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Semi-empirical MNDO study of the structure of some diorganotin (IV) glycylglycinates

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The geometrical structures of some diorganotin glycylglycinates have been obtained using the MNDO semi-empirical method. A good agreement with the experimental diffractometric data was found.

Keywords: Organotin, glycylglycinates, structures, MNDO calculations, tin atomic charge

INTRODUCTION

The aim of this study was to investigate the reliability of the semi-empirical MNDO[1] (Modified Neglect of Diatomic Overlap) calculations in order to obtain good predictions about the geometrical structure of organotin complexes, particularly concerning the environment of the tin atom. Five diorganotin glycylglycinates have been considered, $Me_2Snglygly$ (**1**), $Et_2Snglygly$ (**2**), $n\text{-}Bu_2Snglygly$ (**3**), $t\text{-}Bu_2Snglygly$ (**4**) and $Ph_2Snglygly$ (**5**), where the tin atom is pentacoordinate in a trigonal bipyramidal environment. We have fully optimized at the MNDO level the geometries of the five compounds above by utilizing the AMPAC program package.[2]

RESULTS AND DISCUSSION

Bond lengths and bond angles of the optimized structures, along with experimental data (when available), are reported in Tables 1–3; the adopted numbering scheme is shown in Fig. 1.

A comparison is possible between the geometrical parameters obtained here and the experimental values for the solid phase reported in the literature,[3–7] taking into account that the data obtained for the crystal cannot be strictly compared with those referring to the isolated system; in the case of compounds **1**, **2** and **3**, the experimental data concern systems with a side chain on the C5 atom, whose influence on the structural parameters is to be considered negligible.

Theoretical and experimental values are in good agreement; the average absolute deviation between theoretical and experimental bond length is about 0.04 Å (0.043 Å in the case of Compound **1**; 0.041, 0.038, 0.038 and 0.042 Å for compounds **2**, **3**, **4** and **5**, respectively). In the case of bond angles, the average deviations are 5.0° in the case of Compound **1** and 6.9°, 3.3°, 3.0° and 4.2° for the others. The maximum deviations are observed in the case of the distances between the tin atom and N1 and O3 atoms; this might be due to the intermolecular interactions inside the solid.

The dihedral angle values reported in Table 3 show that all the five structures are predicted to

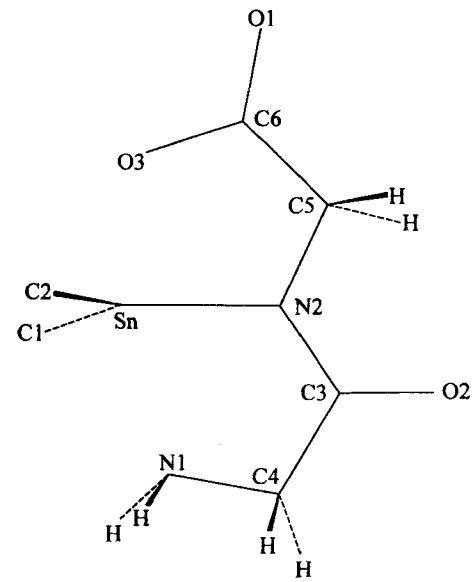

Figure 1 Atom numbering scheme of the systems considered.

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Table 1 Optimized bond lengths (columns a) and experimental values (Å)

