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THE ELECTRONIC STRUCTURE OF DIPHENYLTIN(IV) DICHLORIDE. CALCULATION OF THE MÖSSBAUER ISOMER SHIFT AND THE QUADRUPOLE SPLITTING OF TIN AND THE NUCLEAR QUADRUPOLE RESONANCE FREQUENCY OF CHLORINE

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To M.J.S. Dewar who started me off on $(PNCl_2)_n$ and semi-empirical theories at Q.M.C. Thirty years later I have progressed to Ph_2SnCl_2 and density functional theory.

ABSTRACT

Nonrelativistic and quasirelativistic SCF-MS calculations on the diphenyltin(IV) dichloride monomer and possible "dimer", give theoretical insight into the intermolecular chlorine interaction. This molecule is not a polymer like other diorganotin(IV) dichlorides. A weak interaction occurs in the valence orbital electronic structure; the extent of the interaction is given by the molecular one-electron properties. The isomer shift and the quadrupole splitting of the Mössbauer active ^{119}Sn, and the nuclear quadrupole resonance (n.q.r.) frequency of ^{35}Cl are properties which are helpful in analysing the extent of intermolecular interaction in the "dimer". The calculated isomer shift and quadrupole splitting agree with experiment. The n.q.r. frequency of ^{35}Cl does not agree well with experiment, which is not a single crystal measurement, but nevertheless the weakness of the intermolecular chlorine interaction was confirmed. Further confirmation comes from the total density plot of $(Ph_2SnCl_2)_2$.

INTRODUCTION

Several diorganotin(IV) dihalides occur as linear chain polymers with intermolecular halide bridging[1,2]. Intermolecular chlorine bridging in diphenyltin dichloride is in doubt[3-5], even though Ph_2SnCl_2 was considered polymeric in Mössbauer spectroscopic interpretations[3]. The crystal structure of Ph_2SnCl_2 of Greene and Bryan[4] showed two discrete molecules, with slightly different bond distances and bond angles, but of identical geometry and no intermolecular bridging. However, Bokii et al.[5] suggested the existence of an intermolecular chlorine interaction because of the difference in the two Sn–Cl bond distances. Alcock and Sawyer[2] considered Ph_2SnCl_2 to be an example of weak secondary bonding and of chelating bridge systems. Despite the considerable interests to understand and interpret the nature of the intermolecular chlorine interaction in the Ph_2SnCl_2 molecule, there has been no theoretical molecular electronic structure calculation to analyse the chemical bonding and the extent of the interactions in this molecule.

SCF-multiple scattering (MS)[6] calculations have been applied to both description of Ph_2SnCl_2, to investigate the molecular electronic structure and give theoretical insight to the chemical bondings. The monomer is considered to be Greene and Bryan's isolated molecule[4], Fig. 1(a), the "dimer" is represented by Bokii et al.'s description[5] of the molecular interaction through chlorine bridging, Fig. 1(b). The total energies may be calculated for different geometries but these calculations are time consuming for systems like the "dimer" of Ph_2SnCl_2, which has 50 atoms and 332 electrons. The total energies from SCF-MS calculations are not accurate because of the muffin-tin approximation, however, the quality of the SCF-MS wave functions is good[6c,7]. The present paper studies the molecular electronic structure of Ph_2SnCl_2, and uses the fairly accurate wave function properties to describe the intermolecular chlorine interactions. The isomer shift and quadrupole splitting of Mössbauer active, ^{119}Sn and the nuclear quadrupole resonance frequencies of ^{35}Cl are wave function properties which are helpful in assessing the extent of intermolecular interaction. The SCF-MS programme[8] calculates the electric field gradients of the nuclei in the molecules and has proved accurate for isomer shift and quadrupole splitting for the iron containing ionic cluster[9].

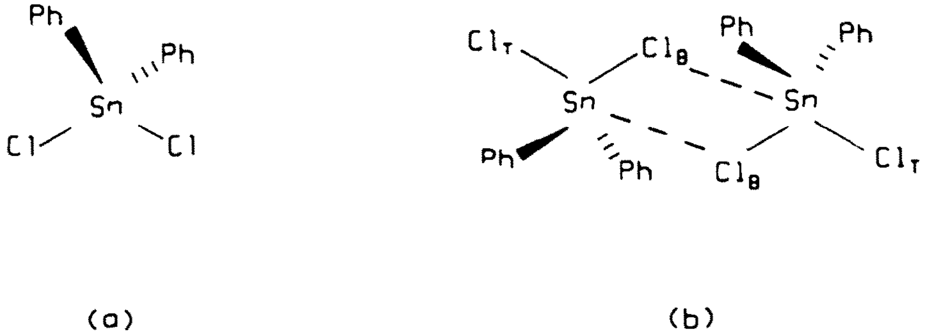

Figure 1. Schematical representations of C_{2v} monomer (a) and C_{2h} "dimer" (b). The bond lengths and bond angles were taken from Ref. 4 and mean values are used for the monomer. In (b) the distances between Sn-Cl_B, Sn...Cl_B and Sn-Cl_T are 2.336, 3.770 and 2.357 Å, respectively. The Cl_B...Cl_B distance was taken from ref. 2 as 4.280 Å.

COMPUTATIONAL DETAILS

Sphere sizes used the Norman criteria[10] (Table 1). The partial waves, ℓ, were taken as 4 for the outer sphere, 2 for Sn and Cl, 1 for C, and zero for H. The preferred Vosko-Wilk-Nusair(VWN)[11] exchange-correlation potential was used and not Slater's Xα exchange potential[6]. The calculations were performed with and without quasirelativistic wave functions[12] for Sn.

To find the isomer shift of ^{119}Sn, a reference molecule which contains the tin nucleus is needed. Therefore an SCF-MS calculation has been applied to the Td $SnCl_4$ molecule, using experimental bond distances[13]. The partial waves and the sphere sizes are chosen in exactly the same manner as for Ph_2SnCl_2.

