INVESTIGATION OF THE STRUCTURE OF ORGANOSILICON COMPOUNDS BY ω-TECHNIQUE, II

By

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In the previous paper of the authors [1] the energy matrices for the π systems of trimethyl-vinyl-silane (I), trimethyl-phenyl-silane (II) p-bis-trimethyl-silyl-benzene (III) and trimethyl-benzyl-silane (IV) have been given along with the block diagram of a computer program. In Tables 1 to 4 most important data obtained by computation using different values of ω are summarized. In the tables E means the energy of molecular orbitals, (which can be given in the form $E = \alpha + k\,\beta$; the tables only contain the value of k), Δm is the energy corresponding to the transfer of an electron from the highest filled molecular orbital to the lowest vacant molecular orbital in β units, Σe denotes the sum of the energy of electrons situated on the filled orbitals, and q the partial charges on the atoms (for the numbering of atoms see Fig. 1 in [1]). To the value $\omega = 0$ belong the data of the 0th approximation.

For any value of ω the calculations result in the molecular orbitals of minimum energy belonging to the given ω, owing to the application of the principle of energy minimum. In the 0th approximation, however, the interactions of electrons are not taken into consideration. The application of

Table 1

Data calculated for trimethyl-vinyl-silane

			ω		
	0.0	0.3	0.5	0.7	1.0
E_1	1.052459	1.054420	1.055741	1.057057	1.058809
E_2	−0.967461	−0.965548	−0.964348	−0.963182	−0.961684
E_3	−1.900238	−1.904116	−1.906633	−1.909115	−1.91278
Δm	−2.019920 β	−2.019968 β	−2.020089 β	−2.02039 β	−2.020493 β
Σe	2α+2.104918 β	2α+2.108840 β	2α+2.111482 β	2α+1.14114 β	2α+2.118618 β
q_1	−0.014010	−0.013892	−0.013827	−0.013768	−0.013695
q_2	−0.012082	−0.007829	−0.005950	−0.004499	−0.002835
q_3	+0.026092	+0.021721	+0.019777	+0.018268	+0.016530

Table 2

Data calculated for trimethyl-phenyl-silane

	ω					
	0 0	0.5	0 7	0.9	1.0	1.2
E_1	2.082172	2.078456	2.077597	2.076958	2.076704	2.076345
E_2	1.138127	1.126145	1.122720	1.111982	1.118527	1.116298
E_3	1.000000	1.012894	1.016955	1.020555	1.022208	1.025341
E_4	-0.843840	-0.850970	-0.853437	-0.855763	-0.854491	-0.858658
E_5	-1.000000	-0.987219	-0.983204	-0.979641	-0.977004	-0.975064
E_6	-1.789707	-1.789635	-1.789782	-1.790005	-1.790143	-1.790482
E_7	-2.028825	-2.031742	-2.032921	-2.034093	-2.034676	-2.055808
Δm	$-1.843840\,\beta$	$-1.863864\,\beta$	$-1.870392\,\beta$	$-1.876218\,\beta$	$-1.878899\,\beta$	$-1.883999\,\beta$
Σe	$6\alpha+8.440600\,\beta$	$6\alpha+8.434990\,\beta$	$6\alpha+8.434544\,\beta$	$6\alpha+8.434660\,\beta$	$6\alpha+8.434878\,\beta$	$6\alpha+8.435968\,\beta$
q_1	0.012315	-0.012102	-0.012037	-0.011979	-0.011952	-0.011900
q_2	-0.153500	-0.121780	-0.112664	-0.104886	-0.101373	-0.090005
q_3	$+0.065116$	$+0.046936$	$+0.042239$	-0.038399	$+0.036730$	$+0.033757$
q_4	-0.003726	$+0.004412$	$+0.004976$	$+0.007059$	$+0.007475$	$+0.010831$
q_5	$+0.043034$	$+0.031186$	$+0.028273$	$+0.025927$	$+0.024920$	$+0.023111$
q_6	-0.003726	$+0.004412$	$+0.005976$	$+0.007059$	$+0.007475$	$+0.010831$
q_7	$+0.065116$	$+0.046936$	$+0.042239$	$+0.039399$	$+0.036830$	$+0.033757$

