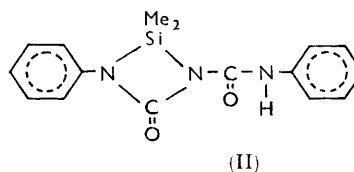
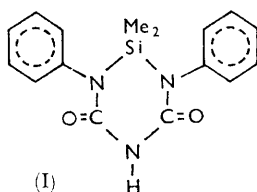


953. The Chemistry of the Silicon-Nitrogen Bond. Part VI.¹ The Molecular Structure of 2,6-Di-*p*-bromophenyl-1,1-dimethyl-1-sila-2,4,6-triazacyclohexane-3,5-dione.

By J. J. DALY and W. FINK.

Single crystal *X*-ray diffraction methods have been used to prove that one reaction product of *p*-bromophenyl isocyanate with hexamethylcyclotrisilazane is the six-membered ring compound, 2,6-di-*p*-bromophenyl-1,1-dimethyl-1-sila-2,4,6-triazacyclohexane-3,5-dione. The crystals examined contain acetone of crystallization.

THE reaction of phenyl isocyanate with hexamethylcyclotrisilazane² produces a compound $C_{16}H_{17}N_3O_2Si$. Chemical and physical evidence were insufficient to distinguish between the two possible structures (I) and (II).² In order to determine the correct



structure by *X*-ray methods, the analogous di-*p*-bromo-compound was synthesized by the method used for the parent compound.²

EXPERIMENTAL

$C_{16}H_{15}Br_2N_3O_2Si \cdot CH_3 \cdot CO \cdot CH_3$. $M = 527.3$. Monoclinic. $a = 25.33$, $b = 15.04$, $c = 6.10$ Å, $\beta = 99.37^\circ$, $U = 2291$ Å³. $D_c = 1.53$ g./c.c., $D_m = 1.5$ g./c.c., $Z = 4$. Space group $P2_1/a$, (No. 14). The atomic scattering factors are mean atomic scattering factors derived from self-consistent or variational wave functions;³ the bromine scattering-factor curve has been corrected for the real part of anomalous dispersion.⁴

p-Bromophenyl isocyanate 19.9 g. (0.1 mole) was dissolved in toluene (30 ml.) and treated with hexamethylcyclotrisilazane (5 g., 0.025 mole). When the strongly exothermic reaction (ice-water cooling) has died down, the temperature was held at 90° for 3 hr., after which the precipitate was filtered off and dissolved in hot benzene. After the insoluble *NN'*-di-*p*-bromophenylurea (m. p. 330°) had been removed, the 2,6-di-*p*-bromodiphenyl-1,1-dimethyl-1-sila-2,4,6-triazacyclohexane-3,5-dione crystallized in long needles. Recrystallization from acetone followed by drying for 1 hr. at $60-70^\circ$ at 0.1 mm. gave the pure compound, m. p. 215° (decomp.) (7.3 g. 62.4%) [Found: C, 41.0; H, 3.2; Br, 33.85; N, 9.2; Si, 5.58%; M , 473 (ebullioscopic in acetone). $C_{16}H_{15}Br_2N_3O_2Si \cdot C_3H_6O$ requires C, 40.95; H, 3.2; Br, 34.1; N, 8.95; Si, 5.99%].

The crystals were long hollow columns, which sometimes contained occluded solvent (acetone). They turned to powder during 48 hr., perhaps owing to loss of solvent of crystallization, but retained their shape. The *hkO* intensity data were recorded photographically within 24 hr. with a Weissenberg goniometer. The intensities were estimated by eye with the aid of a calibration strip.

The structure was solved by the heavy-atom method, the *X* and *Y* co-ordinates of the

¹ Part V, Fink, *Chem. Ber.*, 1964, **97**, 1433.

² Part IV, Fink, *Chem. Ber.*, 1964, **97**, 1424.

³ "International Tables for *X*-ray Crystallography," Vol. III, Kynoch Press, 1962, p. 214.

⁴ *Op. cit.*, p. 202.