The energy of the 4d core orbital of atomic Sn is very close to the energy of the valence 5s orbital, consequently the 4d orbital was treated as a valence orbital in the calculations. The $4d_{yz}$, $4d_{z^2}$, $4d_{xz}$, $4d_{x^2-y^2}$ and $4d_{xy}$ orbitals of Sn were resolved as $1b_2$, $1a_1$, $1b_1$, $2a_1$ and $1a_2$ in the C_{2v} monomer. The $1b_2$, $1a_1$, $1b_1$, $2a_1$ and $1a_2$ levels spanned[14] into $1b_u+1a_g$, $2a_g+2b_u$, $1b_g+1a_u$, $3a_g+3b_u$ and $2a_u+2b_g$ in the C_{2h} "dimer".

Table 1. Sphere sizes used in SCF-MS calculation

MONOMER

R_{out}	R_{Sn}	R_{Cl}	R_{C_1}	$R_{C_2}^a$	$R_{C_3}^b$	R_{C_4}	$R_{H_2}^c$	$R_{H_3}^d$	R_{H_4}
11.1369	2.6472	2.6247	1.7174	1.6874	1.6885	1.6886	1.2679	1.2698	1.2699

"DIMER"

R_{out}	R_{Sn}	R_{Cl_B}	R_{Cl_T}	R_{C_1}	R_{C_2}	R_{C_3}	$R_{C_4}^e$	R_{H_2}	R_{H_3}	$R_{H_4}^f$
13.3209	2.6439	2.5325	2.6166	1.7173	1.6862	1.6874	1.6885	1.2557	1.2679	1.2698

[a] R_{C_6} is same as R_{C_2}; [b] R_{C_5} is same as R_{C_3}; [c] R_{H_6} is same as R_{H_2}; [d] R_{H_5} is same as R_{H_3}.
[e] R_{C_6} and R_{C_5} are same as R_{C_4}; [f] R_{H_6} and R_{H_5} are same as R_{H_4}.

RESULTS AND DISCUSSION

Electronic Structure and Bonding

The one-electron energies of the core orbitals of Sn in the monomer and "dimer" from the quasirelativistic calculation are more stable than the nonrelativistic energies; the percent differences between the energies are 3.7, 5.9, 6.2 and 7.3 % for the 1s, 2s, 3s and 4s orbitals of Sn, and 2.0, 2.3 and 2.4 % for the 2p, 3p and 4p orbitals and 1.3 % for the 3d of Sn. The quasirelativistic energies of the 4d orbitals of Sn are about 4.3 % more positive than the nonrelativistic calculation. Despite the significant changes in the energies of the core orbitals of Sn, the quasirelativistic one-electron energies and the population of the valence orbitals did not differ much from the nonrelativistic calculations. In addition to the five Sn(4d) orbitals in the monomer, there are 38 which become ten and 76 valence orbitals respectively, in the "dimer". The one-electron energies and the population of all (38) monomer orbitals and population of some of the "dimer" orbitals are given in Table 2 and Table 3, respectively. The results in Tables 2 and 3 are from the quasirelativistic wave function calculation. The $7a_1$ orbital energy of the monomer is stabilized about 0.3 eV since this orbital has the highest Sn contribution, while the other valence orbitals of the monomer are changed about 0.02 eV by the quasirelativistic calculation. A similar change (0.3 eV) of the "dimer" valence orbitals occur in the $11a_g$ and $11b_u$ orbitals which correlate with the $7a_1$ of the monomer.

Table 2. The percentage compositions and one-electron energies of Ph_2SnCl_2

		Sn			2 × Cl			12 × C		10 × H
M.O	−e(eV)	s	p	d	s	p	d	s	p	s
$15a_1^*$	4.064	15.10	13.34	1.26	4.22	22.90	14.94	4.96	22.58	0.74
$8a_2$	5.691	-	-	0.00	-	0.04	0.00	0.00	99.96	0.00
$10b_2$	5.708	-	0.03	0.01	0.00	0.00	0.00	0.00	99.96	0.00
$11b_1$	6.060	-	0.03	0.78	-	0.14	0.06	0.06	98.90	0.00
$14a_1$	6.189	0.14	1.39	1.53	0.16	1.36	0.32	0.02	95.02	0.00
$10b_1$	8.825	-	0.92	0.81	-	0.04	0.00	0.22	97.52	0.46
$13a_1$	8.901	0.18	0.01	1.34	0.04	1.80	0.02	0.06	96.44	0.12

$9b_1$	9.287	-	19.71	1.91	-	15.14	0.36	2.52	53.20	7.14
$9b_2$	10.244	-	0.00	0.58	0.00	98.24	0.04	0.00	0.72	0.40
$12a_1$	10.253	3.47	6.23	2.24	0.00	57.68	0.02	0.12	24.26	6.00
$7a_2$	10.396	-	-	0.86	-	98.24	0.02	0.08	0.50	0.36
$8b_1$	10.688	-	4.38	0.31	-	72.10	0.12	0.01	16.64	6.44
$11a_1$	10.802	2.69	4.75	0.40	0.00	47.06	0.10	0.12	32.06	12.78
$6a_2$	10.854	-	-	0.02	-	0.30	0.00	0.16	67.92	31.64
$8b_2$	10.861	-	0.00	0.01	0.00	0.58	0.00	0.16	67.74	31.52
$7b_1$	11.972	-	8.09	0.40	-	3.96	0.12	5.98	55.46	26.00
$10a_1$	11.986	0.62	10.62	1.40	0.20	22.50	0.40	4.38	40.92	18.98
$7b_2$	12.152	-	17.31	3.42	1.02	74.28	1.46	0.12	1.90	0.52
$5a_2$	12.913	-	-	0.00	-	0.08	0.00	0.72	65.12	34.08
$6b_2$	12.929	-	0.36	0.01	0.04	0.26	0.02	0.76	62.20	33.76
$9a_1$	13.248	0.02	0.25	0.09	0.04	0.70	0.02	15.52	40.32	43.02
$6b_1$	13.256	-	0.31	0.04	-	0.00	0.00	16.98	38.52	44.14
$4a_2$	14.522	-	-	0.11	-	0.00	0.00	1.16	96.39	2.36
$5b_2$	14.543	-	0.36	0.01	0.04	0.26	0.02	1.28	95.58	2.44
$8a_1$	14.730	6.34	1.29	0.26	0.98	8.02	0.62	6.70	44.38	31.42
$5b_1$	15.061	-	1.61	0.20	-	0.14	0.02	4.18	57.60	36.22
$7a_1$	16.231	36.79	0.15	0.00	5.38	15.54	1.76	3.10	26.98	10.28
$4b_1$	17.449	-	0.76	0.16	-	0.00	0.00	40.80	43.46	14.82
$6a_1$	17.625	8.40	0.13	0.17	1.28	1.56	0.24	38.66	37.28	12.28
$3a_2$	17.871	-	-	0.13	-	0.00	0.00	40.72	44.16	15.08
$4b_2$	17.889	-	0.36	0.01	0.04	0.26	0.02	1.28	95.58	2.44
$3b_1$	21.060	-	0.63	0.22	-	0.00	0.00	76.76	15.56	6.82
$2a_2$	21.062	-	-	0.06	-	0.00	0.00	74.56	15.26	10.08
$3b_2$	21.066	-	0.03	0.03	0.18	0.00	0.00	74.40	15.30	10.08
$5a_1$	21.092	1.12	0.27	0.30	1.28	0.04	0.02	75.36	15.02	6.60
$2b_2$	21.520	-	2.87	2.58	94.04	0.20	0.08	0.16	0.10	0.04
$4a_1$	22.998	7.19	1.87	0.97	86.14	1.12	0.38	2.50	0.70	0.12
$2b_1$	23.943	-	0.30	0.20	-	0.00	0.00	84.18	12.80	2.50
$3a_1$	23.981	1.23	0.01	0.09	1.40	0.08	0.02	82.56	12.18	2.44

