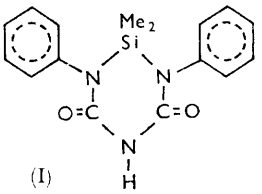
953. *The Chemistry of the Silicon–Nitrogen Bond. Part VI.*[1] *The Molecular Structure of* 2,6-*Di*-p-*bromophenyl*-1,1-*dimethyl*-1-*sila*-2,4,6-*triazacyclohexane*-3,5-*dione.*

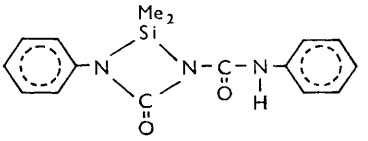
By J. J. Daly and W. Fink.

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 hexamethylcyclotrisilazane [2] 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



(I)



(II)

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

Experimental

$C_{16}H_{15}Br_2N_3O_2Si,CH_3{\cdot}CO{\cdot}CH_3$. $M = 527{\cdot}3$. Monoclinic. $a = 25{\cdot}33$, $b = 15{\cdot}04$, $c = 6{\cdot}10$ Å, $\beta = 99°37'$, $U = 2291$ A^3. $D_c = 1{\cdot}53$ g./c.c., $D_m = 1{\cdot}5$ 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° 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). $C_{16}H_{15}Br_2N_3O_2Si,C_3H_6O$ 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 photographicaly 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.

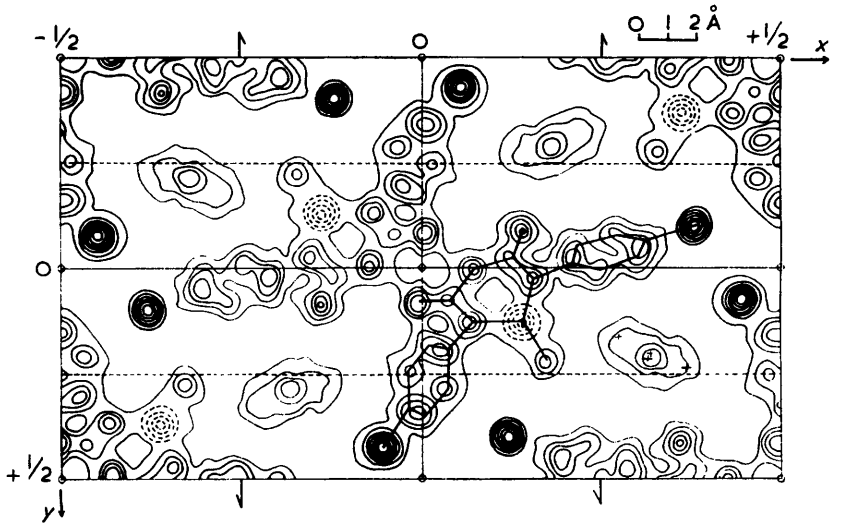


FIG. 1. The electron density of the *c*-axis projection. Contours on bromine at intervals of $8e/A^2$; contours on Si, dashed lines, at intervals of $5e/A^2$; contours on other atoms at $2{\cdot}5e/A^2$.

TABLE 1.