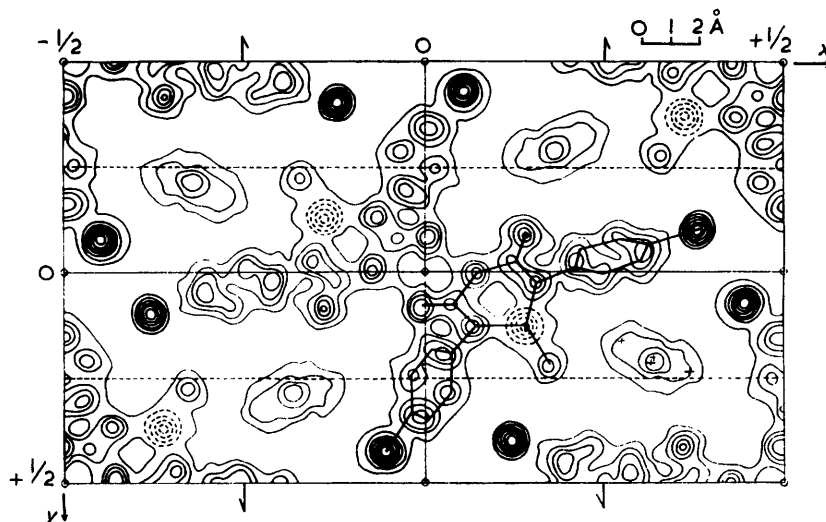


FIG. 1. The electron density of the *c*-axis projection. Contours on bromine at intervals of $8e/\text{\AA}^2$; contours on Si, dashed lines, at intervals of $5e/\text{\AA}^2$; contours on other atoms at $2.5e/\text{\AA}^2$.

TABLE I.