Table 3

Data calculated for bis-trimethyl-silyl-benzene

	ω					
	0.0	0.1	0.5	0.8	1.0	1.4*
E_1	2.146437	2.145782	2.144205	2.143756	2.143682	2.1441
E_2	1.285115	1.279047	1.259612	1.248752	1.242783	1.2331
E_3	1.000000	1.005942	1.025722	1.037439	1.044163	1.0560
E_4	−0.700689	−0.70494	−0.717084	−0.724403	−0.728518	−0.07354
E_5	−1.000000	−0.994057	−0.974344	−0.962562	−0.955837	−0.9440
E_6	−1.683950	−1.683353	−1.681729	−1.681065	−1.680825	−1.6807
E_7	−1.887822	−1.889297	−1.894908	−1.898865	−1.901398	−1.9060
E_8	−2.043235	−2.043714	−2.045692	−2.047194	−2.048193	−2.0498
Δm	−1.700689 β	−1.710436 β	−1.742806 β	−1.761842 β	−1.772681 β	−1.7914 β
Σe	$6\alpha + 8.863104\,\beta$	$6\alpha + 8.861542\,\beta$	$6\alpha + 8.859078\,\beta$	$6\alpha + 8.859894\,\beta$	$6\alpha + 8.861256\,\beta$	$6\alpha + 8.8664\,\beta$
q_1	− 0.0011358	−0.011340	−0.011270	−0.011220	−0.011189	−0.0110
q_2	−0.112340	−0.107498	−0.091562	−0.082301	−0.077067	−0.0680
q_3	+0.061849	+0.059419	+0.051416	+0.046761	+0.044128	+0.0398
q_4	+0.061849	+0.059419	+0.051416	+0.046761	+0.044128	+0.0398
q_5	−0.112340	−0.107498	−0.091562	−0.082301	−0.077067	−0.0680
q_6	−0.011358	−0.011340	−0.011270	−0.011220	−0.011189	−0.0110
q_7	+0.061849	+0.059419	+0.051416	+0.046761	+0.044128	+0.0398
q_8	+0.061849	+0.059419	+0.051416	+0.046761	+0.044128	+0.0398

* Calculations were only made to four places of decimals

ω-technique consists in the empirical consideration for electronic interactions, in this case the energy of electrons has to increase owing to mutual repulsion. The sum of the energy of electrons occurring on the filled orbitals of compound II, III and IV were plotted as function of ω (Fig. 1). The electron energy

Table 4

Data calculated for trimethyl-benzyl-silane

	ω				
	0.0	0.3	0.5	1.0	1.4
E^1	2.996888	2.995827	2.995378	2.994895	2.994778
E_2	1.951346	1.951440	1.951505	1.951658	1.951790
E_3	1.000000	0.999544	0.999297	0.998810	0.998486
E_4	0.961837	0.962409	0.962723	0.962723	0.963758
E_5	—0.980336	—0.979708	—0.979378	—0.978733	—0.978306
E_6	—1.000000	—1.000461	—1.000702	—1.001195	—1.001515
E_7	—1.787994	—1.789373	—1.790316	—1.792730	—1.794670
E_8	—2.003400	2.003688	—2.003885	—2.004389	—2.004806
E_9	—3.453541	—3.451191	—3.449821	—3.446852	—3.444713
$\varDelta m$	—1.942173 β	—1.942117 β	—1.942101 β	—1.942069 β	—1.942064 β
$\varSigma e$	$8\alpha+13.820142\,\beta$	$8\alpha+13.818440\,\beta$	$8\alpha+13.817806\,\beta$	$8\alpha+13.816398\,\beta$	$8\alpha+13.817624\,\beta$
q_1	—0.007027	—0.006995	—0.006976	—0.006933	—0.006900
q_2	—0.078526	—0.071320	—0.067181	—0.058567	—0.052217
q_3	+0.090663	+0.083099	+0.078754	+0.069708	+0.063041
q_4	+0.004388	+0.003345	+0.002847	+0.001967	+0.001506
q_5	—0.003637	—0.002881	—0.002542	—0.001915	—0.001645
q_6	+0.000187	—0.000151	—0.000269	—0.000468	—0.000460
q_7	—0.002595	—0.002063	—0.001823	—0.001409	—0.001220
q_8	+0.000187	—0.000151	—0.000269	—0.000468	—0.000460
q_9	—0.003637	—0.002881	—0.002535	—0.001915	—0.001645

