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The Crystal Structure of Bis(triphenylsilyl)chromate

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The crystal structure of bis(triphenylsilyl)chromate, $((C_6H_5)_3Si)_2CrO_4$, has been determined from three-dimensional X-ray film data and refined by three-dimensional Fourier methods and least-squares techniques. The structure is monoclinic, space group $P2_1/b$. The elementary cell contains four formula units and has the dimensions:

$a = 11.536 \pm 4$ Å
$b = 17.394 \pm 5$ Å
$c = 16.113 \pm 5$ Å
$\gamma = 96.51° \pm 2$

The crystals are built up of molecules, each of which is formed by a CrO_4 tetrahedron which is linked to the silicon atoms by oxygen bridges. In addition to the oxygen contact each silicon atom is also in contact with three aromatic rings which project from it like propeller blades.

Metal organo-silyl esters with the general formula, $[R_1R_2R_3SiO]_xM_yO_{z-x}$ where R_1, R_2, and R_3 are alkyl, aryl, aralkyl, or heterocyclic radicals and where M is chromium(VI), molybdenum(VI), wolfram(VI), or vanadium(V) have been reported [1] to be good corrosion inhibitors. Especially the compound bis(triphenylsilyl)chromate, is cited as having shown superior ability to inhibit corrosion and also as being more stable than the comparable carbon compound. The present article will give a description of an X-ray investigation of the structure of bis(triphenylsilyl)chromate, $[(C_6H_5)_3Si]_2CrO_4$.

From a crystalline preparation, kindly supplied by Drs. C. Hare, R. N. Hammer and J. B. Kinsinger of the Michigan State University, unregular shaped orange coloured single crystals were obtained.

X-RAY DIFFRACTION DATA AND COMPUTING METHODS

The powder pattern of $[(C_6H_5)_3Si]_2CrO_4$ was completely indexed on the basis of a monoclinic unit cell. The cell parameters were calculated from a photograph taken with strictly monochromatized Cu$K\alpha_1$ radiation ($\lambda = 1.54050$ Å) in a focusing camera of the Guinier-Hägg type. Potassium chloride

Table 1. X-ray powder data for $[(C_6H_5)_3Si]_2CrO_4$. Cu$K\alpha$ radiation. $\lambda(CuK\alpha_1) = 1.54050$ Å.

hkl	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I_{obs}
011	432	427	w
101	680	681	m
020	793	795	m
002	919	915	m
021	1026	1024	m
$\bar{1}21$	1341	1341	m
022	1718	1711	m
$\bar{1}22$	—	2088	—
201	2039	2038	m
013	—	2259	—
$\bar{1}31$	2268	2268	m
032	—	2706	—
202	2718	2725	m
113	2784	2779	vw
$\bar{2}12$	—	2788	—
023	2854	2856	vw
$\bar{1}32$	2959	2955	vst
212	3055	3060	vst
$\bar{1}23$	—	3172	—
040	3182	3183	m
$\bar{2}22$	3241	3249	vvw
132	—	3363	—
$\bar{1}40$	3373	3364	vvw
$\bar{1}41$	3598	3593	m
004	3673	3662	w
222	3787	3793	w
$\bar{2}13$	3934	3932	vw
300	4082	4071	m
$\bar{3}11$	—	4295	—
301	4307	4300	m
114	—	4382	—
$\bar{2}23$	4397	4393	w
133	4508	4507	w
$\bar{3}21$	4694	4688	w

The powder photograph was measured and interpreted up to $\sin^2\theta = 0.17$. Reflections systematically absent in space group $P2_1/b$ have been omitted.

($a = 6.29228$ Å)[2] was used as an internal standard. Least-squares refinement gave the following unit-cell dimensions (see Table 1) at 25°C:

$$a = 11.536 \pm 4 \text{ Å}$$
$$b = 17.394 \pm 5 \text{ Å}$$
$$c = 16.113 \pm 5 \text{ Å}$$
$$\gamma = 96.51° \pm 2$$
$$V = 3212 \text{ Å}^3$$

The theoretical value of the density based on four formula units in the unit cell is 1.32 g/cm³.

Rotation and Weissenberg photographs (*0kl*—*5kl*, *h0l*—*h9l*) of two single crystals (rotation axes *a* and *b*, respectively) were taken with Cu$K\alpha$ radiation.

To prevent the slow decomposition of the compound when exposed to daylight the crystals were kept in darkness also during the X-ray examination. The reflections systematically absent in the photographs are $hk0$ with $k=2n+1$ and $00l$ with $l=2n+1$, which is characteristic of the space group $P2_1/b$.

The reflections were recorded photographically with the multiple film technique. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographic recording of a reflection with different exposure times. A total of 710 independent reflections of non-zero intensity were measured.

The computational work involved in the refinement of lattice constants (Program Pirum [3]), correction absorption (No. 6019) and for Lorentz-polarization effects (No. 6024), scaling of reflections recorded from different crystals (Program SFALE [4]), Fourier summation (No. 6015), least-squares refinement (block diagonal matrix approximation, isotropic temperature factors, No. 6023), least-squares refinement of rigid groups (full matrix calculation [5]), and calculation of interatomic distances (Program DIST [6]) was performed on the electronic computers CD 3600, IBM 1800 or IBM 7090. (The program numbers refer to the world list of crystallographic computer programs [7]).

A linear absorption coefficient $\mu=40.3$ cm^{-1} was used in the calculation of the absorption factor for each reflection.