100 F_o , 100 F_c , and 100 Δ . Planes marked with an asterisk were not included in least-squares totals.

<i>h</i>	<i>k</i>	<i>l</i>	100 F_o	100 F_c	100 Δ	<i>h</i>	<i>k</i>	<i>l</i>	100 F_o	100 F_c	100 Δ	<i>h</i>	<i>k</i>	<i>l</i>	100 F_o	100 F_c	100 Δ
2	0	0	8984	10,857	-1873	15	2	0	-2095	-1293	-802	16	4	0	-5553	-5178	-375
4	0	0	-4081	-4235	154	16	2	0	4464	4378	86	17	4	0	4432	4459	-27
6	0	0	8929	7831	1098	17	2	0	1067	1292	-225	18	4	0	-1619	-1606	-13
8	0	0	7329	6428	811	18	2	0	2719	2325	394	19	4	0	3244	2443	801
10	0	0	-8295	-8319	24	19	2	0	3912	3390	522	20	4	0	1515	837	678
12	0	0	-13,039	-12,357	-682	20	2	0	2588	2566	22	21	4	0	-1718	-1846	128
14	0	0	3901	3495	406	22	2	0	-941	-898	-43	22	4	0	-1656	-1928	292
16	0	0	11,485	9784	1701	23	2	0	-4235	-3823	-412	23	4	0	-1718	-1798	80
18	0	0	3102	2806	296	24	2	0	935	625	307				-9592	-9212	-380
24	0	0	1214	1080	134	25	2	0	-913	-1093	180	2	5	0	-9170	-9228	68
						27	2	0	2511	1749	762	3	5	0	952	1151	-199
						31	2	0	-952	-513	-439	4	5	0	-8306	-7972	-334
1	1	0	2413	4431	-2018				-3622	-3257	-365	5	5	0	8782	7993	784
2	1	0	7020	7121	-101	1	3	0	10,604	10,741	-137	7	5	0	5083	4501	582
3	1	0	3611	3490	121	2	3	0	3288	3389	-101	8	5	0	-3813	-3733	-80
4	1	0	1324	1638	-314	4	3	0	-12,306	-12,161	-145	9	5	0	-1898	-1607	-291
5	1	0	-2752	-2929	177	5	3	0	-1849	-1828	-21	10	5	0	-2451	-2095	-356
6	1	0	-10,560	-10,330	-230	6	3	0	-16,858	-16,716	-142	11	5	0	4432	3889	543
7	1	0	-8968	-8727	-241	8	3	0	-5324	-4946	-378	12	5	0	5739	5583	156
8	1	0	-908	-721	-187	9	3	0	-6215	-5403	-812	14	5	0	4612	4645	-35
10	1	0	5745	6012	-267	10	3	0	5333	7989	344	16	5	0	-1203	-1203	0
11	1	0	-2205	-2219	14	12	3	0	5499	5799	-300	17	5	0	-6976	-6666	-310
12	1	0	1521	1456	65	14	3	0	952	370	582	18	5	0	-1378	-825	-553
13	1	0	-10,801	-10,128	-673	15	3	0	1340	1555	-215	19	5	0	-2062	-2300	247
14	1	0	-2500	-2086	-414	16	3	0	1614	2178	-564	20	5	0	3458	2496	962
15	1	0	-1674	-1525	-149	17	3	0	-1532	-1429	-103	21	5	0	-941	-1172	231
17	1	0	8032	8178	-146	18	3	0	4585	4294	291	22	5	0	-2878	-2568	-310
18	1	0	1772	1437	335	20	3	0	-919	-1081	162	24	5	0	-2520	-1662	-658
19	1	0	2281	2702	-421	21	3	0	2763	2583	180	25	5	0	1816	1561	255
20	1	0	-908	-1299	391	22	3	0	-2440	-2422	-18						
21	1	0	-1072	-472	-600	24	3	0	-2949	-3142	193	0	6	0	-12,371	-13,213	842
22	1	0	-2434	-2495	59	25	3	0	-1280	-1409	129	1	6	0	-1526	-1756	230
23	1	0	-946	-904	-42	26	3	0	984	651	333	2	6	0	-7321	-6870	-451
24	1	0	-1712	-1507	-205	28	3	0				3	6	0	-4092	-4468	376
25	1	0	1187	857	330							4	6	0	5345	5323	22
27	1	0	-1285	-1171	-114	0	4	0	-8256	-8620	364	5	6	0	-776	-117	-659
29	1	0	-2631	-2436	-195	1	4	0	13,843	13,879	-36	6	6	0	1389	1842	47
						2	4	0	-9094	-8660	-434	7	6	0	-979	-755	-294
0	2	0	13,942	14,330	-397	3	4	0	8360	7782	-578	8	6	0	-1772	-1652	-120
* 1	2	0	-1873	-359	-1114	4	4	0	10,462	10,574	-112	9	6	0	3879	3942	-63
2	2	0	-3392	-3181	-211	5	4	0	-14,735	-14,346	-389	10	6	0	7151	7345	-194
3	2	0	-7080	-7343	263	6	4	0	1008	1318	-312	12	6	0	-2292	-2370	78
4	2	0	-3605	-3865	60	7	4	0	-8054	-7754	-300	14	6	0	2686	2307	370
5	2	0	-13,126	-13,046	-80	8	4	0	-11,206	-10,401	-805	15	6	0	4448	4436	12
6	2	0	-11,447	-11,688	241	9	4	0	1105	1184	-79	16	6	0	-3950	-3735	-215
7	2	0	-16,800	-16,622	-287	10	4	0	1510	1544	-34	17	6	0	1800	2237	-437
8	2	0	-2270	-2284	14	11	4	0	11,550	9956	1594	18	6	0	-4514	-4138	-376
10	2	0	-3012	-3453	-459	12	4	0	6325	6041	284	19	6	0	-2292	-2638	346
11	2	0	12,798	12,863	-65	13	4	0	3819	3822	197	22	6	0	-766	-1148	382
12	2	0	-5646	-6521	876	14	4	0	-3266	-3363	-903						
13	2	0	3950	3534	416	15	4	0	2155	2650	-504						
14	2	0	3283	3561	-278												

TABLE I. (Continued.)