* Lowest unoccupied molecular orbital

Table 3. The percentage compositions of some M.O.'s of $(Ph_2SnCl_2)_2$

	2 × Sn			2 × Cl_B			2 × Cl_T			24 × C		20 × H
	s	p	d	s	p	d	s	p	d	s	p	s
$25b_u^*$	14.68	14.86	1.40	2.14	12.38	11.76	1.36	8.94	4.28	4.24	23.12	0.88
$19b_g$	-	0.00	0.02	-	0.18	0.06	-	0.04	0.00	0.00	99.68	0.00
$24b_u$	0.00	0.02	0.04	0.06	0.02	0.04	0.00	0.00	0.00	0.04	99.72	0.04
$19a_u$	-	0.00	0.02	-	0.14	0.10	-	0.06	0.00	0.04	99.64	0.04
$24a_g$	0.00	0.18	0.00	0.08	0.02	0.06	0.00	0.02	0.00	0.00	99.56	0.04
$18b_g$	-	0.02	0.72	-	0.14	0.00	-	0.14	0.00	0.04	98.88	0.00
$18a_u$	-	0.04	0.86	-	0.00	0.12	-	0.16	0.04	0.04	98.72	0.00
$23a_g$	0.06	0.92	1.66	0.02	0.80	0.08	0.04	0.54	0.06	0.04	95.76	0.04
$23b_u$	0.18	1.92	1.50	0.22	0.52	0.40	0.06	1.02	0.12	0.04	94.08	0.00
$17b_g$	-	0.02	0.18	-	0.90	0.02	-	4.00	0.00	0.00	94.80	0.08
$17a_u$	-	0.30	0.60	-	0.54	0.06	-	3.60	0.00	0.08	94.56	0.24

$16b_g$	-	9.92	2.46	-	2.58	0.10	-	44.84	0.08	1.84	33.48	4.68
$22b_u$	0.12	0.26	1.30	0.10	0.50	0.08	0.00	2.46	0.00	0.04	95.04	0.12
$22a_g$	0.18	0.12	1.46	0.00	1.76	0.02	0.00	2.66	0.00	0.12	93.24	0.40
$16a_u$	-	8.66	2.34	-	0.18	0.06	-	56.06	0.06	1.44	27.80	3.44
$21b_u$	0.24	0.20	1.34	0.04	3.90	0.04	0.00	92.48	0.00	0.08	1.56	0.08
$21a_g$	0.02	0.24	1.20	0.06	2.52	0.08	0.00	93.74	0.00	0.04	1.96	0.12
$15b_g$	-	10.00	0.42	-	13.64	0.08	-	38.54	0.10	0.72	29.20	7.32
$15a_u$	-	15.44	0.36	-	2.76	0.16	-	28.84	0.16	0.64	42.44	9.24
$20a_g$	3.26	10.98	2.34	0.04	11.62	0.04	0.10	29.02	0.22	0.16	32.76	9.48
$20b_u$	3.28	12.14	1.08	0.00	11.06	0.24	0.08	19.10	0.16	0.04	40.04	12.78
$14b_g$	-	1.66	0.02	-	18.76	0.06	-	0.62	0.02	0.36	53.88	24.60
$14a_u$	-	0.64	0.26	-	37.48	0.06	-	0.52	0.00	0.36	41.48	19.20
$19b_u$	0.20	0.14	0.20	0.20	35.18	0.04	0.00	0.60	0.02	0.20	42.84	20.40
$19a_g$	0.14	1.00	0.08	0.02	0.44	0.04	0.02	1.84	0.04	0.20	66.16	30.00
$18b_u$	0.72	1.12	0.26	0.02	43.54	0.08	0.02	1.88	0.02	0.20	35.84	16.28
$13a_u$	-	0.18	0.30	-	32.30	0.00	-	0.04	0.00	0.16	46.52	20.36
$18a_g$	0.82	1.40	1.34	0.02	26.60	0.04	0.08	8.46	0.22	1.80	39.96	19.32
$13b_g$	-	2.04	0.20	-	44.40	0.04	-	0.50	0.02	1.00	35.48	16.36
$17b_u$	0.16	10.62	1.64	0.06	1.22	0.12	0.64	28.88	0.76	3.16	35.48	17.28
$12b_g$	-	9.16	0.52	-	0.56	0.08	-	0.92	0.06	5.96	56.80	26.00
$12a_u$	-	8.56	0.32	-	6.78	0.06	-	0.82	0.06	7.64	49.72	26.00
$17a_g$	0.02	11.58	0.72	0.02	49.28	0.20	0.68	17.16	0.72	1.72	11.64	6.32
$16b_u$	2.58	14.78	2.64	0.26	45.78	0.36	0.36	9.26	0.46	1.24	16.24	6.08
$16a_g$	2.62	14.42	2.82	0.24	48.04	0.30	0.20	4.92	0.30	1.88	17.32	6.92
$11a_g$	34.30	0.00	0.06	3.38	7.38	0.42	3.26	4.80	0.70	1.72	31.32	12.60
$11b_u$	34.22	0.28	0.08	0.90	10.30	1.00	3.52	4.32	0.64	3.68	29.64	11.44
$6b_u$	5.10	2.22	1.54	2.54	0.20	0.04	81.86	0.68	0.26	4.24	1.00	0.36
$6a_g$	4.78	2.52	1.40	1.70	0.16	0.04	82.94	0.70	0.26	4.00	0.96	0.52
$5b_u$	3.74	1.90	1.56	89.40	0.36	0.14	1.56	0.18	0.08	0.48	0.16	0.40
$5a_g$	1.94	1.64	1.38	65.64	0.30	0.08	0.54	0.06	0.02	22.92	4.84	0.60
$3b_g$	-	0.32	0.20	-	0.00	0.00	-	0.00	0.00	84.12	12.76	2.56
$3a_u$	-	0.34	0.20	-	0.04	0.00	-	0.00	0.00	84.04	12.44	2.88
$4b_u$	0.76	0.08	0.20	0.12	0.04	0.02	0.12	0.02	0.00	83.64	12.36	2.60
$4a_g$	2.90	0.24	0.16	19.96	0.16	0.02	0.46	0.06	0.02	64.56	8.52	2.92

