

Molecular Packing and Metal Coordination in the Crystal Structure of Thallium(I) Diethyldithiocarbamate

HANS PRITZKOW^a and PER JENNISCHE^b

^a Institute of Inorganic Chemistry, University of Heidelberg, 69 Heidelberg 1, Im Neuenheimer Feld 7, Germany and ^b Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The crystal structure of thallium(I) diethyldithiocarbamate, $\text{Tl(I)S}_2\text{CN}(\text{C}_2\text{H}_5)_2$, has been determined from three-dimensional X-ray data collected on a 2-circle Weissenberg diffractometer. The crystals are triclinic, space group $P\bar{1}$, with four formula units in the cell. Unit cell parameters are $a=11.353(3)$ Å, $b=14.735(4)$ Å, $c=5.997(2)$ Å, $\alpha=99.80(3)^\circ$, $\beta=103.50(3)^\circ$ and $\gamma=91.22(3)^\circ$. The final R -value is 0.037.

The structure consists of dimeric molecules with four-fold Tl—S coordination which are linked in chains by weaker Tl—S bonds. The six coordinated sulfur atoms form elongated trigonal prisms. There are only van der Waals forces between the chains.

The dimeric molecules are similar to those in the methyl, propyl and isopropyl homologues, but the metal-ligand linkage between the dimers is quite different. The relation between metal coordination and molecular packing is discussed using packing surfaces obtained from a computer simulation program.

The crystal structures of the dipropyl-, diisopropyl- and dimethyldithiocarbamates of thallium(I)¹⁻³ were determined as part of a systematic investigation of compounds with the composition AX . The structures contain dimeric molecules which are linked by Tl—S coordination. Layers are formed in the methyl compound and chains in the propyl and isopropyl compounds. The central parts of the molecules are the same so that the type of linkage is determined by the alkyl groups. The determination of the structure of thallium(I) diethyldithiocarbamate was undertaken to increase the understanding of these structures.

EXPERIMENTAL

The sample was prepared by Dr. S. Åkerström. Colourless needles were obtained from benzene with [001] as principal axis. Weissenberg and precession photographs showed that most of the crystals were twinned. The crystals decomposed slowly, turning yellow after exposure to light or X-rays. The density was measured by flotation in aqueous K_2HgI_4 . The cell parameters were determined from single crystal photographs and refined to fit a Guinier-Hägg powder photograph taken with $\text{CuK}\alpha_1$ radiation and silicon for calibration ($a=5.4305$ Å).⁵ Crystal data are given in Table 1.

Three crystals were used because of the decomposition and they were all cut from a long crystal needle (cross section 0.15×0.16 mm²) to a length of appr. 0.3 mm. The crystals were mounted in identical orientation and were used for two layers each.

The STOE Weissenberg diffractometer was controlled by a PDP 8/E computer and equipped with a graphite monochromator for $\text{MoK}\alpha$ radiation. The equatorial layer was measured in $\omega-2\theta$ scan, the higher layers in ω scan. The

Table 1. Crystal data.

Formula unit: $\text{Tl(I)S}_2\text{CN}(\text{C}_2\text{H}_5)_2$
Diffraction symmetry: $\bar{1}$
Crystal system: triclinic
Unit cell parameters:
$a=11.353(3)$ Å, $b=14.735(4)$ Å, $c=5.997(2)$ Å,
$\alpha=99.80(3)^\circ$, $\beta=103.50(3)^\circ$, $\gamma=91.22(3)^\circ$
Cell volume: 959 Å ³
Density, measured: 2.41 g cm ⁻³ .
Number of formula units: 4
Density, calculated: 2.44 g cm ⁻³
Space group: $P\bar{1}$
Linear absorption coefficient ($\text{MoK}\alpha$):
173.6 cm ⁻¹

background was counted before and after the scan and the scanning speed was 0.6°/min. The scanning interval was constant in the two lowest layers, $\Delta\omega = 1.3$ and 1.6° , and calculated as $\Delta\omega = A + B \sin \mu \tan(v/2)$ in the higher layers (μ is the equi-inclination angle and v the counter angle). A and B were determined for each layer from the intensity profiles of a few reflections. Pre-scans were performed to determine if the reflections should be skipped or measured with attenuation filters. Two test reflections were measured in each layer after every twenty reflections. Their densities decreased by about 5 % during the two days needed for the layer.