STRUCTURE DETERMINATION

From the three-dimensional Patterson function approximate parameter values were derived for the four chromium and the eight silicon atoms (situated in point positions $4(e)$: $\pm(xyz)$; $\pm(x,\frac{1}{2}+y,\frac{1}{2}-z)$). Three-dimensional electron density calculations were then performed, using the signs of the observed structure factors derived from the chromium and silicon contributions only. (In this and subsequent calculations atomic scattering curves for Cr^{3+} and un-ionized silicon, oxygen, and carbon atoms were used. The real part of the anomalous dispersion correction [8] was applied to the scattering curves [9]). In addition to the Cr and Si atoms the Fourier maps thus obtained also showed the positions of the sixteen oxygen atoms occupying four sets of $4(e)$ point positions. From subsequent three-dimensional calculations approximate positions of the twentyfour aromatic rings were deduced.

A refinement of the coordinates so obtained was then performed using a least-squares block diagonal matrix program with isotropic temperature factors for all of the atoms refined, *viz.* chromium, silicon, oxygen, and carbon. Including the scale factors, a total of 181 parameters were involved in the refinement which, in comparison with the total number of independent reflections, only gives an over-determination by a factor of about four. Therefore, a complete refinement by means of this method was possible to reduce the index discrepancy index R, defined in the usual way, from, initially, 0.44 to 0.14. From this result and since the interatomic distances based on the coordinates obtained, from the last cycle were found to be of reasonable lengths, it was concluded that the atomic parameters arrived at were likely to represent an adequate description of the architecture of the structure, which was the primary interest of this investigation.

Table 2. Atomic coordinates for $[(C_6H_5)_3Si]_2CrO_4$.

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
Cr	0.8260 ± 3	0.5591 ± 2	0.8474 ± 2	5.68 ± 10
Si1	0.6171 ± 4	0.4861 ± 2	0.7416 ± 3	3.71 ± 12
Si2	1.0480 ± 4	0.6289 ± 2	0.7331 ± 3	3.64 ± 13
O1	0.7350 ± 9	0.4856 ± 5	0.7939 ± 6	5.36 ± 25
O2	0.9287 ± 9	0.6050 ± 5	0.7828 ± 6	5.66 ± 27
O3	0.8895 ± 10	0.5203 ± 7	0.9196 ± 7	8.65 ± 34
O4	0.7476 ± 11	0.6144 ± 7	0.8843 ± 8	10.84 ± 39
C11	0.3694 ± 6	0.5811 ± 4	0.3498 ± 4	6.77 ± 22
C12	0.3070	0.6439	0.3372	
C13	0.3022	0.6989	0.3994	
C14	0.3598	0.6910	0.4742	
C15	0.4223	0.6282	0.4868	
C16	0.4271	0.5732	0.4246	
C21	0.3982 ± 6	0.2592 ± 4	0.3546 ± 4	6.31 ± 22
C22	0.4828	0.2911	0.2993	
C23	0.4804	0.3664	0.2710	
C24	0.3935	0.4097	0.2981	
C25	0.3089	0.3777	0.3534	
C26	0.3112	0.3023	0.3816	
C31	0.6907 ± 6	0.6096 ± 3	010901 ± 4	5.20 ± 19
C32	0.7063	0.6048	0.1754	
C33	0.6131	0.5773	0.2259	
C34	0.5042	0.5547	0.1912	
C35	0.4887	0.5595	0.1059	
C35	0.4887	0.5595	0.1059	
C36	0.5819	0.5870	0.0553	
C41	1.0208 ± 5	0.1613 ± 4	0.4303 ± 5	7.11 ± 23
C42	0.9768	0.2246	0.4663	
C43	0.9571	0.2879	0.4178	
C44	0.9814	0.2880	0.3333	
C45	1.0254	0.2247	0.2973	
C46	1.0451	0.1614	0.3457	
C51	0.9241 ± 6	0.4526 ± 4	0.3353 ± 3	6.04 ± 20
C52	1.0137	0.5107	0.3530	
C53	0.9918	0.5734	0.4018	
C54	0.8804	0.5779	0.4330	
C55	0.7809	0.5198	0.4153	
C56	0.8127	0.4572	0.3665	
C61	0.6621 ± 6	0.3154 ± 4	0.0703 ± 4	6.25 ± 22
C62	0.6939	0.2556	0.1194	
C63	0.7774	0.2709	0.1812	
C64	0.8291	0.3461	0.1939	
C65	0.7973	0.4060	0.1447	
C66	0.7138	0.3907	0.0829	

Better accuracy in structural details was obtained by means of a least-squares refinement of the paramters using a rigid group program.[5] The number of parameters was then reduced to 77 which gives a more favourable ratio between the number of reflections and the number of parameters. After a few cycles, when the parameter shifts were less than 5 % of the standard deviations, the refinement was considered complete.

Scheringer's weighting function

$$w = (\Delta^2+4.0)^{-1} \text{ where } \Delta = ||F_{obs}|-|F_{calc}||$$

was used in the refinement. The positional parameters and the isotropic temperature factors are given in Table 2 together with the standard deviations which are throughout smaller than those obtained from the preliminary refinement described above. This is considered to indicate that the data given in Table 2 represent the better description of the molecular structure.

However, the discrepancy index R comes out as 0.14 for both procedures of refinement.