[*] Lowest unoccupied molecular orbital

When two monomers are brought together, the monomer orbitals correlate with the "dimer" orbitals. The four highest occupied valence orbitals from $8a_2$ to $14a_1$ (table 2) have shown about 98% C(3p) of phenyl contribution and correlate to the 8 highest occupied valence orbitals (from $19b_g$ to $23b_u$) of the "dimer", which have the same percentage C(2p) of phenyl contribution (Table 3) and are non-bonding. The next 13 monomer orbitals from $10b_1$ to $7b_2$ are the bonding between Sn(5p) and Cl(3p) and also C(2p) and H(1s) of the phenyl group. These orbitals correlate to the 26 orbitals of the "dimer" (from $17b_g$ to $16a_g$ in Table 3) which have the same character. The next group of monomer orbitals starting from $5a_2$ to $5a_1$ (except $7a_1$) are related to the bonding in the phenyl group and correlate to the orbitals of the "dimer" which have the same character (these 32 orbitals are not given in Table 3). The $7a_1$ orbital of the monomer, which has the highest Sn(5s) contribution (about 37 %), bonds between Sn(5s) and Cl(3s+3p) and correlates to $11a_g$ and $11b_u$ of the "dimer", which both have about 34 % of Sn(5s) (Table 3). The interest lies in the low-lying orbitals: since the electronegativity of chlorine is higher than tin, the low-lying bonding orbitals are localized on the chlorines in the monomer and in the "dimer". The $2b_2$ and $4a_1$ monomer orbitals have 94 and 85 % of Cl(3s) contribution (Table 2) and correlate to $6b_u$, $6a_g$, $5b_u$ and $5a_g$ of the "dimer". The $6b_u$ and $6a_g$ orbitals (Table 3) are localized on the terminal chlorines having almost equal percentage of Cl_T(3s) (82 and 83 %), while $5b_u$ and $5a_g$ are localized on the bridge chlorines and have different percentage of Cl_B(3s) (89 and 66 %). Symmetric and strong bridging in the "dimer" would require the $5a_g$ orbital of the "dimer" to have the same percentage of Cl_B(3s) as the $5b_u$ orbital. The presence of another "dimer" orbital, $4a_g$ energetically close to $5a_g$ with the right symmetry removes about 20 % of Cl_B(3s) character from the $5a_g$ orbital. This might be considered a very weak intermolecular interaction between the monomers, causing perturbation and mixing of the levels with the same symmetry. The electrons will distribute between these two orbitals. The terminal chlorines Cl_T in the dimer system are not involved in the intermolecular interaction, and consequently there is no mixing of the levels in the Sn-Cl_T bond; thus the $6a_g$ and $6b_u$ orbitals of the dimer have equal Cl_T(3s) character. The presence of the unequal population distribution on the Sn-Cl_B bonding orbitals may support Alcock and Sawyer's idea[2] of weak secondary bonding in Ph_2SnCl_2.

When two atoms are brought together to form a molecule, the atomic orbitals mix and interact to give molecular orbitals. Some of the molecular orbitals are stabilized, while others destabilized, with respect to the atomic orbitals. Similarly when two molecules (like AlX_3) are brought together to make a strong dimer (Al_2X_6), some of the dimer orbitals are stabilized and some of them destabilized with respect to their monomer counterparts[18]. The situation is different for clusters; addition of the atoms into the cluster only increases the number of orbitals; it does not split them with respect to their constituent orbitals unless there is interaction with a different atom or molecule[19]. The case of Ph_2SnCl_2 "dimer" resembles the cluster situation; none of the orbitals are split with respect to their monomer counterparts: they are however shifted down. The one-electron energies of the valence orbitals near the highest occupied orbital of the monomer and the "dimer", are given in Fig. 2 to demonstrate the slight stabilization of the "dimer" orbitals without splitting; the stabilization varies between 0.3 and 1.8 eV. Therefore the presence of a second monomer does not change the nature of the bonding in the either monomers. The contour maps of some of the selected monomer and "dimer" bonding orbitals from the quasirelativistic calculation are in Fig. 3. Fig. 3(a) and 3(b) give the monomer $4a_1$ and $7a_1$ bonding orbitals on the tin-chlorine plane, which show the localization of the charge on chlorine and tin respectively. Fig. 3(c) and 3(d) give the $5a_g$ and $5b_u$ bonding orbitals of the "dimer" which are the counterparts of the $4a_1$ orbital of the monomer, after correlation. The localization of the charge on the chlorine at the bridge positions are is clearly shown. Fig. 3(e) and 3(f) are the $11a_g$ and $11b_u$ orbitals of the "dimer", the counterparts of the monomer $7a_1$ orbital. In these figures it can be seen that the charge around the tin nuclei is slightly disturbed by the presence of other bridge chlorine.