increases with ω, reaches a maximum at a singular value (ω_{max}), and thereafter decreases. It seems probable that the optimum value of ω lies near ω_{max}. The electron energy is in fact twice the sum of the energies of the filled orbitals, so the shape of the curve is determined by the change of the energies of the orbitals with ω. In Fig. 2 the energies of the four molecular orbitals of compound II are plotted against ω. As shown by the curves, the energy of some orbitals increases, that of others decreases with increasing ω. The same is shown by Fig. 3 in connection with the five molecular orbitals of compound IV. Thus the sum of the energies of filled molecular orbitals can be described by a curve passing through a maximum with the exception of compound I containing a single filled molecular orbital, thus the energy increases monoto-
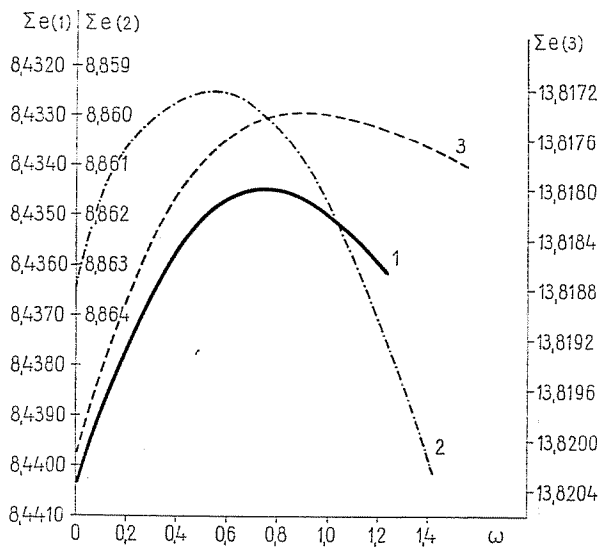
Fig. 1. Variation of total electron energy as function of ω. 1. trimethyl-phenyl-silane; 2. p-bis-trimethyl-silyl-benzene; 3. trimethyl-benzyl-silane
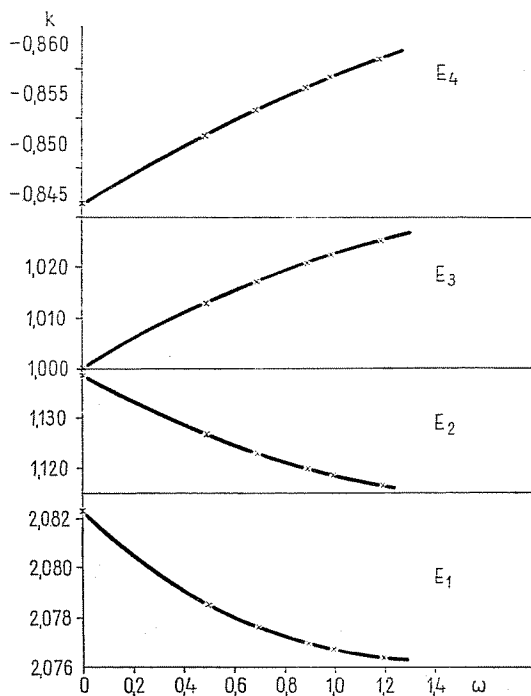