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

h	*k*	*l*	100 F_o	100 F_c	100 Δ	*h*	*k*	*l*	100 F_o	100 F_c	100 Δ	*h*	*k*	*l*	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	−1636	−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	628	307						
24	0	0	1214	1080	134	25	2	0	−913	−1095	180	1	5	0	−9592	−9212	−380
						27	2	0	2511	1749	762	2	5	0	−9170	−9228	58
1	1	0	2413	4431	−2018	31	2	0	−952	−513	−439	3	5	0	952	1151	−199
2	1	0	7020	7121	−101							4	5	0	−8306	−7972	−334
3	1	0	3611	3490	121	1	3	0	−3622	−3257	−365	5	5	0	8782	7998	784
4	1	0	1324	1638	−314	2	3	0	10,604	10,741	−137	7	5	0	5083	4501	582
5	1	0	−2752	−2929	177	3	3	0	3288	3389	−101	8	5	0	−3813	−3733	−80
6	1	0	−10,560	−10,330	−230	4	3	0	−12,306	−12,161	−145	9	5	0	−1898	−1607	−291
7	1	0	−8968	−8727	−241	5	3	0	−1849	−1828	−21	10	5	0	−2451	−2095	−356
8	1	0	−908	−721	−187	6	3	0	−16,858	−16,716	−142	11	5	0	4432	3889	543
10	1	0	5745	6012	−267	8	3	0	−5324	−4946	−378	12	5	0	5417	5526	−109
11	1	0	−2205	−2219	14	9	3	0	−6215	−5403	−812	13	5	0	5739	5583	156
12	1	0	1521	1456	65	10	3	0	8333	7989	344	14	5	0	4612	4645	−33
13	1	0	−10,801	−10,128	−673	12	3	0	5499	5799	−300	16	5	0	−1205	−1203	0
14	1	0	−2500	−2086	−414	14	3	0	952	370	582	17	5	0	−6976	−6666	−310
15	1	0	−1674	−1525	−149	15	3	0	1340	1555	−215	18	5	0	−1378	−825	−553
17	1	0	8032	8178	−146	16	3	0	1614	2178	−564	19	5	0	−2062	−2309	247
18	1	0	1772	1437	335	17	3	0	−1532	−1429	−103	21	5	0	3458	2496	962
19	1	0	2281	2702	−421	18	3	0	4585	4294	291	22	5	0	−941	−1172	231
20	1	0	−908	−1299	391	20	3	0	−919	−1081	162	24	5	0	−2878	−2568	−310
21	1	0	−1072	−472	−600	21	3	0	2763	2583	180	25	5	0	−2320	−1662	−658
22	1	0	−2434	−2493	59	22	3	0	−2440	−2422	−18	29	5	0	1816	1561	255
23	1	0	−946	−904	−42	24	3	0	−2949	−3142	193						
24	1	0	−1712	−1507	−205	25	3	0	−1280	−1409	129	0	6	0	−12,371	−13,213	842
25	1	0	1187	857	330	28	3	0	984	651	333	1	6	0	−1526	−1756	230
27	1	0	−1285	−1171	−114							2	6	0	−7321	−6870	−451
29	1	0	−2631	−2436	−195	0	4	0	−8256	−8620	364	3	6	0	−4092	−4468	376
						1	4	0	13,843	13,879	−36	4	6	0	5345	5323	22
0	2	0	15,942	14,339	−397	2	4	0	−9094	−8660	−434	*5	6	0	−776	−117	−659
*1	2	0	−1373	−259	−1114	3	4	0	−8360	−7782	−578	6	6	0	1389	1342	47
2	2	0	−3392	−3181	−211	4	4	0	10,462	10,574	−112	7	6	0	−979	−755	−224
3	2	0	−7080	−7343	263	5	4	0	−14,735	−14,346	−389	9	6	0	−1772	−1652	−120
4	2	0	−3605	−3665	60	6	4	0	1006	1318	−312	10	6	0	3879	3942	−63
5	2	0	−13,126	−13,046	−80	7	4	0	−8054	−7754	−300	12	6	0	7151	7345	−194
6	2	0	−11,447	−11,688	241	8	4	0	−11,206	−10,401	−805	13	6	0	−2292	−2370	78
7	2	0	−16,809	−16,522	−287	9	4	0	1105	1184	−79	14	6	0	2686	2307	379
8	2	0	−2270	−2284	14	10	4	0	1510	1544	−34	15	6	0	4448	4436	12
10	2	0	−3912	−3453	−459	11	4	0	11,550	9956	1594	16	6	0	−3950	−3735	−215
11	2	0	12,798	12,863	−65	12	4	0	6325	6041	284	17	6	0	1800	2237	−437
12	2	0	−5646	−6521	875	13	4	0	3819	3622	197	18	6	0	−4514	−4138	−376
13	2	0	3950	3534	416	14	4	0	−3266	−2363	−903	19	6	0	−2292	−2638	346
14	2	0	3283	3561	−278	15	4	0	2155	2659	−504	22	6	0	−766	−1148	382

TABLE 1. (*Continued.*)