	1		2		3		4		5	
	a	b	a	c	a	d	a	e	a	f
Sn–N2	2.069	2.071	2.070	2.077	2.071	2.097	2.090	2.085	2.067	2.082
N2–C5	1.459	1.458	1.459	1.452	1.459	1.456	1.461	1.45	1.459	1.457
C5–C6	1.547	1.543	1.546	1.518	1.546	1.530	1.542	1.485	1.547	1.549
C6–O1	1.232	1.221	1.232	1.236	1.232	1.233	1.233	1.24	1.232	1.200
C6–O3	1.329	1.269	1.329	1.278	1.329	1.287	1.327	1.303	1.329	1.293
Sn–O3	2.022	2.161	2.023	2.191	2.023	2.140	2.027	2.196	2.023	2.157
N2–C3	1.385	1.322	1.385	1.335	1.385	1.305	1.386	1.34	1.383	1.330
C3–O2	1.233	1.241	1.233	1.224	1.233	1.230	1.234	1.23	1.234	1.240
C3–C4	1.541	1.518	1.541	1.505	1.541	1.528	1.538	1.51	1.541	1.506
C4–N1	1.479	1.447	1.480	1.446	1.479	1.474	1.477	1.49	1.481	1.499
Sn–N1	2.412	2.249	2.404	2.288	2.407	2.272	2.468	2.293	2.372	2.273
Sn–C1	2.078	2.112	2.099	2.104	2.105	2.119	2.210	2.18	2.052	2.116
Sn–C2	2.076	2.092	2.102	2.123	2.107	2.146	2.204	2.18	2.050	2.100
C5–H(av.)	1.119	—	1.119	—	1.119	—	1.119	—	1.119	—
C4–H (av.)	1.118	—	1.118	—	1.118	—	1.118	—	1.118	—
N1–H (av.)	1.012	—	1.012	—	1.012	—	1.012	—	1.013	—

a, This work; b, from Ref. 3; c, from Ref. 4; d, from Ref. 5; e, from Ref. 6; f, from Ref. 7. 1 Å = 10 nm.

be a distorted trigonal bipyramid, with the tin atom and the glycylglycinate group approximately on a plane and the C1 and C2 atoms above and below this plane, inclined about 30° with respect to the normal to the glycylglycinate plane; in the case of the diphenyl compound, the glycylglycinate group and the tin atom show minimum deviation from planarity.

Table 2 Optimized bond angles (columns a) and experimental values (degrees)

	1		2		3		4		5	
	a	b	a	c	a	d	a	e	a	f
C1–Sn–C2	122.1	123.8	117.6	131.4	116.5	125.3	124.6	121.7	123.2	117.5
C1–Sn–N1	90.5	96.1	93.6	101.1	93.3	96.6	92.9	99.2	91.5	98.8
C1–Sn–N2	118.9	115.3	119.9	115.7	121.0	118.7	118.7	124.3	117.6	124.3
C1–Sn–O3	100.1	98.0	100.8	94.7	101.4	97.8	98.1	92.5	99.6	94.4
C2–Sn–N1	92.2	96.4	91.7	92.4	91.9	94.0	97.0	100.2	89.5	99.8
C2–Sn–N2	117.3	120.9	121.2	112.8	121.1	115.8	116.2	113.7	117.4	117.9
C2–Sn–O3	101.4	94.7	99.8	94.1	99.8	97.6	98.5	97.2	101.7	94.7
N1–Sn–N2	73.7	76.8	73.9	76.6	73.9	74.3	71.8	75.2	74.8	77.6
N1–Sn–O3	154.5	153.0	154.5	152.2	154.5	151.3	151.1	149.6	156.0	153.2
N2–Sn–O3	80.9	76.5	80.8	75.9	80.8	77.0	79.5	75.0	81.2	75.7
Sn–N2–C3	124.1	121.5	124.2	121.3	124.3	119.6	125.2	123.3	124.0	120.3
N2–C3–O2	123.4	126.5	123.4	124.8	123.4	127.8	123.5	124.4	123.2	122.4
O2–C3–C4	120.7	118.6	120.5	120.4	120.4	117.2	120.5	121.0	120.1	119.7
C3–C4–N1	110.0	113.9	110.2	116.4	110.3	111.5	109.3	113.2	111.4	113.2
Sn–N2–C5	114.6	118.9	114.7	118.5	114.7	116.7	115.2	119.3	114.6	120.1
N2–C5–C6	109.9	108.5	109.9	110.0	109.9	109.1	109.8	110.3	110.0	108.2
C5–C6–O1	124.2	118.4	124.1	119.0	124.2	118.9	124.6	120.2	124.0	118.3
O1–C6–O3	118.8	123.5	118.9	123.0	118.8	123.3	119.0	121.9	118.8	124.7
Sn–O3–C6	117.3	117.7	117.4	117.1	117.3	117.4	118.8	117.1	117.0	118.9
Sn–N1–C4	110.3	112.9	111.1	109.7	111.3	107.3	110.2	110.7	113.0	109.9

a, This work; b, from Ref. 3; c, from Ref. 4; d, from Ref. 5; e, from Ref. 6; f, from Ref. 7.