The calculated interatomic distances and their standard deviations are given in Table 3. All distances lie within normal ranges, thus supporting the correctness of the coordinates arrived at in the last cycle.

Table 3. Interatomic distances (Å) and standard deviations ($\pm\sigma$ in Å) and some angles in $[(C_6H_5)_3Si]_2CrO_4$. The distances are uncorrected for thermal motion.

Cr –O1	1.782±10	O2 –Cr –O1	111.22±46°
Cr –O2	1.706±10	O1 –Cr –O3	108.43±53
Cr –O3	1.568±12	O1 –Cr –O4	107.44±60
Cr –O4	1.514±13	O2 –Cr –O3	108.67±55
		O2 –Cr –O4	112.06±60
Si1–O1	1.601±11	O3 –Cr –O4	108.93±66
Si2–O2	1.605±11		
		Cr –O1–Si1	133.06±58°
Si1–C11	1.897±8	Cr –O2–Si2	162.71±67
Si1–C24	1.939±8		
Si1–C34	1.847±8	O1 –Si1–C11	106.05±44°
		O1 –Si1–C24	108.79±43
Si2–C44	1.861±8	O1 –Si1–C34	107.26±46
Si2–C51	1.852±8	C11–Si1–C24	109.79±35
Si2–C64	1.856±8	C11–Si1–C34	109.26±34
		C24–Si1–C34	115.27±34
		O2 –Si2–C44	105.15±44°
		O2 –Si2–C51	108.50±45
		O2^1–Si2–C64	110.72±47
		C44–Si2–C51	108.35±37
		C44–Si2–C64	112.58±36
		C51–Si2–C64	111.27±37

A list of the observed and calculated structure factors is presented in Table 4.

In the unit cell there are also 120 hydrogen atoms. It was not possible to determine their parameters from the present set of experimental data.

Table 4. Observed and calculated structure factors for $[(C_6H_5)_3Si]_2CrO_4$.