1900 reflections with θ less than 20° (sin $\theta/\lambda = 0.48 \text{ \AA}^{-1}$) were measured in the layers hkl to $hkl5$ and 440 reflections at higher angles in

the two highest layers. The intensities were corrected for Lorentz and polarization effects, including monochromator polarization, and for absorption. 180 of the 2340 reflections were excluded since their intensities were less than the estimated standard deviations, $\sigma_1 = (N + 0.05^2 I^2)^{1/2}$. Approximate relative scale factors were obtained from measurements of certain hkl reflections for each crystal.

DETERMINATION OF THE STRUCTURE

The thallium positions were determined from a three-dimensional Patterson synthesis. A difference synthesis revealed the positions of the remaining atoms except the hydrogens and the

Table 2. Atomic coordinates and thermal parameters, B or β_{ij} . The anisotropic temperature factor is defined as $\exp(-h^2\beta_{11} - 2hk\beta_{12} - \dots)$.

Atom	x	y	z	$B(\text{\AA}^2)$		
Dimer A						
Tl	-0.06677(4)	0.04093(3)	0.24175(7)			
S1	0.2078(3)	0.0136(2)	0.2757(6)			
S2	0.0307(2)	-0.1477(2)	0.1376(5)			
C1	0.1765(8)	-0.1014(7)	0.2644(15)			4.2(2)
N1	0.2630(7)	-0.1547(5)	0.3442(13)			4.6(2)
C2	0.2393(12)	-0.2568(9)	0.3294(22)			7.1(3)
C3	0.3908(10)	-0.1191(8)	0.4439(19)			5.9(2)
C4	0.2502(15)	-0.3082(12)	0.0969(29)			9.8(4)
C5	0.4204(15)	-0.0957(12)	0.7153(27)			9.5(4)
Dimer B						
Tl	0.42802(4)	0.46184(3)	0.19590(7)			
S1	0.2951(3)	0.5065(2)	0.5838(6)			
S2	0.4483(2)	0.3470(2)	0.5735(5)			
C1	0.3136(8)	0.3934(6)	0.6004(15)			4.1(2)
N1	0.2250(7)	0.3395(6)	0.6365(14)			5.0(2)
C2	0.2325(12)	0.2385(9)	0.6348(21)			6.7(3)
C3	0.1084(11)	0.3769(9)	0.6743(20)			6.6(3)
C4	0.2902(13)	0.2170(10)	0.8773(23)			7.6(3)
C5	0.0197(17)	0.3691(13)	0.4409(33)			11.0(5)
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Dimer A						
Tl	0.01266(5)	0.00793(3)	0.0419(2)	0.00487(3)	0.00845(7)	0.00507(5)
S1	0.0098(3)	0.0035(2)	0.064(1)	0.0007(2)	0.0004(4)	0.0026(3)
S2	0.0069(3)	0.0050(2)	0.060(1)	0.0005(2)	0.0023(4)	0.0046(3)
Dimer B						
Tl	0.01135(5)	0.00693(3)	0.03916(2)	-0.00209(3)	0.00395(6)	0.00185(5)
S1	0.0089(2)	0.0038(1)	0.064(1)	0.0013(1)	0.0089(5)	0.0037(4)
S2	0.0073(3)	0.0048(2)	0.062(1)	0.0012(2)	0.0068(4)	0.0044(3)

Table 3. Observed and calculated structure amplitudes. Reflections marked with an asterisk were not included in the refinement.