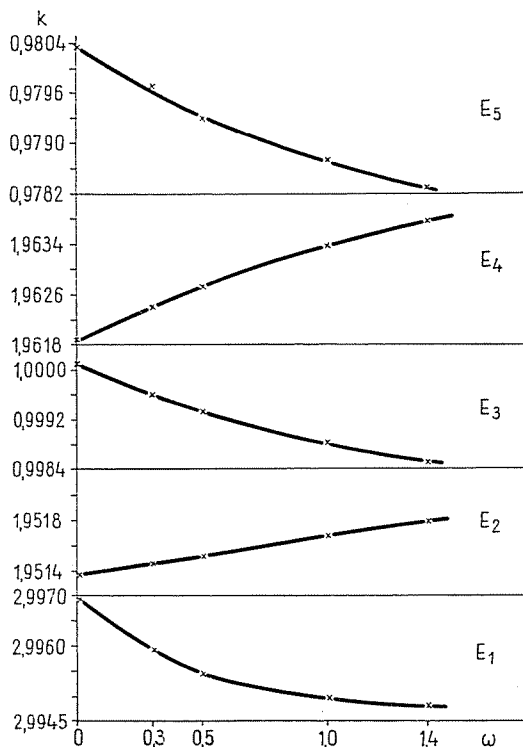**Fig. 2.** Variation of the energies of the molecular orbitals of trimethyl-phenyl-silane as function of ω

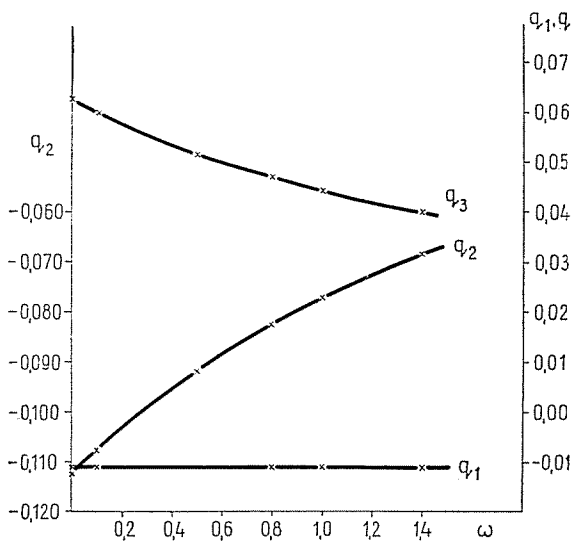**Fig. 3.** Variation of the energies of the molecular orbitals of trimethyl-benzyl-silane as function of ω

Fig. 4. Variation of the partial charges of p-bis-trimethyl-silyl-benzene as function of ω

nously with ω. With the three other compounds ω_{max} ranges from 0.6 to 0.9, the average being 0.8.

Curves similar to the former are obtained when partial charges are plotted against ω (Figs. 4, 5). The partial charges belonging to the silicon atom (q_1) decrease slowly with increasing ω.

The change of the linear coefficients (c_1) is presented for three different values of ω, on the example of trimethyl phenyl silane (Table 5). The bond orders (p_{ij}) calculated on the basis of the linear coefficients are summarized in Table 6 for a single ω. The change of these data is similar in the case of the other compounds studied.

The data in the table show that the bond orders, eigenvalues change slightly with ω. The electron transfer energies Δm and the linear coefficients