H	K	L	FOBS	FCAL
0	0	2	147.87	193.77
0	0	4	146.06	147.00
0	0	6	27.70	27.32
0	0	10	53.70	40.29
0	1	3	59.97	61.51
0	1	4	61.23	59.15
0	1	6	55.32	48.51
0	1	8	19.54	21.83
0	1	9	32.94	32.50
0	2	0	125.77	131.72
0	2	1	127.74	118.54
0	2	2	71.79	86.18
0	2	3	88.22	103.88
0	2	4	21.75	20.39
0	2	5	63.51	57.43
0	2	6	32.62	35.76
0	2	7	32.62	30.95
0	2	8	21.08	21.44
0	2	9	38.61	34.22
0	2	10	41.61	39.64
0	2	12	29.79	27.98
0	3	2	80.61	106.39
0	3	3	16.55	16.10
0	3	4	29.43	22.57
0	3	5	45.27	45.42
0	3	6	50.00	47.84
0	3	8	49.88	47.16
0	3	9	22.14	21.85
0	4	0	44.13	43.74
0	4	1	33.02	31.63
0	4	2	9.38	4.94
0	4	3	13.63	5.11
0	4	4	21.36	23.57
0	4	5	97.16	93.20
0	4	7	40.70	42.09
0	4	9	59.73	56.20
0	5	1	56.19	56.68
0	5	2	47.95	46.87
0	5	3	56.79	58.77
0	5	4	29.12	15.42
0	5	5	41.80	40.20
0	5	6	43.10	41.13
0	5	7	22.26	26.87
0	5	12	49.09	46.17
0	6	0	98.82	88.29
0	6	1	41.21	39.86
0	6	3	103.47	86.84
0	6	4	87.12	79.73
0	6	5	121.28	118.04
0	6	6	43.81	44.02
0	6	7	68.28	66.15
0	7	1	16.71	2.91
0	7	2	27.03	7.56
0	7	3	18.91	34.30
0	7	5	55.75	55.32
0	7	6	24.23	25.08
0	7	7	30.73	28.68
0	8	1	31.91	40.26
0	8	2	48.70	63.95
0	8	3	33.88	31.81
0	8	4	84.55	83.63
0	8	6	53.90	49.97
0	8	8	42.16	34.60
0	9	3	51.38	41.02
0	9	7	24.35	24.51
0	10	1	21.75	27.30
0	10	4	32.62	34.52
0	10	6	49.17	48.72
0	11	2	23.56	27.09
0	11	4	34.59	33.30
0	12	1	35.07	36.81
0	12	3	25.37	28.31
0	14	0	27.27	25.96
0	14	1	38.61	55.23
1	0	0	51.15	43.23
1	0	1	82.24	88.15
1	0	2	16.62	9.66
1	0	3	37.86	35.84
1	0	4	66.39	61.35
1	0	5	74.89	65.97
1	0	6	27.95	20.94
1	0	8	29.25	19.25
1	0	9	57.12	60.34
1	0	10	28.45	24.85
1	-1	2	15.85	7.53
1	-1	3	36.72	28.61
1	-1	4	68.57	69.65
1	-1	5	28.06	29.29
1	-1	6	44.37	43.45
1	-2	1	85.07	192.38
1	-2	2	49.96	59.76
1	-2	3	69.72	101.85
1	-2	4	50.50	48.11
1	-2	6	41.88	32.73
1	-2	9	32.85	34.80
1	-2	11	37.86	31.70
1	-3	1	86.94	154.20
1	-3	2	153.29	279.27
1	-3	3	112.10	163.75
1	-3	5	59.72	44.21
1	-3	6	29.40	25.51
1	-3	7	74.27	71.42
1	-3	9	27.34	16.58
1	-3	10	36.98	31.75
1	-4	0	117.07	116.21
1	-4	1	117.15	166.56
1	-4	2	72.59	87.17
1	-4	3	28.60	38.58
1	-4	4	31.62	30.63
1	-4	5	48.51	46.75
1	-4	6	36.83	33.01
1	-4	11	21.98	30.62
1	-5	2	100.04	97.99
1	-5	3	75.11	72.36
1	-5	7	69.41	73.96
1	-5	9	52.45	50.52
1	-6	0	47.55	43.84
1	-6	1	67.92	51.73
1	-6	3	38.32	38.29
1	-6	4	36.06	32.26
1	-6	10	21.75	25.76
1	-7	3	57.50	48.95
1	-7	4	18.76	29.15
1	-7	5	34.07	19.13
1	-7	7	60.18	63.14
1	-7	8	36.14	41.73
1	-7	9	21.21	12.34
1	-7	10	22.36	12.02
1	-7	11	23.35	29.51
1	-8	0	57.20	54.20
1	-8	1	22.59	5.83
1	-8	2	44.03	52.95
1	-8	3	66.23	64.43
1	-8	4	49.08	58.75
1	-8	5	51.15	48.96
1	-8	6	33.46	31.76
1	-9	2	60.87	67.73
1	-9	4	41.50	42.10
1	-9	5	27.26	28.50
1	-9	6	20.06	7.34
1	-10	1	18.68	25.47
1	-10	2	37.75	30.69
1	-10	3	43.11	50.16
1	-10	4	19.83	14.98
1	-10	5	70.75	65.66
1	-10	7	49.00	52.33
1	-11	2	40.43	39.20
1	-11	3	29.10	30.29
1	-12	3	29.10	33.00
1	-13	3	45.79	34.14
1	1	2	47.89	47.83
1	1	3	23.16	21.29
1	1	4	44.22	42.49
1	1	5	55.78	47.82
1	1	7	34.76	29.99
1	1	8	34.00	24.34
1	2	1	21.48	26.30
1	2	2	23.81	23.63
1	2	3	26.84	21.92
1	2	4	121.06	132.55
1	2	6	53.68	45.82
1	2	7	18.03	13.31
1	2	8	25.92	11.57
1	3	1	24.77	24.93
1	3	2	43.07	48.65
1	3	3	79.36	79.89
1	3	4	20.79	15.32
1	3	5	30.78	28.48
1	3	6	25.04	33.10
1	3	7	17.53	16.27
1	3	8	35.34	29.85
1	3	11	25.34	29.16
1	3	13	39.51	40.21
1	4	0	118.68	142.22
1	4	1	82.31	82.53
1	4	2	85.34	94.33
1	4	3	42.96	47.18
1	4	4	71.90	76.92
1	4	5	115.31	76.40
1	4	6	71.52	69.20
1	4	7	16.85	28.24
1	4	8	60.68	68.38
1	5	1	37.90	45.73
1	5	2	45.41	47.79
1	6	2	14.70	27.14
1	6	3	57.31	49.91
1	6	4	52.11	54.45
1	6	5	88.86	84.61
1	6	6	36.94	26.47
1	6	7	26.57	23.85
1	6	8	20.18	19.24
1	7	1	39.43	37.77
1	7	2	25.27	10.80
1	7	4	32.58	26.24
1	7	5	35.15	34.01
1	7	6	32.12	29.92
1	7	7	19.30	21.93
1	7	8	36.72	34.68
1	8	0	30.59	35.85