M	K	L	O	P	M	K	L	O	P	M	K	L	O	P	M	K	L	O	P	M	K	L	O	P			
				0																							
2	0	1261	1295	-3	-7	1763	1702	-7	-10	443	448	-3	-3	1756	1802	4	3	311	309	-2	11	249	246	7	-7	73	83
2	0	254	249	-3	-7	1840	1555	-10	-10	421	403	-2	-2	536	594	3	3	397	390	-1	11	322	326	8	-7	205	174
2	0	271	259	-2	-7	1109	1349	-5	-10	219	234	-5	-10	219	234	3	3	849	811	0	10	363	362	-10	-4	144	146
0	0	326	323	0	7	1538	1483	-3	-10	158	133	-3	-3	903	946	7	3	656	679	2	11	377	27	-8	-6	375	356
0	0	1099	1000	2	0	733	1163	-1	-10	738	733	-3	-3	2245	2225	-10	-4	938	927	-6	11	163	172	-6	-6	345	347
0	0	190	184	3	7	562	581	3	-10	245	239	3	-10	276	264	-9	-4	833	861	3	11	525	523	-9	-6	1212	1202
0	0	1259	1090	2	0	1378	1393	-1	-10	426	435	5	-3	666	639	9	4	689	678	-8	12	126	118	-6	-4	381	390
0	0	331	37	3	7	111	104	2	-10	722	688	6	-3	733	687	-7	-4	938	948	-6	12	95	505	-3	-6	1095	1079
-10	0	154	176	6	7	307	376	3	-10	398	303	7	3	254	219	-4	-4	293	252	-3	12	71	33	-2	-1	402	332
-10	0	1	94	3	0	451	3	0	-10	545	529	8	-3	216	207	-5	-3	1044	1022	0	12	231	238	1	-4	958	939
-7	1	1458	1456	-7	8	203	184	6	-10	558	552	-10	-2	463	430	-2	-4	614	610	1	12	95	64	-2	-6	86	84
-4	1	356	346	-6	8	208	224	-6	-10	468	441	-9	-2	155	185	-1	-1	2366	2388	2	12	415	444	3	-6	1389	1410
-4	1	612	626	-6	8	1076	1061	-7	-10	444	433	-8	-2	136	135	0	4	142	145	3	12	168	159	6	-8	483	465
-4	1	960	978	-6	8	33	2	-4	-10	405	425	-7	-2	593	593	1	4	1776	1071	-3	13	476	480	5	-2	321	339
-4	1	473	444	-3	8	1353	1362	-5	-10	372	371	-4	-2	776	767	2	4	776	760	-2	13	124	137	6	-6	624	615
-4	1	517	523	-2	8	552	559	-4	-10	176	156	-5	-2	276	269	3	4	541	528	-1	13	202	183	7	-4	114	126
-2	1	630	648	-1	8	700	692	-3	-10	568	528	-4	-2	2599	2242	4	4	443	461	0	13	165	156	8	-6	30	20
0	1	390	370	0	8	134	146	-2	-10	358	343	-3	-2	203	178	5	4	894	873	1	13	334	364	9	-6	353	373
0	1	758	844	2	8	929	874	2	-10	3	2	118	2	103	104	6	6	885	866	6	13	522	522	-10	-3	251	262
0	1	571	595	2	8	728	710	0	-10	1313	1323	-1	-2	371	367	7	4	819	896	1	12	9	2	-9	-5	200	171
0	1	577	590	3	8	1201	1249	1	-10	432	437	0	-2	379	353	8	4	163	162	-3	-14	76	17	-8	-5	142	137
0	1	1362	1376	3	8	37	74	2	-10	90	82	1	-2	721	632	9	4	467	463	-3	-14	76	17	-8	-5	552	543
0	1	217	214	3	8	868	842	3	-10	545	531	2	-2	1831	1824	-10	5	477	473	-2	-14	345	352	-6	-3	751	71
0	1	434	423	6	8	480	488	6	-10	466	459	3	-2	241	223	-9	5	205	197	-1	-14	355	11	-5	-3	395	404
-10	1	184	184	2	8	148	148	2	-10	518	503	-2	-2	169	172	-8	2	722	628	0	-12	61	6	-4	-3	114	126
-10	1	398	397	8	8	313	296	6	-10	752	744	5	-2	129	128	-7	5	413	406	-1	-14	103	91	-2	-5	212	191