Table 5

Linear coefficients of trimethyl-phenyl-silane

$\omega = 0.5$	c_1	c_2	c_3	c_4	c_5	c_6	c_7
E_1	0.041594	0.480764	0.417536	0.377275	0.365774	0.377275	0.417536
E_2	0.065734	0.574244	0.222586	0.328798	−0.592129	−0.323798	−0.222586
E_2	0.000000	0.000000	0.502644	0.497342	0.000000	−0.497342	−0.502644
E_4	0.189691	0.545535	−0.349306	−0.240096	0.554155	−0.240096	−0.349306
E_5	0.000000	0.000000	0.497339	−0.502646	0.000000	0.502646	−0.497339
E_6	0.769613	0.082152	−0.214813	0.309772	−0.341673	0.309772	−0.214813
E_7	0.60430	−0.372685	0.329053	−0.307986	0.299401	−0.307986	0.329053
$\omega = 0.7$							
E_1	0.041179	0.476047	0.417508	0.379044	0.368387	0.379044	0.41508
E_2	0.065753	0.574205	0.226733	−0.326339	−0.591738	−0.326339	0.226733
E_3	0.000000	0.000000	0.503150	0.496830	0.000000	−0.496830	−0.503150
E_4	0.190464	0.547706	−0.346456	−0.241802	0.553843	−0.241802	−0.346456
E_5	0.000000	0.000000	0.496830	−0.503150	0.000000	0.503150	−0.496830
E_6	0.779760	0.073160	−0.208432	0.304746	−0.337630	0.304746	−0.208432
E_7	0.591557	−0.368984	0.332662	−0.314700	0.307427	−0.314700	0.332662
$\omega = 0.9$							
E_1	0.040797	0.4719400	0.417415	0.380619	0.370668	0.380619	0.417415
E_2	0.065765	0.574200	0.230341	−0.324203	−0.591305	−0.324203	0.230341
E_3	0.000000	0.000000	0.503496	0.496479	0.000000	−0.496479	−0.503496
E_4	0.191055	0.549477	−0.343923	−0.243334	0.553700	−0.243334	−0.343924
E_5	0.000000	0.000000	0.496482	−0.503494	0.000000	0.503494	−0.496482
E_6	0.774528	0.077783	−0.211716	0.307391	−0.339749	0.307391	−0.211715
E_7	0.598176	−0.370993	0.330790	−0.311241	0.303256	−0.311241	0.330790

show a greater change, while partial charges change remarkably with ω. In consequence of the last-mentioned fact the calculated values of dipole moments highly depend on ω. Bis-trimethyl-silyl-benzene has no resultant dipole moment. For the other three compounds σ dipole moments have been calculated by the modified method of DEL RE [2], the dipole moment

Table 6

Bond orders of trimethyl-phenyl-silane

	$\omega = 0.5$	$\omega = 0.7$	$\omega = 0.9$
p_{12}	0.115488	0.114718	0.114032
p_{23}	0.657110	0.657888	0.658514
p_{34}	0.668652	0.668484	0.668384
p_{45}	0.665376	0.665484	0.665572

Table 7

Calculated and experimental dipole moments

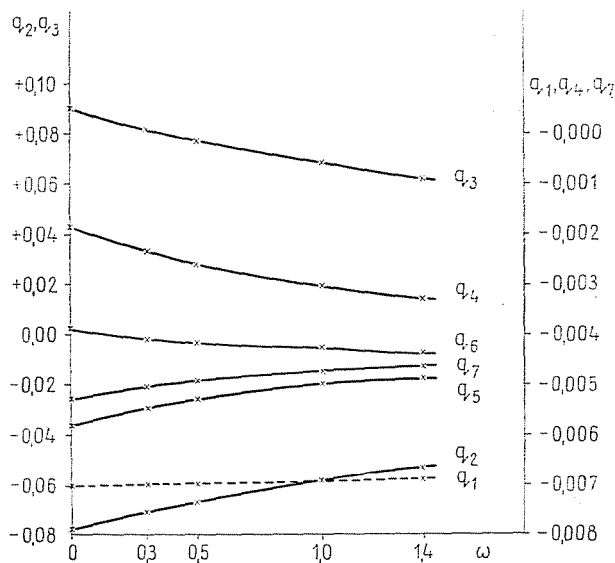| Compound	$\mu_{calculated}$ (D)								$\mu_{experimental}$ (D)
	$\omega = 0$	0.3	0.5	0.7	0.9	1.0	1.2	1.4	
I	0.129	0.106	0.097	0.090		0.083		0.080	0.229
II	0.741		0.622	0.583	0.546	0.529	0.494		0.250
III	0.495	0.487	0.452			0.411		0.396	0.550