1	8	1	42.88	29.00
1	8	2	37.86	32.51
1	8	5	18.53	30.72
1	8	6	27.34	25.14
1	9	2	47.63	44.40
1	9	3	18.45	18.66
1	9	6	54.06	51.68
1	9	8	58.58	53.67
1	10	0	53.83	60.23
1	10	2	54.67	51.83
1	10	4	20.21	33.05
1	12	0	30.63	41.21
1	12	2	31.01	38.42
2	0	0	42.42	41.22
2	0	1	104.14	102.19
2	0	2	42.34	35.98
2	0	3	56.08	47.47
2	0	4	150.41	147.60
2	0	5	23.03	31.13
2	0	6	59.33	56.43
2	0	7	27.41	23.86
2	-1	1	47.93	47.70
2	-1	2	63.26	63.53
2	-1	3	114.64	130.50
2	-1	4	30.17	26.21
2	-1	11	27.09	31.38
2	-1	12	28.71	35.25
2	-1	13	29.93	34.83
2	-2	0	50.77	50.95
2	-2	1	17.52	13.37
2	-2	2	62.49	59.55
2	-2	3	97.00	94.71
2	-2	4	16.63	0.00
2	-2	5	23.48	13.57
2	-2	6	40.59	40.06
2	-2	7	32.93	28.15
2	-2	12	27.57	11.97
2	-3	1	46.11	43.44
2	-3	3	67.96	73.23
2	-3	4	28.79	4.32
2	-3	5	52.35	50.34
2	-3	7	55.88	61.66
2	-3	9	32.73	21.20
2	-4	0	59.53	69.80
2	-4	1	73.60	85.17
2	-4	2	66.42	75.38
2	-4	3	41.24	27.30
2	-4	4	31.95	32.22
2	-4	6	45.58	43.40
2	-4	7	33.33	34.88
2	-5	2	57.34	56.46
2	-5	3	91.73	82.41
2	-5	4	65.82	72.41
2	-5	5	59.41	56.28
2	-5	7	69.71	68.04
2	-5	8	46.35	44.27
2	-5	9	46.72	46.84
2	-6	0	89.46	86.73
2	-6	1	97.89	118.74
2	-6	3	106.04	113.28
2	-6	4	43.03	40.04
2	-6	5	39.25	29.96
2	-6	6	52.88	55.08
2	-6	9	52.92	52.32
2	-7	1	29.12	11.02
2	-7	2	96.39	78.44
2	-7	3	20.48	17.99
2	-7	4	41.24	16.97
2	-7	8	39.42	38.39
2	-7	10	28.30	43.58
2	-8	0	45.74	42.20
2	-8	1	46.11	58.22
2	-8	3	57.66	61.72
2	-8	4	31.06	29.31
2	-8	5	22.95	17.44
2	-8	6	24.09	19.69
2	-8	8	26.60	30.86
2	-8	9	48.34	38.31
2	-9	1	48.91	52.46
2	-9	2	31.39	17.30
2	-9	3	22.79	26.59
2	-9	6	25.39	23.97
2	-9	8	27.66	26.68
2	-10	4	27.66	34.46
2	-10	5	25.87	28.89
2	-10	6	59.85	44.60
2	-12	2	54.34	46.57
2	-12	4	68.69	74.58
2	1	1	56.53	57.21
2	1	2	235.93	384.08
2	1	3	25.30	25.72
2	1	4	63.06	57.73
2	1	5	54.50	47.67
2	1	6	69.75	61.06
2	1	12	57.50	57.13
2	1	14	43.47	41.58
2	2	0	37.88	38.24
2	2	1	18.82	18.81
2	2	2	94.40	101.61
2	2	3	151.99	194.76
2	2	4	37.79	35.33
2	2	5	115.77	110.48
2	2	7	51.82	52.25
2	3	1	48.66	40.92
2	3	2	38.08	21.15
2	3	3	35.97	31.26
2	3	4	35.97	27.55
2	3	5	37.31	36.17
2	3	6	42.90	41.37
2	3	7	28.51	20.49
2	3	8	30.86	17.69
2	3	9	24.21	27.74
2	4	0	67.68	67.81
2	4	1	40.19	39.08
2	4	3	66.71	60.37
2	4	4	123.28	122.34
2	4	5	66.42	66.60
2	4	6	32.40	50.32
2	5	1	111.39	107.07
2	5	3	45.01	52.33
2	5	4	19.79	17.13
2	5	5	47.08	49.42
2	5	6	48.46	45.29
2	5	7	68.69	71.30
2	5	8	41.40	33.62
2	6	0	73.11	79.29
2	6	1	18.90	8.00
2	6	2	24.57	24.17
2	6	3	21.65	16.29
2	6	4	44.40	34.58
2	6	5	18.09	16.83
2	6	8	43.84	33.06
2	6	10	57.02	57.71
2	7	1	47.89	42.37
2	7	2	62.94	54.21
2	7	3	35.60	34.20
2	7	5	56.12	53.70
2	7	7	62.21	52.55
2	7	9	66.83	74.70
2	8	0	30.94	33.99
2	8	1	46.84	50.49
2	8	2	39.54	40.04
2	8	3	48.26	46.89
2	8	4	44.40	43.02
2	8	7	26.12	12.20
2	8	8	47.36	36.30
2	8	10	29.52	39.61
2	9	3	23.84	22.02
2	9	8	63.58	58.31
2	10	0	24.57	24.12
2	10	1	65.37	64.05
2	10	4	36.90	31.72
2	11	2	26.60	28.46
2	11	4	39.01	47.82
3	0	0	135.60	134.68
3	0	1	56.54	51.92
3	0	4	36.63	29.99
3	0	6	69.45	67.77
3	0	8	20.53	24.39
3	-1	1	82.95	90.10
3	-1	2	50.33	51.24
3	-1	3	87.13	92.78
3	-1	4	50.25	49.65
3	-1	5	47.64	42.85
3	-1	6	29.55	26.05
3	-1	7	45.65	41.60
3	-1	8	20.53	21.99
3	-2	1	67.96	74.68
3	-2	2	57.08	58.85
3	-2	3	28.68	11.34
3	-2	4	73.22	78.09
3	-2	5	101.12	112.51
3	-2	6	19.58	12.32
3	-2	7	84.89	87.47
3	-2	8	42.67	41.96
3	-3	1	47.97	45.35
3	-3	2	93.71	95.73
3	-3	4	61.75	72.34
3	-3	5	23.34	24.12
3	-3	7	38.25	37.84
3	-3	11	25.83	27.28
3	-3	12	51.41	47.99
3	-4	0	45.78	50.11
3	-4	2	25.41	14.93
3	-4	3	40.15	36.77
3	-4	5	90.02	94.06
3	-4	7	32.66	32.53
3	-4	8	37.42	31.29
3	-5	1	39.20	37.78
3	-5	4	40.65	47.97
3	-5	5	34.77	31.98
3	-5	6	26.49	32.51
3	-5	8	34.19	25.63
3	-5	11	26.57	22.90
3	-6	0	32.70	29.13
3	-6	1	67.92	66.60
3	-6	3	43.21	39.86