-10	1	349	348	-8	8	174	171	7	-10	272	272	6	-2	96	110	-6	-6	966	960	-2	-14	388	26	-2	-2	323	294
-10	1	1234	1048	-2	8	288	283	-2	-10	391	398	-2	-2	391	398	-2	-2	117	117	5	-13	751	3	-3	-3	114	126
-10	1	293	302	-6	8	248	274	-8	-10	245	261	8	-2	419	410	-4	-4	249	239	-4	-13	288	6	-3	-5	409	393
-10	1	1849	1839	-3	8	948	938	-7	-10	711	722	9	-2	109	88	-3	-3	353	337	-3	-13	402	306	1	-3	290	299
-10	1	1094	1021	-2	8	1176	1176	-4	-10	317	317	-4	-4	1176	1176	-4	-4	1176	1176	-4	-13	402	306	1	-3	290	299
-10	1	512	449	-3	8	572	594	-3	-10	293	305	-10	-1	103	57	-1	-1	114	114	-1	-13	606	603	3	-2	381	301
-10	1	1849	1839	-3	8	930	923	-4	-10	381	375	-9	-1	479	468	0	0	2160	2253	0	-13	255	57	6	-6	1035	1043
-10	1	1536	1548	-2	8	704	725	-3	-10	213	232	-6	-6	213	232	-6	-6	213	232	-6	-13	406	246	-10	-4	286	286
-10	1	1123	1130	0	8	109	9	-2	-10	307	291	-7	-1	80	95	2	2	1005	1028	-2	-13	88	99	6	-5	232	280
-10	1	1002	1039	1	8	927	923	-1	-10	1456	1473	-4	-1	80	92	3	3	251	259	-3	-13	95	50	7	-5	622	639
-10	1	1249	1203	4	8	451	451	4	-10	332	346	0	-1	166	166	-2	-2	166	166	-2	-13	406	246	-10	-4	286	286
-10	1	1610	1593	3	8	666	659	1	-10	1118	1166	-4	-1	144	167	5	5	440	436	-5	-12	159	188	-10	-4	70	85
-10	1	966	955	6	8	669	687	2	-10	366	378	-3	-3	1677	1671	6	6	819	863	-2	-12	296	297	-9	-6	93	66
-10	1	1311	1348	2	8	246	264	2	-10	278	278	1	-1	278	278	1	1	278	278	1	-12	246	246	-10	-4	286	286
-10	1	937	951	6	8	17	87	6	-10	470	461	-1	-1	79	60	8	8	567	573	-2	-12	693	686	-7	-4	516	516
-10	1	341	357	7	8	278	287	5	-10	678	666	0	-1	47	64	9	9	198	186	-1	-12	179	40	-6	-6	652	689
-10	1	764	731	-2	8	107	191	6	-10	518	503	-2	-2	249	249	-10	-10	249	249	-10	-12	616	138	-10	-3	749	749
-10	1	180	146	-10	8	954	958	7	-10	956	956	2	-1	116	112	-10	-10	640	653	-1	-12	178	169	-4	-2	52	70
-10	1	123	130	-10	8	396	363	0	-10	244	216	3	-1	2440	2300	-9	-9	378	382	-2	-12	302	313	-3	-6	1176	1179
-10	1	273	243	-10	8	133	113	-8	-10	232	232	-2	-2	339	300	-3	-3	339	300	-3	-12	402	402	-10	-4	121	126
-10	1	153	180	-3	8	1050	813	-8	-10	741	756	5	-1	649	685	-6	-6	451	461	-4	-12	233	229	-1	-4	62	57
-10	1	79	86	-2	10	485	403	-7	-10	373	425	6	-1	44	44	-2	-2	653	636	-9	-12	90	110	0	-6	1388	1423
-10	1	1295	1297	-1	10	298	350	-4	-10	596	588	37	-7	887	875	-7	-7	181	175	-7	-12	116	75	-7	-7	136	143
-10	1	756	724	0	10	483	480	-5	-10	473	475	8	-1	346	33	-3	-3	729	690	-5	-11	118	131	2	-10	140	163
-10	1	616	689	1	10	92	122	-4	-10	73	68	9	-1	597	566	-2	-2	296	279	-5	-11	121	102	3	-6	16	