<i>h</i>	<i>k</i>	<i>l</i>	100 <i>F</i> _o	100 <i>F</i> _c	100 Δ	<i>h</i>	<i>k</i>	<i>l</i>	100 <i>F</i> _o	100 <i>F</i> _c	100 Δ	<i>h</i>	<i>k</i>	<i>l</i>	100 <i>F</i> _o	100 <i>F</i> _c	100 Δ
23	6	0	749	535	214	9	9	0	4705	5355	-650	2	12	0	2620	2822	-202
27	6	0	-1652	-1319	-335	10	9	0	-4333	-3730	-603	3	12	0	4142	4683	-541
28	6	0	1088	1171	-83	11	9	0	705	682	23	4	12	0	2588	2651	-63
						12	9	0	-6139	-5862	-277	6	12	0	-1690	-1412	-278
1	7	0	-10,423	-9511	-912	13	9	0	-2330	-2912	582	7	12	0	-1198	-1484	286
2	7	0	-7463	-7237	-226	14	9	0	-1181	-1443	262	9	12	0	1214	1028	186
3	7	0	4021	4805	-784	15	9	0	-930	-1407	477	11	12	0	1220	988	232
5	7	0	6396	5976	420	16	9	0	2106	1697	409	13	12	0	-2878	-3046	168
6	7	0	7397	7260	137	17	9	0	771	508	263	15	12	0	-2965	-2828	-137
7	7	0	6571	6150	421	21	9	0	-1794	-1731	-63	16	12	0	1045	1360	-315
8	7	0	3704	3860	-156	22	9	0	2062	2433	-371	18	12	0	1778	1501	277
9	7	0	5592	5977	-385	24	9	0	1729	1751	-22	19	12	0	815	965	-150
10	7	0	-6198	-5367	-832	25	9	0	1302	1282	20	20	12	0	634	540	94
11	7	0	6856	7713	-857	28	9	0	-667	-606	-61						
13	7	0	2144	2091	53							1	13	0	2232	1895	337
14	7	0	3988	3943	45	0	10	0	5077	5397	-320	3	13	0	1532	1377	155
15	7	0	-3135	-3012	-123	1	10	0	-2221	-1836	-385	7	13	0	-1290	-1078	-142
16	7	0	2019	1661	558	3	10	0	2839	2924	-35	8	13	0	-1636	-1828	192
17	7	0	-2910	-2498	-412	4	10	0	-3813	-3927	114	9	13	0	-1811	-2047	236
18	7	0	-2703	-2735	80	5	10	0	7813	7792	21	11	13	0	-1428	-1778	350
22	7	0	2385	2157	228	6	10	0	-1367	-1632	265	16	13	0	-1843	-1801	-42
						7	10	0	3332	3647	-315	20	13	0	1127	1230	-103
						8	10	0	3151	3514	-363	21	13	0	891	966	-75
1	8	0	-3107	-2952	-155	9	10	0	-875	-912	37						
2	8	0	-5006	-4736	-270	11	10	0	1384	1534	-150	0	14	0	2440	1908	532
3	8	0	-3233	-3248	15	12	10	0	-2051	-2327	276	1	14	0	1543	1666	-123
4	8	0	-3596	-3706	179	13	10	0	-1198	-1135	-63	2	14	0	1444	1302	142
5	8	0	5860	6032	-172	14	10	0	-1532	-1898	366	3	14	0	1543	1741	-198
7	8	0	7419	7324	95	15	10	0	-2615	-2842	227	4	14	0	1805	2175	-370
8	8	0	6998	6858	340	16	10	0	1811	1770	41	5	14	0	-1329	-1812	483
9	8	0	-6166	-5454	-719	17	10	0	-1882	-2126	244	7	14	0	-935	-1422	487
10	8	0	1225	1404	-179	20	10	0	-1149	-1154	5	8	14	0	-3042	-3055	13
11	8	0	-3534	-3367	-167	21	10	0	853	1300	-447	9	14	0	1192	1563	-371
12	8	0	1083	766	322	22	10	0	-667	-791	124	10	14	0	-1898	-2370	472
14	8	0	2812	2062	750							11	14	0	1269	1180	89
16	8	0	1192	642	550	1	11	0	2380	2551	-171	13	14	0	-1116	-1254	138
17	8	0	-1876	-2162	286	2	11	0	5586	6064	-478						
18	8	0	-2987	-3189	202	3	11	0	-3354	-3830	476	1	15	0	-919	-1058	139
19	8	0	-1729	-1338	-403	4	11	0	3868	4195	-327	2	15	0	-1061	-881	-180
20	8	0	-2424	-2126	-298	5	11	0	-3764	-3685	-79	3	15	0	1296	1532	-236
22	8	0	-1160	-1337	177	6	11	0	1143	886	257	5	15	0	1285	1258	27
23	8	0	1116	859	237	8	11	0	3228	2735	493	7	15	0	-1630	-1498	-132
						10	11	0	1849	1697	152	14	15	0	973	1169	-196
1	9	0	-2648	-2166	-482	11	11	0	-2697	-2971	274	19	15	0	815	742	73
2	9	0	3611	3086	525	12	11	0	-2101	-1581	-320	3	16	0	-1789	-1821	32
3	9	0	-2172	-2224	52	13	11	0	-941	-1442	501	14	16	0	1170	687	483
4	9	0	1811	1715	96	14	11	0	-1811	-2326	515	* 16	16	0	880	108	772
5	9	0	-2358	-2780	422	17	11	0	1683	1386	299						
6	9	0	2172	2333	-161							1	18	0	-651	-1028	377
7	9	0	2768	3389	-621	0	12	0	2817	3200	-383	3	18	0	-1335	-1593	258
8	9	0	3584	3199	385	1	12	0	2817	3061	-244	9	18	0	-824	-956	114
												10	18	0	470	499	-29