Table 4. Continued.

H	K	L	FOBS	FCAL
3	-6	4	21.11	20.74
3	-6	5	44.16	49.17
3	-6	7	21.69	17.47
3	-6	10	41.14	44.72
3	-7	1	52.94	41.76
3	-7	3	35.89	30.56
3	-7	5	28.89	26.38
3	-7	6	26.49	26.36
3	-7	7	46.69	38.29
3	-8	0	94.99	134.01
3	-8	2	64.20	84.90
3	-8	5	21.52	5.97
3	-9	1	28.97	20.82
3	-9	7	49.67	31.41
3	-10	0	65.89	106.78
3	-10	1	31.21	35.78
3	-10	2	44.70	43.22
3	-12	0	25.08	8.45
3	-12	1	35.51	42.89
3	1	1	32.28	23.68
3	1	2	67.26	61.38
3	1	3	142.30	136.29
3	1	4	31.87	37.36
3	1	7	82.24	83.73
3	1	9	22.43	25.84
3	2	0	174.42	171.88
3	2	1	91.10	76.03
3	2	2	82.37	75.37
3	2	3	53.44	39.36
3	2	4	120.70	112.20
3	2	6	33.61	32.89
3	2	7	19.37	18.34
3	2	8	39.28	29.08
3	2	9	33.49	23.50
3	2	10	29.30	24.11
3	2	12	31.04	20.09
3	3	2	33.44	19.75
3	3	4	37.62	27.68
3	3	5	35.80	31.86
3	3	6	49.25	28.74
3	3	7	21.19	21.40
3	3	8	50.91	52.98
3	3	9	29.68	30.24
3	4	0	29.43	9.34
3	4	1	79.68	82.01
3	4	4	52.44	50.33
3	4	5	39.79	41.40
3	4	6	19.29	12.94
3	4	7	63.16	63.18
3	4	9	58.96	76.44
3	4	11	47.02	60.76
3	5	1	30.13	19.80
3	5	2	26.74	21.14
3	5	3	49.67	40.00
3	5	4	34.69	20.31
3	5	6	39.45	24.39
3	5	8	59.19	57.79
3	5	10	38.53	36.13
3	6	0	59.69	58.81
3	6	1	33.61	35.03
3	6	5	37.67	36.68
3	6	7	22.93	16.42
3	6	8	34.19	21.59
3	6	9	59.89	57.37
3	7	1	43.63	38.04
3	7	3	54.39	42.53
3	7	5	31.13	35.81
3	7	7	34.77	33.36
3	8	0	39.90	35.55
3	8	1	40.19	39.41
3	8	2	35.06	32.36
3	8	4	47.10	42.13
3	8	6	33.69	32.12
3	9	1	31.21	27.06
3	9	3	45.61	34.38
3	9	5	24.17	24.18
3	10	0	47.10	41.01
3	10	3	34.35	34.02
3	10	4	49.67	47.99
4	0	0	46.33	42.25
4	0	1	34.90	35.70
4	0	2	17.88	16.04
4	0	4	42.25	48.56
4	0	5	23.67	16.85
4	0	8	22.08	22.49
4	0	9	23.71	21.78
4	0	10	47.30	46.62
4	0	11	46.40	33.99
4	-1	2	73.11	80.51
4	-1	6	41.47	35.84
4	-1	7	35.06	24.34
4	-1	8	57.52	53.08
4	-2	1	29.30	16.18
4	-2	4	31.95	30.65
4	-2	5	55.07	75.00
4	-2	7	40.92	37.17
4	-3	1	15.82	7.78
4	-3	2	41.24	34.36
4	-3	3	31.91	19.76
4	-3	4	64.28	68.53
4	-3	5	28.92	25.55
4	-4	0	18.11	23.76
4	-4	1	27.59	23.62
4	-4	3	30.39	12.24
4	-4	5	79.13	87.96
4	-4	6	85.70	106.19
4	-4	7	41.82	42.71
4	-4	8	42.13	41.97
4	-5	1	21.06	15.43
4	-5	2	21.34	16.78
4	-5	3	33.85	41.26
4	-5	4	25.18	26.00
4	-5	5	60.16	66.55
4	-6	0	50.37	62.24
4	-6	1	16.01	16.48
4	-6	4	68.01	67.43
4	-6	5	39.41	37.40
4	-6	6	71.24	79.16
4	-6	8	33.70	38.26
4	-7	1	31.09	2.22
4	-7	3	46.83	52.54
4	-8	0	51.65	59.83
4	-8	5	22.93	31.85
4	-8	6	35.60	30.49
4	-8	7	25.26	20.17
4	-10	0	32.96	12.26
4	-10	1	52.39	51.53
4	-11	6	39.10	38.43
4	-12	0	64.90	72.21
4	-12	1	37.54	37.30
4	1	3	45.98	36.37
4	1	4	26.20	9.63
4	1	5	79.83	66.67
4	1	6	111.35	124.16
4	1	7	50.14	45.47
4	1	8	51.54	49.18
4	1	9	24.10	24.28
4	2	0	119.47	121.47
4	2	1	35.72	34.84
4	2	2	76.99	73.32
4	2	3	27.98	29.19
4	2	4	49.13	39.52
4	2	6	37.62	31.90
4	2	9	27.13	33.34
4	2	10	57.83	62.06
4	3	1	79.25	76.35
4	3	3	42.29	31.76
4	3	5	60.86	58.09
4	3	6	24.76	23.68
4	3	7	79.44	73.57
4	3	9	61.41	62.98
4	4	1	31.40	31.10
4	4	2	32.45	32.47
4	4	8	30.94	42.72
4	4	10	34.51	46.28
4	5	1	43.37	42.53
