CALCULATION OF DIPOLE MOMENTS FOR SILATRANES

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Summary

Authors carried out some dipole moment calculations of silatranes $(R\overleftarrow{Si(OCH_2CH_2)_3N})$ by bond moments and CNDO/2 methods. We have established by bond moments method that the average value of the $m_{Si \leftarrow N}$ bond moment is at 2.04 D and is independent of the $d_{Si \leftarrow N}$ distance. We have found that the charge displacement is at 0.2 e which indicates that the nitrogen donates 10% of its lone electron pair to the vacant 3 d orbitals of silicon. In dipole moments obtained by the CNDO/2 method the pd atomic dipole average percentage is 7.3 and does not depend on the $d_{Si \leftarrow N}$ distance either.

Introduction

Unusually large dipole moments (> 5 Debye) of silatranes $(R\overleftarrow{Si(OCH_2CH_2)_3N})$ are explained in the literature by the interaction between the silicon and nitrogen atoms [1]. Great many papers have already been published on the calculation of dipole moments, in which the authors gave various data for $m_{Si \leftarrow N}$ bond moments (e.g. [1] Vol. 2. 3). In most cases the main reason of the difference in value is that the calculations were carried out by fictitious geometry: bond distances of other compounds known from the literature and "regular" tetrahedral bond angles. On the other hand, the deviations were caused by the different bond moments used in the calculation. In this work dipole moment calculations of silatranes by the method of bond moments and CNDO/2 are given. In our calculations we used the experimental geometric data determined by X-ray diffraction. According to our previous work [2] further dipole moments of some silatrane derivatives were measured, as well.

Calculations

The geometric data of compounds were taken from the X-ray diffraction structure determinations. In the cases of 1-α-phenylsilatrane and 1-vinylsilatrane the coordinates of hydrogen atoms were originally not determined, thus we have calculated them assuming a 100 pm distance for C—H bond, tetrahedral bond angle (silatrane-skeleton) and trigonal ones (phenyl and vinyl groups), respectively.

We have chosen for geometry of 1-hydrogensilatrane the structural data of 1-hydrogen-3,7,10-trimethylsilatrane. The values of bond moments used by us and other authors are shown in Table 1.-For Si—R group moments of R groups attached to the silicon the following values were employed according to our previous calculations, as well as, data taken from literature: Si-(C_6H_5): 0.445 D [3], Si-(CH═CH_2): 0.34 D [4], Si-(C_{alkyl}): 0.2 D [5], SiH: 1.0 D [6], Si-($C_6H_4CH_3$-p): 0.08 D this was calculated from value of Si-(C_6H_5) and toluene's dipole moment (0.37 D [7]). (1 Debye$=3.33563 \cdot 10^{-30}$ Cm.)

Table 1

Data of bond moments obtained by us and other authors (in Debye)

	[8, 9]	[10]	[6, 11]	[12]	Our data
H—C	0.37	0.28	0.4	0.3	0.4
C—N	0.45	0.53	0.45	0.5	0.48
C'—O	0.74		0.7	0.8	0.77
Si—O	1.54	2.25	1.19; 1.54; 1.7	1.54	1.51

The quantum-chemical calculations were carried out by the use of CNDO/2 program known [13], for the calculation of pd atomic dipole we applied the formula [14] after our correlation.

The results of our calculations on dipole moments are summarized in Table 2.

Discussion

For every silatrane derivative the value of dipole moments calculated by bond moment method has been found about 2 D smaller than the experimental values. This difference can be explained by the interaction between the silicon and nitrogen atoms. The $m_{Si \leftarrow N}$ bond moment usually arises—because of the marked symmetry of silatranes and the assumed pointlike R groups for calculations—from the simplex mathemathical difference between the calculated and the experimental dipole moments. In contrast to the above, in the cases of hydrogensilatrane and p-tolyltrimethylsilatrane the vectors of the $m_{Si \leftarrow N}$ bond moment and the original dipole moment do not coincide: they form an angle of 11.6 and 10.3 degrees, respectively. The $m_{Si \leftarrow N}$ bond moments do not show any correlation with the change of $d_{Si \leftarrow N}$ distances. The charge displacement between the silicon and

Table 2

Results of dipole moment calculations on silatranes
$R\overset{\downarrow}{Si}(OCH_2CH_2)_3N$

R	Bond moment calculations					CNDO/2 calculations		
	$d_{Si \leftarrow N}$ [pm]	μ_{exp} [D]	μ_{calc} [D]	$m_{Si \leftarrow N}$ [D]	δe	μ_{calc} [D]	μ_{pd} [%]	$\mu_{calc}-\mu_{exp}$ [D]
$\gamma-C_6H_5$	213.2 [15]	5.77 [2]	3.64	2.13	0.21	8.47	7.2	2.70
H	214.6* [16]	6.10	4.17	1.97	0.19	9.64	6.8	3.54
						9.73**	6.4	3.63
$CH_2=CH$	215.0 [17]	5.88 [9]	3.64	2.24	0.22	8.59	7.6	2.71
$\beta-C_6H_5$	215.6 [18]	5.77 [2]	3.62	2.15	0.21	8.54	6.9	2.77
CH_3	217.5 [19]	5.38 [2]	3.36	2.02	0.19	7.87	8.0	2.49
$\alpha-C_6H_5$	219.3 [20]	5.77 [2]	3.63	2.14	0.20	8.25	7.6	2.48
C_2H_5	221 [21]	5.34 [23]	3.50	1.84	0.17	8.00	7.0	2.66
$p-CH_3C_6H_4$***	223.6 [22]	5.14	3.31	1.86	0.17			