Table 3. Continued.

M	K	10FO	10FC	M	K	10FO	10FC	M	K	10FO	10FC	M	K	10FO	10FC	M	K	10FO	10FC	
2	0	376	319	2	7	965	969	7	132	341	342	7	-3	340	329	0	4	60	64	
0	0	900	916	4	7	11	11	0	4	726	725	0	4	726	725	0	4	726	725	
0	0	473	469	4	7	753	757	-8	-9	250	223	0	2	17	82	-8	-11	77	75	
5	0	631	644	5	7	182	177	-9	-9	338	343	-11	-2	76	31	3	4	287	301	
0	0	1017	1018	6	7	32	13	-9	-9	184	176	-10	-2	361	358	-6	5	214	218	
7	0	633	646	7	7	314	303	-3	-3	356	343	-9	-2	259	254	5	4	498	508	
0	0	369	365	-9	0	306	294	-4	-4	194	195	-8	-2	58	63	6	4	223	229	
0	0	138	121	-8	0	278	291	-3	-3	153	83	-7	-2	359	34	7	4	398	402	
-11	-1	336	30	-7	0	180	201	-2	-2	1096	1095	-6	-2	1262	1075	8	4	136	116	
-10	-1	106	93	-8	0	293	287	-1	-1	68	77	-5	-2	78	87	-10	5	402	421	
-9	-1	704	706	-5	0	753	757	0	0	821	821	-4	-3	1232	1297	-9	5	235	233	
-9	-1	284	275	-4	0	528	532	1	-1	256	247	-3	-2	271	265	-8	5	432	444	
-7	-1	1138	1147	-3	0	787	756	2	-1	94	93	-2	-2	447	450	-7	5	238	239	
-6	-1	866	866	-2	0	756	763	3	-1	288	308	-1	-2	361	338	-6	5	413	427	
-5	-1	405	394	-1	0	54	60	4	-4	443	434	0	-2	931	930	-5	5	209	51	
-5	-1	661	631	0	0	762	735	5	-9	238	252	1	-2	82	85	-4	5	399	401	
-3	-1	567	559	1	0	564	593	3	-8	661	678	2	-2	1425	1460	-3	9	76	80	
-2	-1	986	992	2	0	589	574	7	-9	179	152	3	-2	119	123	-2	5	1027	1026	
-2	-1	1476	2082	3	0	915	924	-10	-8	179	165	6	-2	741	798	-1	5	65	32	
0	1	1006	1011	4	0	263	268	-8	-8	586	565	5	-2	50	3	0	5	807	823	
1	1	478	485	5	0	43	73	-8	-8	234	227	6	-2	178	192	1	5	155	143	
1	1	730	735	6	0	255	250	-7	-7	370	359	7	-2	46	89	2	5	85	89	
1	1	296	301	6	0	238	238	-6	-6	159	197	8	-2	335	353	3	5	191	181	
4	1	813	837	-7	0	414	418	-5	-5	116	99	9	-2	259	12	4	5	908	584	
4	1	768	791	-6	0	275	267	-6	-6	311	33	-11	-1	374	373	5	5	274	268	
5	1	216	213	-9	0	33	39	-3	-3	966	828	-9	-1	259	234	6	5	373	391	
7	1	329	343	-9	0	620	620	-2	-2	61	68	-8	-1	61	62	7	5	45	7	
8	1	222	229	-3	0	640	637	-1	-1	1425	1431	-7	-1	666	665	-10	6	66	56	