4	5	2	34.82	17.15
4	5	3	58.26	63.34
4	5	4	19.51	26.34
4	5	5	27.67	24.53
4	5	6	27.52	20.19
4	5	7	29.07	14.38
4	5	8	30.70	23.99
4	6	0	46.37	44.30
4	6	1	67.39	66.94
4	6	3	72.60	69.37
4	6	4	24.41	25.00
4	6	5	49.90	48.59
4	6	6	22.50	21.53
4	7	1	24.41	20.75
4	7	2	52.74	56.17
4	7	3	45.24	40.48
4	7	4	31.09	19.59
4	7	5	27.98	18.05
4	8	1	31.56	22.39
4	8	3	60.12	55.79
4	8	5	27.31	26.86
4	8	7	53.40	50.43
4	9	4	35.83	38.66
4	10	4	26.74	42.01
4	10	6	39.56	48.51
5	0	0	70.57	55.25
5	0	1	32.85	36.12
5	0	2	20.84	23.18
5	0	4	20.72	21.33
5	0	6	28.72	28.53
5	0	9	57.74	47.37
5	0	10	55.63	49.78
5	0	11	50.02	36.72
5	-1	1	44.41	41.92
5	-1	2	27.73	6.44
5	-1	4	57.99	54.77
5	-1	7	67.23	71.51
5	-1	9	53.53	50.77
5	-2	0	96.49	92.07
5	-2	2	39.79	47.90
5	-2	5	47.21	45.08
5	-2	6	25.59	25.66
5	-2	8	50.76	57.66
5	-2	10	39.46	45.95
5	-3	1	28.48	25.86
5	-3	2	22.33	25.07
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5	-3	5	22.99	23.36
5	-3	6	29.59	36.15
5	-3	7	64.42	62.41
5	-3	9	35.86	35.53
5	-4	0	73.96	89.56
5	-4	2	24.72	31.70
5	-4	3	20.47	19.58
5	-4	5	34.83	38.32
5	-5	2	50.72	49.09
5	-5	3	40.69	46.30
5	-6	1	41.60	26.29
5	-6	3	31.41	27.82
5	-6	4	23.03	29.24
5	-6	5	65.00	73.52
5	-6	7	36.86	43.19
5	-7	2	49.90	50.72
5	-7	4	50.89	47.11
5	-8	5	61.58	56.80
5	-9	3	30.46	30.39
5	-10	4	33.26	39.26
5	1	6	55.80	41.01
5	1	8	65.04	54.93
5	2	1	34.05	35.50
5	2	5	81.43	73.89
5	2	8	29.96	32.81
5	3	1	41.93	44.11
5	3	2	128.81	123.45
5	3	3	48.33	48.31
5	3	4	22.91	22.28
5	3	5	34.50	34.19
5	3	6	51.92	49.14
5	3	7	25.59	11.77
5	3	8	34.83	34.03
5	4	0	27.07	17.18
5	4	2	46.31	43.57
5	4	3	45.56	38.41
5	4	4	25.18	13.72
5	4	5	27.12	34.80
5	4	6	28.81	24.69
5	5	1	26.91	14.65
5	5	3	56.75	45.66
5	5	4	39.62	38.32
5	6	0	28.06	24.92
5	6	4	68.72	70.37
5	6	6	62.28	59.10
5	7	1	31.16	40.26
5	8	5	47.63	33.42
6	0	0	54.51	51.59
6	0	4	79.28	71.77
6	0	6	51.59	40.46
6	-2	0	43.08	41.88
6	-2	1	43.25	35.33
6	-2	4	37.92	38.34
6	-2	6	28.98	26.70
6	-2	8	31.56	28.21
6	-2	9	32.76	32.23
6	-2	10	33.88	34.64
6	-3	7	27.77	30.47
6	-3	8	64.75	62.81
6	-4	1	26.48	36.57
6	-4	3	47.72	58.67
6	-5	2	29.41	30.52
6	-5	3	30.09	33.27
6	-7	3	51.76	50.08
6	2	0	85.30	75.11
6	2	1	25.80	22.30
6	2	2	37.06	25.88
6	2	3	37.84	32.26
6	2	4	39.64	52.08
6	2	5	28.55	28.56
6	2	6	41.96	43.05
6	2	7	30.87	24.02
6	3	2	64.66	57.80
6	3	3	49.96	47.95
6	3	4	57.44	53.69
6	4	0	39.81	31.57
6	4	3	58.56	68.95
6	4	5	31.04	29.95
6	6	1	35.25	33.24
6	6	5	27.09	26.34
7	0	1	35.25	25.17
7	0	2	50.47	47.49
7	0	3	36.37	27.81
7	0	4	26.31	37.42
7	0	5	57.52	57.96
7	0	7	67.76	35.69
7	-2	1	27.94	44.17
7	-2	3	40.67	40.50
7	-2	5	60.62	59.20
7	-3	2	36.63	35.91
7	-5	3	33.28	36.48
7	-6	0	43.51	51.25
7	2	0	28.63	30.43
7	2	2	29.06	22.13
7	2	3	29.58	24.26
7	2	4	30.27	18.90
7	2	5	31.04	9.29
7	2	6	31.90	35.09
7	3	3	38.86	36.42
7	4	0	31.21	31.15
7	6	1	27.34	43.38
7	6	2	39.04	46.97
7	6	3	39.55	38.77
8	-2	0	30.70	29.69
8	-2	2	31.04	31.04
8	-2	4	45.31	42.79
8	-2	6	47.21	58.47
8	2	1	63.11	60.54
8	4	0	48.15	74.22
8	4	1	48.24	72.93
8	4	2	34.39	50.03