bromine atoms being located from the *c*-axis projection of the Patterson function. Successive cycles of electron-density and structure-factor calculations were carried out. The lighter atoms (with the exception of the solvent) were thus located and the *R* factor fell to 0.21. (Inclusion of one molecule of acetone in an unexplained region of high electron density caused *R* to fall to 0.17. Further refinement of the *X* and *Y* co-ordinates by the least-squares method gave a

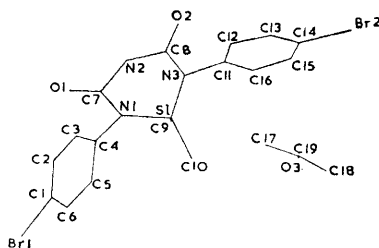


FIG. 2. The labelling of the atoms.

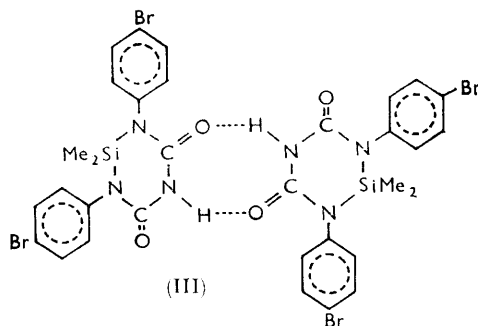
final *R* value of 0.087 for the *h**k**l* planes; 287 planes were used in the final cycle of calculations. Three separate isotropic temperature factors ($U = B/8\pi^2$) were used: one for the bromine atoms ($U = 0.0753 \text{ \AA}^2$), one for the acetone molecule ($U = 0.1600 \text{ \AA}^2$), and one for the remaining atoms ($U = 0.0572 \text{ \AA}^2$). The final list of F_o , F_c , and Δ is shown in Table I.

TABLE 2.

Atomic co-ordinates and σ (rms) in Å.

	<i>X</i>	<i>Y</i>	σ (rms)		<i>X</i>	<i>Y</i>	σ (rms)
Br1	—1.3634	13.9399	0.0052	C6	0.1078	12.8211	0.0373
Br2	9.6302	6.0102	0.0051	C7	1.0058	8.6816	0.0378
Si	3.4801	9.4472	0.0117	C8	3.1374	7.1702	0.0386
O1	—0.1305	8.7421	0.0244	C9	3.5382	9.5356	0.0379
O2	3.5137	6.1830	0.0253	C10	4.3759	10.8389	0.0376
O3	8.1356	10.8260	0.0482	C11	5.2437	7.3811	0.0386
N1	1.7559	9.4696	0.0305	C12	5.4036	6.7489	0.0370
N2	1.7813	7.5756	0.0318	C13	6.8164	6.3519	0.0383
N3	3.8636	7.9386	0.0297	C14	7.8117	6.5499	0.0380
C1	—0.4687	12.4856	0.0388	C15	7.5632	7.1079	0.0394
C2	—0.4995	11.2124	0.0366	C16	6.2582	7.6367	0.0382
C3	0.2100	10.3019	0.0375	C17	6.8496	10.2212	0.0746
C4	0.9255	10.4802	0.0387	C18	9.1104	11.0067	0.0740
C5	0.9014	11.8410	0.0383	C19	8.0965	10.3667	0.0742

Fig. 1 shows the electron density of the *c*-axis projection. This map is based on 285 observed structure factors and shows clearly that the dibromo-compound has a six-membered central ring corresponding to the structure (I). There are four molecules in the cell and the *X* and *Y* co-ordinates of the one which is outlined are given in Table 2. The *X* and *Y* co-



ordinates of one of the four acetone molecules, indicated by crosses in Fig. 1, are also listed in Table 2, which includes the root mean square standard deviations of the atomic co-ordinates. The labelling of the atoms is shown in Fig. 2. The proximity of the O1 and N1 atoms to the centre of symmetry and the shortness of the *c*-axis suggest that, in the solid state, the molecules are held together in pairs by hydrogen bonds (see III).

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