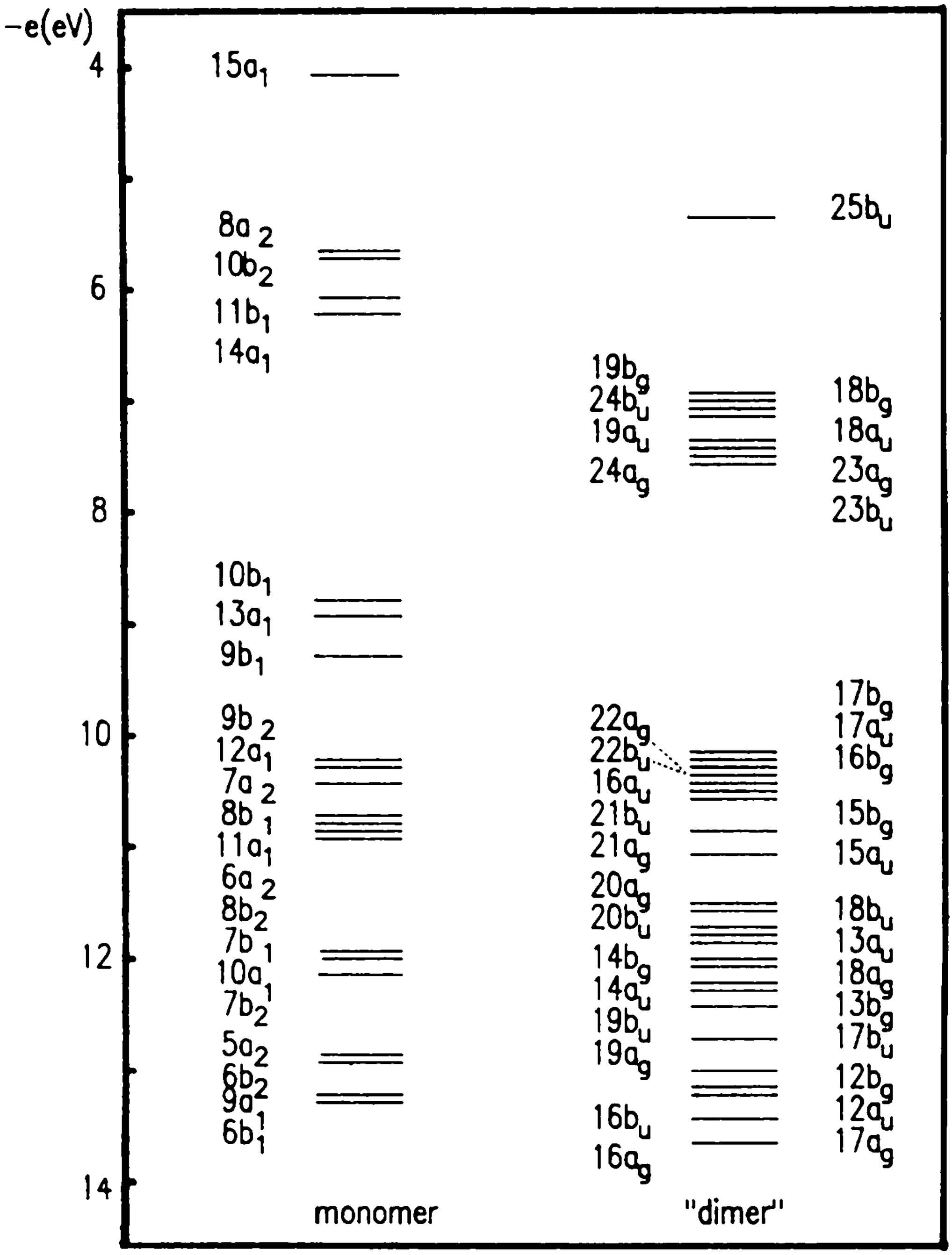

Figure 2. The one-electron energies of the monomer and "dimer" orbitals near to the highest occupied orbitals. The lowest unoccupied orbitals are $15a_1$ and $25b_u$ for the monomer and "dimer" respectively.