Fig. 5. Variation of the partial charges of trimethyl-benzyl-silane as function of ω

of the π-system on the basis of the results of computations with different ω values, and the resultant dipole moment by the vectorial addition of the two vectors (Table 7). In Fig. 6 the change of dipole moments with ω is presented. The dipole moments of all the compounds studied decrease as ω increases. From the plots in Fig. 6 the dipole moments belonging to any value of ω can
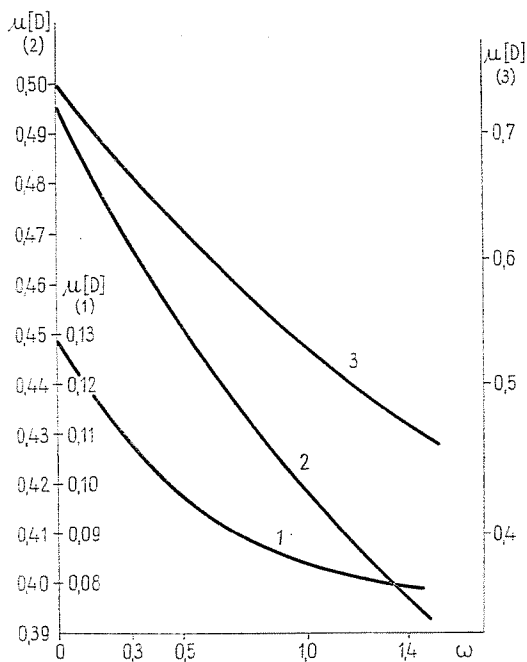

Fig. 6. Variation of dipole moments as function of ω. 1. trimethyl-vinyl-silane; 2. trimethyl-benzyl-silane; 3. trimethyl-phenyl-silane
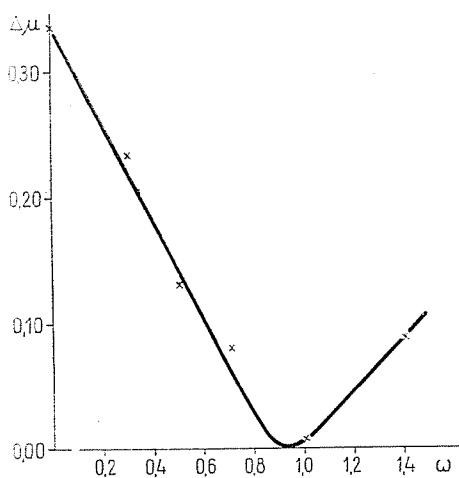

Fig. 7. Average deviation of calculated and experimental dipole moments as function of ω

be read. By taking the average of the differences between experimental and calculated dipole moments at different values of ω for the three compounds (Table 8) and plotting the averages against ω (Fig. 7), a curve having a mini-

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Table 8

Differences between experimental and calculated dipole moments in (D) units

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	$\omega = 0$	0.3	0.5	0.7	1.0	1.4
I	−0.100	−0.123	−0.132	−0.139	−0.146	−0.149
II	+0.391	+0.441*	+0.372	+0.333	+0279	+0.214*
III	−0.055	−0.084*	−0.098	−0.114*	−0.139	−0.154

* Data obtained by interpolation from Fig. 6.

mum at $\omega = 0.9$, i.e. near ω_{max} was obtained. This indicates that best results are obtained in the case of organosilicon compounds when calculating with $\omega = 0.8 - 0.9$.

Summary

Computations have been made using the ω-technique LCAO—MO method for trimethyl-vinyl-silane, trimethyl-phenyl-silane, p-bis-trimethyl-silyl-benzene and trimethyl-benzyl silane. Calculated π-bond orders and Δm electron transitions are the least sensitive, while partial charges the most sensitive to the changes in ω. The total energy of the electrons on the filled orbitals has its maximum in the range $= 0.6$ to 0.9 attributable to the empirical consideration for electronic interactions.

References

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