Table 3 Optimized dihedral angles (degrees)

	1	2	3	4	5
Sn–N2–C5–C6	6.3	4.5	4.3	5.8	1.1
N2–C5–C6–O1	176.8	177.8	178.1	177.8	179.5
N2–C5–C6–O3	−3.3	−2.3	−1.8	−2.0	−0.4
C6–C5–N2–C3	186.0	184.3	183.8	186.8	180.7
C5–N2–C3–O2	−3.7	−3.9	−3.8	−3.4	1.6
C5–N2–C3–C4	175.2	174.9	175.0	175.7	181.7
N2–C3–C4–N1	22.1	19.4	19.1	23.2	−1.2
C6–O3–Sn–C1	120.1	121.8	123.0	120.0	117.2
C6–O3–Sn–C2	245.9	242.6	242.8	247.0	244.2

MNDO ATOMIC CHARGES

Linear correlations between the atomic charge of tin, evaluated using the empirical method of Jolly and Perry,[8,9] and Mössbauer chemical shifts have been proposed,[10,11] for organotin isostructural compounds.

The atomic charge values as obtained by the method quoted above, as observed earlier,[12] cannot be compared with the more realistic Mulliken charges obtainable from an SCF (Self Consistent Field) semiempirical calculation, but it seems interesting to verify if there exists a relationship between these different charge values.

MNDO (Mulliken) charge values on the tin atom are 0.65*e* for each of the alkyl compounds and 0.80*e* for the diphenyl compound, which are to be compared with the values 0.19*e* and 0.25*e*, respectively, obtained from the empirical method by Jolly and Perry. Although the absolute values of the atomic charge are quite different, a constant proportionality ratio between the values obtained from the two methods is to be noted. A more satisfactory answer would require a larger number of charge values but it seems possible to infer, with caution, that the empirical (Jolly) values for the charges can be utilized,when looking for correlations, as well as the Mulliken MNDO charge values.

REFERENCES

1. Dewar, M and Thiel, W *J. Am. Chem. Soc.*, 1977, 99: 4899
2. AMPAC, IBM version, Program No. 523, Q.C.P.E., Bloomington, IN, USA
3. Preut, H, Mundus, B, Huber, F and Barbieri, R *Acta Cryst.*, 1986, C42: 536
4. Vornfeld, M, Huber, F, Preut, H, Ruisi, G and Barbieri, R *Appl. Organomet. Chem.*, 1992, 6: 75
5. Mundus-Glowacki, B, Huber, F and Barbieri, R *Appl. Organomet. Chem.*, 1992, 6: 83
6. Preut, H, Mundus, B, Huber, F and Barbieri, R *Acta Cryst.*, 1989, C45: 728
7. Huber, F, Haupt, H-J, Preut, H, Barbieri, R and LoGiudice, M T *Z. Anorg. Allg. Chem.*, 1977, 432: 51
8. Jolly, W H and Perry, B *J. Am. Chem. Soc.*, 1973, 95: 5442
9. Jolly, W H and Perry, B *Inorg. Chem.*, 1974, 13: 2686
10. Barbieri, R and Silvestri, A *J. Chem. Soc., Dalton Trans.*, 1984: 1019
11. Barbieri, R and Huber, F *Gazz. Chim. It.*, 1993, 123: 223
12. Andersson, M, Blomquist, J, Folkesson, B, Larsson, R and Sundberg, P *J. Electron Spectrosc. Rel. Phenom.*, 1986, 40: 385