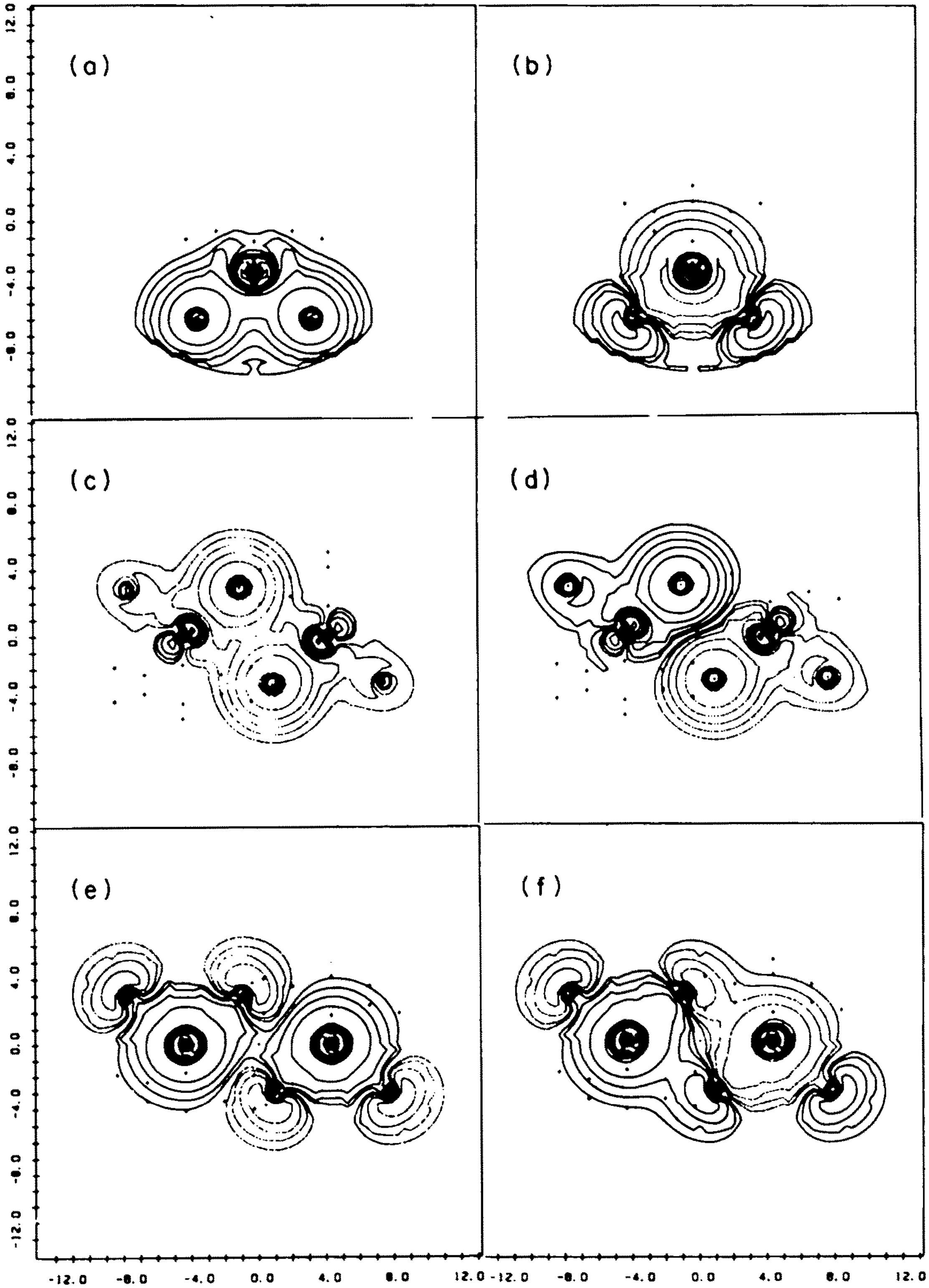

Figure 3. Wave function contour diagrams of selected molecular orbitals of C_{2v} Ph_2SnCl_2 (monomer) and C_{2h} $(Ph_2SnCl_2)_2$ ("dimer") on the tin-chlorine planes. Monomer orbitals are (a) $4a_1$, (b) $7a_1$. "Dimer orbitals are (c) $5a_g$, (d) $5b_u$, (e) $11a_g$ and (f) $11b_u$. The contour values in $(electrons/a_0)^{1/2}$ starting from the outermost are ±0.005, ±0.01, ±0.02, ±0.04, ±0.08 and ±0.16. Positive wave function contours are represented by solid lines

whereas negative contours are indicated by dashed lines. The out of plane positions of carbons and hydrogens in the phenyl groups are shown by dots.

The lowest-unoccupied molecular orbitals (LUMO) of the monomer and the "dimer" are $15a_1$ and $25b_u$. The composition of these orbitals is in Table 2 and 3. The antibonding LUMO's are localized on the tin with inclusion of some chlorine character, while highest occupied molecular orbitals (HOMO's), $8a_2$ of the monomer and $19b_g$ of the "dimer", have phenyl character. The energy difference between HOMO and LUMO is 1.627 and 1.616 eV in the monomer and the "dimer". Note that the Cl(3d) percentages in the virtual orbitals, suggest a metal to ligand charge transfer, whereas the bonding orbitals have no Cl(3d) contribution. However, this is not the case for central (tin) atom on which some of the bonding orbitals such as $7b_2$ and $12a_1$ of the monomer and $16a_g$ and $16b_u$ of the "dimer" have some Sn(5d) contribution. The occurence of some tin(d) contribution in low-lying σ-orbital such as $2b_2$ of the monomer can be explained as the effect of the energetically close 4d orbital of tin.

Although the total energies of SCF-MS calculations are not accurate due to the muffin-tin approximation, it is interesting to note that twice the total energy of the monomer (-30,207.460 Ry) almost equals the total energy of the "dimer" (-30,207.297 Ry).

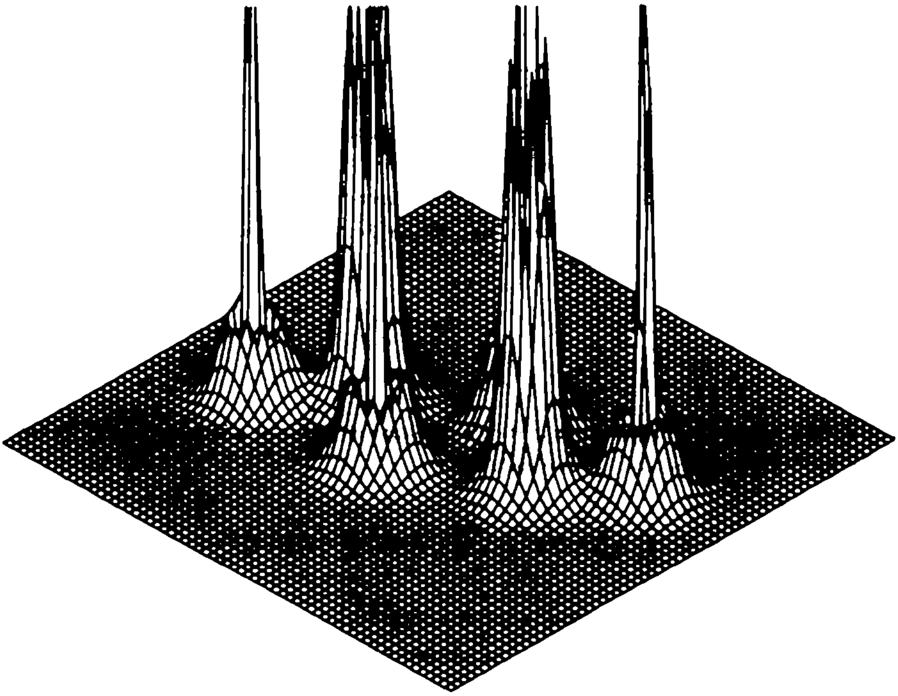

Figure 4. The total density plot of $(Ph_2SnCl_2)_2$ on the tin-chlorine plane. The out of plane positions of carbons and hydrogens in the phenyl groups are not shown.