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of $[(C_6H_5)_3Si]_2CrO_4$ are built up of molecules, each of which is formed by a CrO_4 tetrahedron which is linked to the silicon atoms by oxygen bridges. In addition to the oxygen contact each silicon atom is also in contact with three aromatic rings which project from it like propeller blades. Schematic drawings of the molecule and the packing of the molecules in the unit cell are shown in Figs. 1—2.

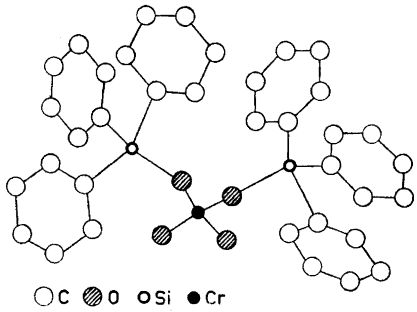

Fig. 1a. The molecular configuration of $[(C_6H_5)_3Si]_2CrO_4$.

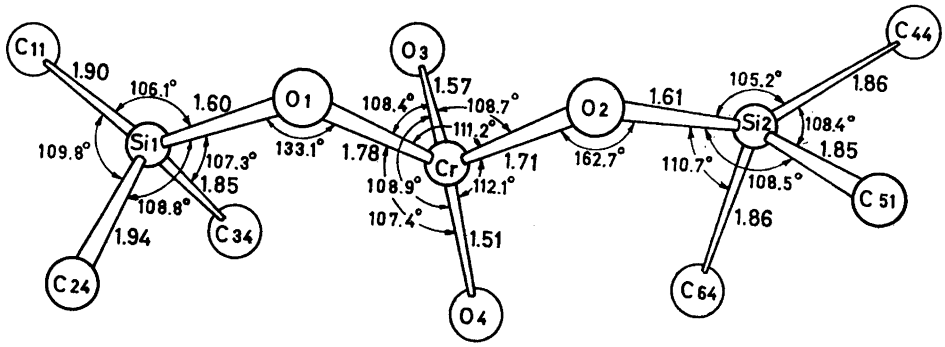

Fig. 1b. Bond lengths and bond angles within the $[(C_6H_5)_3Si]_2CrO_4$ molecule.

The interatomic distances (*cf.* Table 3) within the molecule are, as mentioned above, all within the normal ranges. The average Cr—O distance within the CrO_4 group is 1.64 Å and the average angle O—Cr—O is 109.5°. These values are in good agreement with those found in other chromates.[10] However, two Cr—O distances are much longer (average value of 1.74 Å) than the remaining two in the CrO_4 tetrahedron (average value of 1.54 Å). The former represent the bridge oxygens.

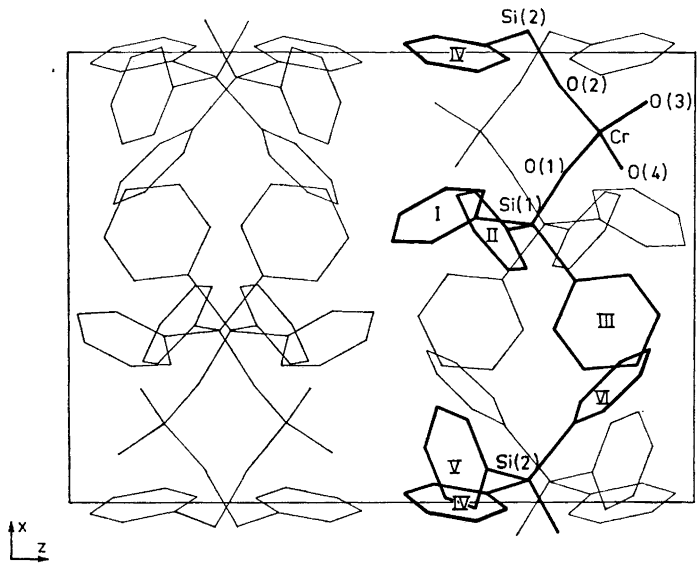

Fig. 2. Schematic drawing of the structure of $[(C_6H_5)_3Si]_2CrO_4$ projected on the *xz* plane. The Roman numerals denote the six aromatic rings.

The Si—O and Si—C distances found (the average values are 1.60 Å and 1.88 Å) are in concordance with the values 1.59 to 1.63 Å (average 1.612 Å) for Si—O and 1.84±1 Å for Si—C, obtained from a large number of determinations given in the *International Tables*.[9]

The aromatic rings, assumed in the refinement to be planar with carbon-carbon distances equal to 1.395 Å, are twisted relative to each other. The angle between adjacent phenyl rings is 74.1° (average value of six angles). This is somewhat bigger than the values 47—54°, estimated on the basis of steric considerations[11] and the values (54.3°) reported for triphenylmethyl perchlorate by Gomes de Mesquita, MacGillavry and Eriks.[12] Larger values ranging from 62° to 112° have been published for tristriphenylphosphine rhodium carbonyl hydride by La Placa and Ibers.[13]

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