h	*k*	*l*	100 F_o	100 F_c	100 Δ
23	6	0	749	535	214
27	6	0	−1652	−1319	−333
28	6	0	1088	1171	−83
1	7	0	−10,423	−9511	−912
2	7	0	−7463	−7237	−226
3	7	0	4021	4805	−784
5	7	0	6396	5976	420
6	7	0	7397	7260	137
7	7	0	6571	6150	421
8	7	0	3704	3860	−156
9	7	0	5592	5977	−385
10	7	0	−6199	−5367	−832
11	7	0	6856	7713	−857
13	7	0	2144	2091	53
14	7	0	3988	3943	45
15	7	0	−3135	−3012	−123
16	7	0	2019	1661	358
17	7	0	−2910	−2498	−412
18	7	0	−2703	−2783	80
22	7	0	2385	2157	228
1	8	0	−3107	−2952	−155
2	8	0	−5006	−4736	−270
3	8	0	−3233	−3248	15
4	8	0	−8536	−8706	170
5	8	0	5860	6032	−172
7	8	0	7419	7324	95
8	8	0	6998	6658	340
9	8	0	−6166	−5454	−712
10	8	0	1225	1404	−179
11	8	0	−3534	−3367	−167
12	8	0	1088	766	322
14	8	0	2812	2062	750
16	8	0	1192	642	550
17	8	0	−1876	−2162	286
18	8	0	−2987	−3189	202
19	8	0	−1729	−1326	−403
20	8	0	−2424	−2126	−298
22	8	0	−1160	−1337	177
23	8	0	1116	859	257
1	9	0	−2648	−2166	−482
2	9	0	3611	3086	525
3	9	0	−2172	−2224	52
4	9	0	1811	1715	96
5	9	0	−2358	−2780	422
6	9	0	2172	2333	−161
7	9	0	2768	3389	−621
8	9	0	3584	3199	385
9	9	0	4705	5355	−650
10	9	0	−4333	−3730	−603
11	9	0	705	682	23
12	9	0	−6139	−5862	−277
13	9	0	−2330	−2912	582
14	9	0	−1181	−1443	262
15	9	0	−930	−1407	477
16	9	0	2106	1697	409
17	9	0	771	508	263
21	9	0	−1794	−1731	−63
22	9	0	2062	2433	−371
24	9	0	1729	1751	−22
25	9	0	1302	1282	20
28	9	0	−667	−606	−61
0	10	0	5077	5397	−320
1	10	0	−2221	−1836	−385
3	10	0	2889	2924	−35
4	10	0	−3813	−3927	114
5	10	0	7813	7792	21
6	10	0	−1367	−1632	265
7	10	0	3332	3647	−315
8	10	0	3151	3514	−363
9	10	0	−875	−912	37
11	10	0	1384	1534	−150
12	10	0	−2051	−2327	276
13	10	0	−1198	−1135	−63
14	10	0	−1532	−1898	366
15	10	0	−2615	−2842	227
16	10	0	1811	1770	41
17	10	0	−1882	−2126	244
20	10	0	−1149	−1154	5
21	10	0	853	1300	−447
22	10	0	−667	−791	124
1	11	0	2380	2551	−171
2	11	0	5586	6064	−478
3	11	0	−3354	−3830	476
4	11	0	3868	4195	−327
5	11	0	−3764	−3685	−79
6	11	0	1143	886	257
8	11	0	3228	2735	493
10	11	0	1849	1697	152
11	11	0	−2697	−2971	274
12	11	0	−2101	−1581	−520
13	11	0	−941	−1442	501
14	11	0	−1811	−2326	515
17	11	0	1685	1386	299
0	12	0	2817	3200	−383
1	12	0	2817	3061	−244
2	12	0	2620	2822	−202
3	12	0	4142	4683	−541
4	12	0	2588	2651	−63
6	12	0	−1690	−1412	−278
7	12	0	−1198	−1484	286
9	12	0	1214	1028	186
11	12	0	1220	988	232
13	12	0	−2878	−3046	168
15	12	0	−2965	−2828	−137
16	12	0	1045	1360	−315
18	12	0	1778	1501	277
19	12	0	815	965	−150
20	12	0	634	540	94
1	13	0	2232	1895	337
3	13	0	1532	1377	155
7	13	0	−1220	−1078	−142
8	13	0	−1636	−1828	192
9	13	0	−1811	−2047	236
11	13	0	−1428	−1778	350
16	13	0	−1843	−1801	−42
20	13	0	1127	1230	−103
21	13	0	891	966	−75
0	14	0	2440	1908	532
1	14	0	1543	1666	−123
2	14	0	1444	1302	142
3	14	0	1543	1741	−198
4	14	0	1805	2175	−370
5	14	0	−1329	−1812	483
7	14	0	−935	−1422	487
8	14	0	−3042	−3055	13
9	14	0	1192	1563	−371
10	14	0	−1898	−2370	472
11	14	0	1269	1180	89
13	14	0	−1116	−1254	138
1	15	0	−919	−1058	139
2	15	0	−1061	−881	−180
3	15	0	1296	1532	−236
5	15	0	1285	1258	27
7	15	0	−1630	−1498	−132
14	15	0	973	1169	−196
19	15	0	815	742	73
3	16	0	−1789	−1821	32
14	16	0	1170	687	483
* 16	16	0	880	108	772
1	18	0	−651	−1028	377
3	18	0	−1335	−1593	258
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

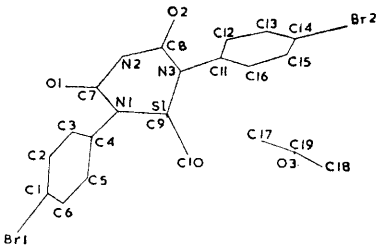


FIG. 2. The labelling of the atoms.

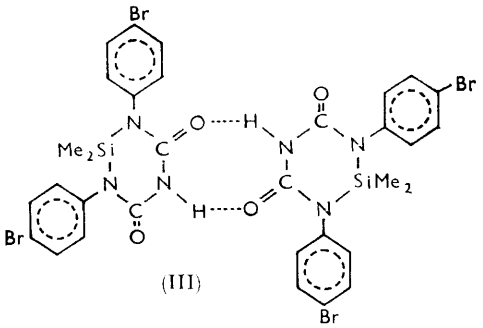
final *R* value of 0·087 for the *hkO* planes; 287 planes were used in the final cycle of calculations. Three separate isotropic temperature factors ($U = B/8\pi^2$) were used: one for the bromine atoms (U = 0·0753 Å^2), one for the acetone molecule (U = 0·1600 Å^2), and one for the remaining atoms (U = 0·0572 Å^2). The final list of F_o, F_c, and Δ is shown in Table 1.

TABLE 2.

Atomic co-ordinates and σ (rms) in Å.

	X	*Y*	σ (rms)		*X*	*Y*	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-



(III)

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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