Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

EVIDENCE FOR Sn–N π-BONDING: DIPOLE MOMENTS OF AMINOSTANNANES

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(Received June 9th, 1969)

The question of the existence of π-bonding in silicon–nitrogen compounds is the subject of controversy. Objections[1,2] are still made to acceptance of this concept although evidence in favour of it has emerged from various detailed physical studies[3,4,5] (for a review see ref. 5). The increase in reactivity when passing from aminosilanes and aminogermanes to aminostannanes[6] indicates a weakening of the metal–nitrogen bond in this series and therefore a decrease in bond strength. Reactivity considerations, however, provide a rather uncertain guide to bond strengths, and better evidence can be derived from force constants calculated for the metal–nitrogen bond in the series $M(NMe_2)_4$ (where M = Si, Ge, Sn, Ti)[7]. These force constants clearly indicate bond orders for all compounds >1, provided no anomalous structures are present and assuming reasonable force constants available for the corresponding metal–nitrogen single bonds. Analogous conclusions were drawn for (dimethylamino)silanes[8] $X_{4-n}Si(NMe_2)_n$ (where X = H, Cl, CH_3; $n = 1$ to 4), extrapolating from bond orders >1 to π-bonding in the metal–nitrogen bond. Additional support for π-bonding in Sn–N-compounds of the type $R_{4-n}Sn(NR_2)_4$ is now given by measurements of the electric dipole moments in solution. The data obtained are summarized in Table 1.

Assuming constant partial moments for the $R_{4-n}Sn$ moiety the trends observed in the series may be rationalized in terms of three factors as follows:

TABLE 1

DIPOLE MOMENTS OF DIALKYLAMINOSTANNANES (IN DEBYE UNITS)

Compound		$R=CH_3$	$R=C_2H_5$	$R=n\text{-}C_4H_9$	$R=C_6H_5$
R_3SnNMe_2		1.09	1.56	1.90	1.02
R_3SnNEt_2		0.85	0.82	0.55	1.08
$R_2Sn(NMe_2)_2$		1.33	1.34	1.47	1.51
$R_2Sn(NEt_2)_2$		0.82	1.05	0.89	1.07
$RSn(NMe_2)_3$		1.36	1.42	1.40	1.24
$RSn(NEt_2)_3$		1.02	1.01	1.04	1.38
$Sn(NMe_2)_4$	1.15				
$C(NMe_2)_4$	0.00				

(*i*) Variation of the Sn–N-bond partial moment in the range of 0.8–1.1 (D).
(*ii*) Contribution of some preferred conformations of the alkyl substituents, *e.g.* in the butyl–tin compounds, to the total dipole moment.
(*iii*) A minor contribution of the Sn–C π-bonding in the (dialkylamino)phenylstannanes as compared with the chloro(phenyl)stannanes[9,10].

The parent compound of amino derivatives of Group IV, tetrakis(dimethylamino)methane, $C(NMe_2)_4$—a detailed investigation of its IR spectrum is now being carried out in these laboratories—has no electric dipole moment in benzene solution; thus the distinct dipole moment of $Sn(NMe_2)_4$ is not in accord with a full T_d symmetry, although the SnN_4 site symmetry is probably tetrahedral, an assumption which was also made by Bürger and Sawodny[7]. The rather low Sn–N bond partial moments for (dialkylamino)stannanes may arise from back-bonding due to different polarity in the Sn–N σ-bonds and the Sn–N π-bonds.

We are carrying out a detailed investigation of other dialkylamides of Group IV and V elements by means of dipole moment measurements, and the results will be presented later.

EXPERIMENTAL

Preparation of compounds

The preparation and properties of aminostannanes and their identification by physical methods has been described in the literature[6,11]; $C[NMe_2]_4$ was prepared according to Weingarten *et al.*[12] and purified by vacuum sublimation. All manipulations were carried out in an atmosphere of dry nitrogen or argon.

Dipole moments

Dipole moments were determined with a commercial WTW Dipolmeter Type DM 01 of Wissenschaftlich-Technische Werkstätten, Weilheim, West Germany, fitted with a 20 cc cell. Benzene was distilled from potassium and passed through molecular sieves before use.