8	1	704	706	-5	0	753	757	0	0	821	821	-4	-3	1232	1297	-9	5	235	233	
-11	-2	251	237	-1	0	609	653	1	-8	485	491	-5	-14	1543	1543	-8	6	277	305	
-10	-2	180	199	0	0	309	292	-2	-2	62	69	-6	-1	151	137	-7	6	756	766	
-9	-2	847	849	1	0	727	731	-4	-4	187	201	-1	-1	172	181	-1	5	192	201	
-8	-2	923	910	2	0	246	241	-6	-6	83	64	-2	-1	173	168	-5	6	239	253	
-8	-2	563	537	3	0	126	113	5	-8	483	485	0	-1	33	51	-6	6	198	177	
-7	-2	452	460	4	0	119	127	-4	-4	488	85	-5	-1	177	174	-6	6	197	174	
-6	-2	838	825	5	0	335	310	7	-8	425	331	2	-1	226	229	-2	6	149	171	
-6	-2	158	168	6	0	104	199	8	-8	167	123	2	-1	124	1318	-1	6	876	875	
-5	-2	1096	1096	-7	10	12	11	-2	-2	153	135	0	7	-1	1	0	7	11	11	
-2	-2	1157	1182	-6	10	462	474	-9	-7	198	188	5	-1	337	350	1	6	449	449	
-2	-2	244	248	-5	10	102	79	-7	-7	848	640	6	-1	66	65	2	6	106	86	
-2	-2	1251	1181	-10	10	42	31	-2	-2	153	61	-1	-1	121	139	-2	6	169	169	
-2	-2	1100	1095	-3	10	304	323	-6	-7	96	95	0	-1	174	173	4	6	299	303	
2	2	110	112	-10	10	491	499	-5	-7	159	158	9	-1	311	310	5	6	447	446	
2	2	896	896	-10	10	42	31	-2	-2	153	61	-1	-1	121	139	-2	6	169	169	
4	2	440	441	0	10	635	612	-3	-7	366	362	-10	0	298	300	7	6	247	247	
5	2	615	604	1	10	184	187	-2	-2	1476	1476	-9	0	426	426	-10	7	286	276	
5	2	735	736	1	10	336	319	-10	-10	105	105	-9	0	291	290	-6	6	172	172	
7	2	196	199	8	10	49	44	0	-7	1386	1093	-7	0	438	435	-8	7	330	328	
7	2	88	85	4	10	230	263	1	-7	587	562	-6	0	119	116	-7	7	277	277	
7	2	363	367	10	10	96	90	9	-9	80	97	0	0	23	26	-6	7	313	322	
-11	-3	10	107	-6	11	105	117	3	-7	288	273	-4	0	1493	1517	-5	7	276	289	
-11	-3	491	476	-5	11	259	267	-7	-7	455	457	-6	0	540	523	-6	7	284	289	
-11	-3	433	410	-4	11	185	193	5	-5	288	281	-2	0	240	228	-3	6	443	443	
-9	-3	32	34	-3	11	335	354	-7	-7	737	733	-1	0	361	375	-2	7	628	617	
-9	-3	713	712	-2	11	71	71	-2	-2	195	187	0	0	86	79	-1	7	84	82	
-9	-3	188	182	-6	11	88	85	0	0	818	818	0	0	815	815	0	7	464	436	