* $d_{Si \leftarrow N}$ value taken from X-ray structure $H\overset{\downarrow}{Si}[OCH(CH_3)CH_2]_3N$

** Calculated by X-ray structure of vinylsilatrane

*** $p-CH_3C_6H_4\overset{\downarrow}{Si}[OCH(CH_3)CH_2]_3N$

nitrogen was calculated from the bond moment according to the next equation:

$$\delta e = \frac{m_{Si \leftarrow N}}{4.803\ d_{Si \leftarrow N}} \cdot 10^2$$

We have got for the charge displacement a value about 0.2 e which means that the nitrogen donates 10% of its lone electron pair to the vacant 3 d orbitals of silicon in a σ type n—d interaction.

The average values of our calculations ($\bar{m}_{Si \leftarrow N}$: 2.04 D, $\bar{\delta} e$: 0.20) well correlate with the results given by PESTUNOVICH et al. [11] which are recently accepted and widely referred to by many other authors (m: 2.2 D, δe: 0.2 e). (They obtained them likewise from bond moments calculations).

Our quantum-chemical calculations made by CNDO/2 method gave results for dipole moments by some 2.6 D larger values than the experimental ones. The pd atomic dipole (μ_{pd}) percentage is about 7.4 in the calculated values for each silatrane molecule. This pd atomic dipole reveals the participation of 3 d orbitals of silicon atom in the bond structure of the molecule. The pd atomic dipole is in the direction of Si←N, which is due to the fact that the nitrogen donates its electron pair to the originally vacant d orbitals of silicon. In the case of hydrogensilatrane the dipole moment determined by CNDO/2 method was by 3.5 D higher than the experimental value. We performed a calculation using the coordinates of vinylsilatrane in which the Si←N distance is very similar to that in hydrogensilatrane. The question was whether the unexpected higher dipole moment is due to the distorted silatrane-skeleton. This calculation has resulted in nearly the same values. Accordingly we may explain our results by the known fact namely that the parameters of CNDO/2 method are not capable for the calculation of charge distribution and dipole moment on compounds involving Si—H bond. For the charge of the hydrogen atom linked to the silicon we have obtained large negative values: —0.1461 and —0.1325, respectively.

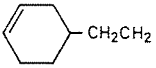
Experimental

The dipole moment measurements were carried out at 25 °C in benzene solutions. The relative permittivity of solutions was determined by a WTW Dipolmeter DM 01 instrument. The dipole moment was calculated by HEDESTRAND method, the experimental molar refraction values multiplied by 1.10 were considered as the sum of atom polarization and electron polarization. The measured data and calculated values required for determination of the dipole moments of the investigated compounds, as well as, the experimental dipole moments are shown in Table 3. The experimental dipole

Table 3

Experimental dipole moments of silatranes, as well as, the measured and calculated data necessary for the calculations (t = 25 °C)

$R\overset{\swarrow}{Si}(OCH_2CH_2)_3N$

R	x · 10³	d[gcm⁻³]	ε	n_D	
H	0	0.87322	2.2727	1.49824	$MR_D = 39.60\ cm^3$
	1.0990	0.87399	2.3300	1.49829	$\mu_{exp} = 6.10$ D
$p\text{—}CH_3C_6H_4$*	0	0.87303	2.2728	1.49800	$MR_D = 70.75\ cm^3$
	7.562	0.87723	2.5536	1.49869	$\mu_{exp} = 5.14$ D
	15.086	0.88248	2.8332	1.49922	
	22.453	0.88786	3.1122	1.49997	
C_3H_7	0	0.87357	2.2727	1.49813	$MR_D = 54.25\ cm^3$
	4.66	0.87636	2.4643	1.49807	$\mu_{exp} = 5.40$ D
	11.98	0.88060	2.7618	1.49803	
	13.39	0.88163	2.8313	1.49803	
$C_6H_5(CH_2)_3$	0	0.87370	2.2727	1.49798	$MR_D = 82.42\ cm^3$
	2.7282	0.87589	2.3946	1.49838	$\mu_{exp} = 5.51$ D
	8.3534	0.88061	2.6367	1.49916	
	10.3969	0.88203	2.7227	1.49970	
$p\text{—}ClC_6H_4CH_2CH_2$	0	0.87331	2.2734	1.49813	$MR_D = 78.98\ cm^3$
	4.6524	0.87881	2.5285	1.49900	$\mu_{exp} = 6.21$ D
	5.8972	0.88011	2.5961	1.49933	
	0	0.87370	2.2727	1.49797	$MR_D = 76.13\ cm^3$
	7.8011	0.87949	2.6089	1.49869	$\mu_{exp} = 5.52$ D
	10.565	0.88177	2.7269	1.49896	
C_6H_5*	0	0.87370	2.2727	1.49801	$MR_D = 80.97\ cm^3$
	8.1118	0.87955	2.6835	1.49896	$\mu_{exp} = 5.99$ D (5.96 D [24])
	10.1484	0.88124	2.7867	1.49911	

* Derivatives of 3, 7, 10-trimethylsilatranes: $R\overset{\swarrow}{Si}[OCH(CH_3)CH_2]_3N$

moments shown in Table 3 are higher than 5 D in every case, similarly to the values known so far from the literature. These large experimental values may be interpreted as a result of the interaction between silicon and nitrogen.

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