The total density plot of the "dimer" from the quasirelativistic calculation is given in Fig. 4 in which phenyl groups are out of the plane and the electron charge density is most dense at Sn and Cl, becoming less dense away from the nuclei, especially between Cl_B and the second Sn. The total density plot gives no evidence of dimerization. The total electron distribution from both nonrelativistic and quasirelativistic calculation is given for monomer and "dimer" in Table 4. There is no real difference between the total charge distribution from both nonrelativistic and quasirelativistic wave function calculation:

quasirelativistic tin has only 0.08 and 0.07 electron more in the monomer and "dimer" than the nonrelativistic tin.

Table 4. Total charge distribution

Monomer	Sn	Cl	Ph
Non-Rel.	49.24	17.24	41.06
Quasirel.	49.32	17.23	41.02

"Dimer"	Sn	Cl_B	Cl_T	Ph
Non-Rel.	49.32	17.07	17.14	41.21
Quasirel.	49.39	17.05	17.14	41.16

The experimental ionization potentials, I.P.'s for Ph_2SnCl_2 molecule have not been published. Nevertheless Slater's transition state calculation[8] has been applied to the Ph_2SnCl_2 system to give ionization potentials. Such a calculation gives good agreement with experiment in many molecules[7,17]. The approximate ionization potentials[17] of the monomer and "dimer" are calculated removing half an electron from the highest occupied molecular orbitals $8a_2$ and $19b_g$ of the monomer and "dimer" respectively. The I.P.'s of monomer are in the range of 7.4 and 25.8 eV for $8a_2$ and $3a_1$, while for the "dimer", the I.P.'s are about 1.0 or 1.5 eV higher than the monomer.

Isomer Shift

The electric monopole interaction between a nucleus and the electron shell is measured in Mössbauer spectroscopy by the isomer shift[18] as

$$\delta = (c/E_\gamma)\,\frac{4}{5}\,\pi\, Z\, e^2\, R^2\, \frac{\delta R}{R}\,[\Sigma|\psi(0)|^2_a - \Sigma|\psi(0)|^2_s]\ . \qquad (1)$$

R is the nuclear radius which is taken as $1.2 \times (A)^{1/3} \times 10^{-13}$ cm approximately. $\Delta R/R$ is the change of the nuclear radius between the ground and exited states upon the exitation to a level E_γ (23.8 KeV for Sn). $\Sigma|\psi(0)|^2_a$ and $\Sigma|\psi(0)|^2_s$ are the s-electron densities at the nucleus for a reference absorber and a given source. This linear relationship eq. (1) between isomer shift and electronic structure of Sn-containing molecules can be rewritten taking $\delta R/R$[18] as 1.16×10^{-4} for ^{119}Sn.

$$\delta(\text{mm/sec}) = 0.0643\,[\Sigma|\psi(0)|^2_a - \Sigma|\psi(0)|^2_s]\ . \qquad (2)$$

The s-electron densities at the tin-nuclei of Ph_2SnCl_2 monomer and "dimer", and reference absorber $SnCl_4$ are calculated using the quasirelativistic wave functions for Sn from the one-electron properties.

Table 5 gives the calculated s-electron densities and the comparison between calculated and experimental Mössbauer isomer shift of Ph_2SnCl_2 with respect to the $SnCl_4$ reference absorber. The experimental isomer shift of Ph_2SnCl_2 with respect to $SnCl_4$ is calculated from the difference between experimental isomer shift of $SnCl_4$ with respect to α-Sn (-1.30 mm/sec)[19] and Ph_2SnCl_2 with respect to α-Sn[20]. The agreement between calculated and experimental isomer shift of Ph_2SnCl_2 is very good. The absolute value of isomer shift of the "dimer" is slightly (0.02 mm/sec) higher than that of the monomer. This shows that only a very weak intermolecular chlorine interaction can occur in the "dimer", which must be caused by the presence of the chlorine at the bridge position giving the central atom Sn more charge around the nucleus. The extent of the effect of the bridge chlorine on the Sn nucleus is very small (Table 5). The "dimer" s-electron density is 0.33 $(a.u.)^{-3}$ higher than in the monomer.

Table 5. The comparison of the calculated and experimental Mössbauer isomer shift of Sn (in mm/sec)

	Ph_2SnCl_2		$SnCl_4$
	Monomer	"Dimer"	Reference
$\Sigma\lvert\psi(0)\rvert$	125,556.72	125,557.06	125,549.03
δcal	-0.50	-0.52	0.00
δexp.[*]	-0.60[a], -0.51[b], -0.62[c]		0.00

[*] Experimental isomer shift of Ph_2SnCl_2 w.r.t. $SnCl_4$ is calculated from the difference between the experimental isomer shift of $SnCl_4$ w.r.t. α-Sn (-1.30 mm/sec at 80 °K from ref. 19) and Ph_2SnCl_2 w.r.t. α-Sn.

[a] -0.70 mm/sec at 77 °K (ref. 20a)

[b] -0.79 mm/sec at 78 °K (ref. 20b)

[c] -0.68 mm/sec at 80 °K (ref. 20c)

Quadrupole Splitting

The quadrupole splitting is caused by the interaction of the quadrupole moment of the nucleus and the electric field gradient. For ^{119}Sn (I = 3/2), the magnitude of the splitting[21] is

$$\Delta E_q = \frac{1}{2} e^2 q_z Q \left(1+\eta^2/3\right)^{1/2} . \qquad (3)$$

Where eQ is the nuclear quadrupole moment, eq_z $(=V_{zz})$ is the maximum principal component of the electric field gradient tensor and η is the asymmetry parameter defined as $|V_{xx} - V_{yy}|/|V_{zz}|$. The principal components of electric field gradients are calculated using the Case, Cook and Karplus charge partitioning method[22] from the one-electron properties.