-9	-3	302	324	-10	11	76	96	-10	-10	149	149	2	0	1513	1500	-1	7	223	230	
-9	-3	1272	1272	1	11	145	145	0	0	371	371	3	0	390	403	3	7	316	311	
-2	-3	960	949	3	11	96	88	-7	-7	495	488	5	0	353	359	4	7	351	373	
-2	-3	158	158	1	11	145	145	0	0	371	371	3	0	390	403	3	7	316	311	
0	3	618	670	-9	12	111	108	-5	-5	126	123	7	0	271	277	6	7	235	237	
1	3	596	586	-5	12	35	28	-4	-4	662	633	0	0	260	278	-9	8	290	288	
1	3	1033	1056	-2	12	103	103	-2	-2	856	865	-11	0	236	247	-9	8	180	185	
3	3	219	224	-1	12	51	42	-2	-2	335	333	-11	0	123	125	-10	7	409	408	
4	3	778	776	0	12	366	369	-1	-1	1366	1390	-1	0	92	95	-6	8	335	356	
4	3	962	917	-5	12	61	61	-5	-5	603	567	-8	0	187	182	-7	7	173	165	
5	3	94	101	-2	12	178	167	1	-1	955	976	-7	1	833	854	-6	8	482	470	
7	3	360	321	-2	13	62	49	2	-1	711	729	-6	1	415	421	-3	8	521	527	
8	3	349	377	-2	13	293	281	6	-6	556	554	-4	1	709	721	-2	8	315	323	
0	3	334	337	0	13	33	33	0	0	576	576	-1	0	448	448	-6	7	461	465	
-10	-4	76	14	L = 3	5	6	659	688	3	1	966	1004	0	0	303	292	-3	7	138	127
-10	-4	415	406	-9	13	415	406	-9	-9	61	28	-2	1	79	78	-2	8	352	341	
-10	-4	541	536	-4	-14	331	313	5	-5	366	349	-1	1	309	294	-1	7	342	336	
-7	-4	926	913	-3	-14	358	318	8	-8	246	233	0	1	1140	1126	3	8	332	344	
-7	-4	230	313	-11	-14	151	163	-5	-5	151	163	-5	1	1209	1215	-5	8	172	177	
-5	-4	1121	1083	-1	-14	158	163	-10	-10	321	321	2	1	245	232	5	8	255	274	
-4	-4	359	318	0	-14	179	183	-9	-9	86	87	3	1	1010	1009	-8	9	262	252	
-4	-4	1360	1364	-1	-14	180	180	-1	-1	417	413	6	4	493	485	-6	9	345	345	
-2	-4	798	775	-2	-14	403	393	-7	-7	427	407	5	1	185	187	-6	9	302	287	
-1	-4	119	137	-6	-13	87	82	-6	-6	189	186	6	1	533	505	-5	9	467	460	
-1	-4	250	216	-4	-13	89	84	-4	-4	175	175	7	2	205	205	-5	9	395	395	
2	-4	1069	1066	-6	-13	50	49	-6	-6	323	313	0	1	343	333	-3	9	482	480	
2	-4	38	39	-3	-13	138	156	-3	-3	701	699	-11	2	277	287	-2	9	306	303	
2	-4	1217	1216	-1	-13	196														

