2.0062
	UB3LYP/N07D//UMP2	2.0057
2c$^{-\bullet}$(Si←O)	UTPSSh/IGLOIII//UB3PW91	2.0048
	UB3LYP/IGLOIII//UB3PW91	2.0051
	UB3LYP/TZVP//UB3PW91	2.0051
	UB3LYP/N07D//UB3PW91	2.0048
	UTPSSh/IGLOIII//UMP2	2.0053
	UB3LYP/IGLOIII//UMP2	2.0056

UB3LYP/TZVP//UMP2	2.0056
UB3LYP/N07D//UMP2	2.0053

[a] Geometry optimization was carried out at the UB3PW91/6-31+G(d,p) and UMP2/6-31+G(d,p) levels of theory in acetonitrile solution (C-PCM model).