Table 6 gives both nonrelativistic and quasirelativistic calculations of the maximum principal component of the electric field gradients, and the asymmetry parameters of Sn-nucleus in monomer and "dimer". The quadrupole splitting is calculated from eq. (3) using given eQ for ^{119}Sn (-0.065 barns)[23] and compared with the experimental quadrupole splitting[20] (Table 6). The agreement between calculated and experimental quadrupole splitting is very good, however better agreement is obtained with the quasirelativistic calculations. In the "dimer" the chlorines at the bridging position cause deviation from cylindrical symmetry of Sn-nuclei, resulting in a larger asymmetry parameter and consequently larger quadrupole splitting for the "dimer" comparing to the monomer (Table 6).

however the extent of the interaction is small; the difference between the quadrupole splitting of monomer and "dimer" is about 4.4 %. It can be seen from Table 6 that the effect of changing from the nonrelativistic to quasirelativistic wave function on the quadrupole splitting is bigger (about 12.2 %) than the difference between monomer and "dimer" quadrupole splitting.

Table 6. The comparison of the calculated and experimental Mössbauer quadrupole splitting of Sn (in mm/sec)

Ph_2SnCl_2	SCF-MS Calculation		
	Non-Rel.	Quasirel.	Exp.*
	eq_z = −4.4688	eq_z = −5.0678	
Monomer	η = 0.6223	η = 0.5971	
	ΔE_q = 1.88	ΔE_q = 2.12	ΔE_q = 2.80[a]
			2.66[b]
	eq_z = −4.4481	eq_z = −5.0253	2.98[c]
"Dimer"	η = 0.8546	η = 0.8474	
	ΔE_q = 1.96	ΔE_q = 2.22	

[*] The experimental ΔE_q for Sn in Ph_2SnCl_2 is taken from

[a] ref. 20a at 77 °K

[b] ref. 20b at 78 °K

[c] ref. 20c at 80 °K

Nuclear Quadrupole Resonance Frequencies

The nuclear quadrupole resonance (n.q.r.) frequencies of ^{35}Cl in the Ph_2SnCl_2 molecule has been measured by Green and Graybeal[24]. The calculated n.q.r. frequencies and asymmetry parameters of ^{35}Cl are given along with the experimental frequencies in Table 7. The n.q.r. frequencies are calculated from the maximum principal component of the electric field gradients and asymmetry parameter, taking the nuclear quadrupole moment eQ as −0.082 barns for ^{35}Cl from ref. 23. The calculated resonance frequencies are about twice of the experimental frequencies. It is well known[25] that the frequencies of bridge halides are always lower than the terminal halides and asymmetry parameters are almost zero for the terminal halides in the strong dimers. In Table 7, calculated frequencies for bridge chlorine are lower than the terminal chlorine and also asymmetry parameters are almost zero for terminal chlorine but are not very big for the bridge chlorine, about 0.13 which must be by the very weak intermolecular interaction in the "dimer". If the interaction were not weak, the asymmetry parameter for the bridge chlorine would be closer to one. Experimentally four n.q.r. frequencies are given[24], they are all close to each other but two slightly lower ones (17.440, 17.902 MHz) should correspond to the bridge chloride while the others (18.020, 18.772 MHz) correspond to the terminal chlorines.

The calculated frequencies are higher than the experiment because the experimental results reflect solid state effects while the theoretical wave function is for a single isolated molecule (monomer and "dimer").

Table 7. The comparison of the calculated and experimental Nuclear Quadrupole Resonance frequencies of ^{35}Cl (in MHz)*

Ph_2SnCl_2	SCF-MS Calculation Non-Rel.	SCF-MS Calculation Quasirel.	Exp.**
	eq_z = 3.3918	eq_z = 3.4154	
Monomer	η = 0.0223	η = 0.0226	
	ν = 32.669	ν = 32.896	ν = 17.440
"Dimer"	eq_z = 3.1185	eq_z = 3.1328	17.902
Cl_B	η = 0.1374	η = 0.1364	18.020
	ν = 30.034	ν = 30.272	18.772
	eq_z = 3.7626	eq_z = 3.8150	
Cl_T	η = 0.0420	η = 0.0424	
	ν = 35.973	ν = 36.256	

* The n.q.r. frequencies of ^{35}Cl are calculated using $\nu = \frac{e^2qQ}{2}(1 + \eta^2/3)^{½}$.

** ref. 24.

CONCLUSIONS

The detailed SCF-MS analysis of the molecular electronic structures of diphenyltin(IV) dichloride together with the Mössbauer isomer shift and quadrupole splitting of ^{119}Sn and the n.q.r. frequencies of ^{35}Cl, gives interesting insight to the electronic structures and chemical bonding in the Ph_2SnCl_2 monomer and "dimer". It predicts no strong bridging in the "dimer"; the total density map gives no evidence of strong dimerization and the population analysis predicts at the most a small intermolecular interaction supporting the idea of the secondary bonding. The calculated Mössbauer isomer shift and quadrupole splitting of Ph_2SnCl_2 are in good agreement with experiment, the "dimer" values being slightly larger than for the monomer again evidence that these interactions are very small. The comparison between the nonrelativistic and quasirelativistic wave function calculations of the quadrupole splitting shows the importance of using quasirelativistic wave function on Sn nucleus, since the molecular properties, like quadrupole splitting and isomer shift, are sensitive to the charge distribution on the nucleus, which changes more since the core orbitals of the Sn nucleus are affected more than the valence orbitals of the molecule by the relativistic effect.

The SCF-MS calculations predict the n.q.r. resonance frequencies of ^{35}Cl about twice as big as experimental: single crystal measurements are needed to compare with the calculation. Nevertheless n.q.r. frequency calculations support the idea of very weak intermolecular interaction because the asymmetry parameter of the chlorine at the bridge position is very close to zero rather than one.

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