TABLE 2

EXPERIMENTAL DATA

Compound (Mol.wt.)	ω	ε	a_n	a	P_0	μ
Me_3SnNMe_2	0.010213	0.007280	0.0881	0.6247	24.43	1.09
(207.883)						
Me_3SnNEt_2	0.007132	0.001927		0.2702	15.34	0.87
(235.937)	0.010156	0.002826		0.2487	14.12	0.83
$Me_2Sn(NMe_2)_2$	0.007322	0.007298	0.2049	0.7918	35.29	1.31
(236.926)	0.007302	0.007298	0.1643	0.8351	37.22	1.35
$Me_2Sn(NEt_2)_2$	0.006030	0.001841	0.04981	0.2556	14.09	0.83
(293.034)	0.008132	0.002569	0.0738	0.2422	13.35	0.81
$MeSn(NMe_2)_3$	0.006303	0.005026	0.0476	0.7497	37.51	1.35
(265.969)	0.008951	0.007123	0.0335	0.7623	38.14	1.37

TABLE 2 (*continued*)

Compound (Mol.wt.)	ω	ε	a_n	a	P_o	μ
$MeSn(NEt_2)_3$	0.006519	0.002141	—	0.3285	21.63	1.03
(350.129)	0.006677	0.002098	—	0.3142	20.69	1.01
Et_3SnNMe_2	0.004856	0.004810	0.0617	1.0522	49.46	1.56
(249.964)	0.005783	0.005843	0.0518	1.0622	49.94	1.56
Et_3SnNEt_2	0.012240	0.004064	0.0245	0.3075	16.08	0.89
(278.018)	0.008880	0.002535	0.0676	0.2179	11.39	0.75
$Et_2Sn(NMe_2)_2$	0.011958	0.007672	0.0752	0.7167	35.72	1.32
(264.980)	0.006055	0.004015	0.0990	0.7620	37.98	1.36
$Et_2Sn(NEt_2)_2$	0.018115	0.006337	—	0.3498	21.13	1.02
(321.086)	0.007252	0.003496	0.0827	0.3994	24.12	1.09
$EtSn(NMe_2)_3$	0.005334	0.003498	0.1124	0.7680	40.45	1.41
(279.996)	0.004590	0.003061	0.1307	0.7974	42.00	1.43
$EtSn(NEt_2)_3$	0.006333	0.002360	0.0474	0.3252	22.28	1.04
(364.154)	0.007524	0.002797	0.0798	0.2920	20.00	0.99
$n\text{-}Bu_3SnNMe_2$	0.005497	0.005923	0.1091	1.1866	74.49	1.91
(334.126)	0.004189	0.004333	0.1432	1.1777	73.93	1.90
$n\text{-}Bu_3SnNEt_2$	0.008356	0.001355	0.0718	0.0903	6.15	0.55
(362.184)	0.008161	0.001311	0.0735	0.0871	5.94	0.54
$n\text{-}Bu_2Sn(NMe_2)_2$	0.007780	0.006949	0.0385	0.7334	44.30	1.47
(321.088)	0.007077	0.006909	0.0424	0.7333	44.29	1.47
$n\text{-}Bu_2Sn(NEt_2)_2$	0.007651	0.002316	0.0784	0.2243	15.91	0.88
(377.200)	0.008646	0.002578	0.0694	0.2288	16.23	0.89
$n\text{-}BuSn(NMe_2)_3$	0.009535	0.006281	0.0314	0.6901	39.98	1.40
(308.050)	0.009788	0.006519	0.0306	0.6966	40.36	1.40
$n\text{-}BuSn(NEt_2)_3$	0.006696	0.002272	0.0448	0.2945	21.73	1.03
(392.216)	0.008819	0.003278	0.0680	0.3036	22.40	1.04
Ph_3SnNMe_2	0.007471	0.004015	0.2409	0.2964	21.97	1.04
(394.098)	0.006447	0.003538	0.2792	0.2695	19.98	0.99
Ph_3SnNEt_2	0.005480	0.002447	0.1642	0.2823	22.42	1.05
(422.148)	0.005531	0.002360	0.1085	0.1085	25.26	1.11
$Ph_2Sn(NMe_2)_2$	0.004346	0.002464	0.1380	0.7051	47.93	1.53
(361.068)	0.003258	0.001908	0.0920	0.6775	46.02	1.50
$Ph_2Sn(NEt_2)_2$	0.007478	0.003321	0.1204	0.3238	25.41	1.11
(417.176)	0.006308	0.002316	0.0951	0.2721	21.35	1.02
$PhSn(NMe_2)_3$	0.010819	0.005923	0.0277	0.5197	32.07	1.25
(328.040)	0.008709	0.004651	0.0344	0.4996	30.83	1.23
$PhSn(NEt_2)_3$	0.007318	0.004545	0.1229	0.4980	38.62	1.37
(412.204)	0.008334	0.005463	0.1440	0.5114	39.66	1.39
$Sn(NMe_2)_4$	0.006569	0.002663	0.0913	0.4967	26.93	1.15
(295.012)	0.014555	0.005645	0.0824	0.4885	27.11	1.15

Dipole moments were calculated following the procedure of Guggenheim[13]. Experimental data are listed in Table 2; ω=mole fraction; ε=dielectric constant of solution; a_n and a=slopes of concentration dependences of dielectric constants and of specific volumes; P_0=molar polarisation of the compound studied extrapolated to infinite solution; μ=Dipole moment in Debye units. Results are obtained at 25° ; standard deviations are assumed to be ±0.05 D. No corrections for atomic polarisations have been made.

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