Table 3. Continued.

M	K	10FO	10FC	M	K	10FO	10FC	M	K	10FO	10FC	M	K	10FO	10FC	M	K	10FO	10FC	
5	3	137	154	5	7	192	192	-4	-11	230	222	1	-7	300	310	-5	-3	598	619	
6	3	103	96	-8	6	245	258	-3	-11	209	25	2	-7	109	96	-4	-3	99	105	
-7	3	379	17	-7	8	119	96	-2	-11	419	423	3	-7	170	171	-3	-3	280	297	
-7	4	356	8	-6	6	379	24	-1	-11	79	70	4	-7	274	295	-2	-3	196	210	
-9	4	51	36	-8	8	241	228	-11	-11	111	116	5	-7	79	30	-1	-1	495	5	
-8	4	102	88	-4	8	296	300	1	-11	232	226	6	-7	163	182	0	-3	149	3	
-4	4	619	640	-3	6	316	336	-2	-11	122	120	-10	-8	99	110	1	-3	661	657	
-6	4	91	101	-2	8	402	398	3	-11	132	145	-9	-6	256	272	2	-3	68	26	
-3	4	836	845	-1	8	153	173	6	-11	249	262	-8	-6	199	181	3	-3	474	473	
-1	4	53	61	0	9	91	213	-5	-10	109	115	-4	-6	261	267	7	-3	181	168	
-3	4	527	532	1	8	135	137	-7	-10	109	115	-4	-6	259	322	5	-3	62	68	
-2	4	73	59	2	8	88	91	-6	-10	166	155	-5	-6	135	163	6	-3	13	17	
-9	4	419	425	3	9	11	213	-5	-10	135	156	-4	-6	261	267	7	-3	181	168	
0	4	53	26	4	8	190	182	-8	-10	139	22	-3	-6	440	634	-11	-11	7	3	
1	4	785	773	-7	9	276	270	-3	-10	493	496	-2	-6	68	102	-10	-2	98	71	
2	4	120	116	-4	9	55	71	-2	-10	138	50	-1	-6	360	362	-9	-2	139	21	
3	4	424	413	-9	9	120	88	-9	-10	421	421	0	-6	628	651	-9	-2	367	368	
4	4	336	52	-4	9	218	217	0	-10	168	58	1	-6	316	51	-7	-2	111	127	
5	4	140	156	-3	9	299	292	1	-10	346	18	2	-6	317	312	-2	-6	442	476	
6	4	59	58	-2	9	446	23	-2	-10	111	121	3	-6	191	199	-5	-2	96	101	
-10	5	189	190	-1	9	370	372	3	-10	253	233	4	-6	98	92	-2	-6	495	513	
-9	5	73	63	0	9	163	174	6	-10	408	46	5	-6	232	223	-3	-2	239	248	
-8	5	310	326	1	9	187	169	-10	-10	308	305	6	-6	186	178	-1	-2	111	124	
-7	5	366	56	2	9	54	32	-9	-9	9	9	-11	-5	172	165	0	-2	654	642	
-8	5	645	656	3	9	71	103	-8	-9	181	172	-10	-5	195	206	1	-2	83	86	
-5	5	190	199	+6	10	138	131	-7	-9	644	21	-9	-5	4	22	2	-2	621	615	
-4	5	736	737	-5	10	55	42	-6	-9	326	16	-8	-5	210	213	3	-2	149	156	
-3	5	176	165	-4	10	132	139	-5	-9	56	17	-7	-5	361	328	6	-2	249	240	
-2	5	61	96	-3	10	379	107	-4	-9	424	435	-6	-5	53	22	5	-2	68	63	
-1	5	235	232	-2	10	319	327	-3	-9	107	119	-5	-5	438	428	6	-2	127	141	
0	5	561	573	-1	10	98	102	-2	-9	576	565	-4	-5	268	277	-7	-2	92	86	
1	5	212	206	0	10	252	252	-1	-9	163	168	-3	-5	241	239	-11	-1	181	162	
2	5	627	644	1	10	499	63	3	-9	271	280	-2	-5	407	395	-10	-1	65	60	
3	5	336	41	-4	11	399	42	1	-9	338	17	-2	-5	365	340	-9	-1	136	130	
4	5	349	343	-3	11	242	263	2	-9	135	162	0	-5	166	165	-8	-1	191	212	
5	5	121	136	-2	11	446	43	3	-9	346	33	1	-5	461	463	-7	-1	522	537	
-10	6	166	168	L = 5	4	9	307	299	2	-5	216	40	-6	-1	78	76	-10	3	296	289
-8	6	133	142	-1	10	88	42	4	-9	84	42	4	-5	205	209	-4	-1	257	236	
-7	6	407	412	-3	-14	88	50	-9	-8	261	285	5	-5	70	74	-3	-1	231	227	
-6	6	102	95	-2	-14	318	35	-8	-8	168	65	6	-5	137	116	-3	-1	231	227	
-5	6	598	606	-1	-14	376	33	-7	-8	124	116	-11	-4	113	125	-1	-1	455	442	
-4	6	359	368	-0	-14	158	151	-6	-8	88	59	-10	-4	133	161	0	-1	255	237	
-3	6	406	400	-5	-13	183	181	-2	-8	206	201	-8	-4	142	169	1	-1	464	469	
-2	6	353	344	-4	-13	70	57	-6	-8	192	194	-8	-4	244	243	2	-1	61	69	
-1	6	267	259	-3	-13	356	15	-3	-8	578	605	-7	-4	45	49	3	-1	386	360	
0	6	381	356	-2	-13	114	118	-1	-8	60	66	-6	-4	520	550	4	-1	238	238	
1	6	487	501	-1	-13	167	134	-1	-8	461	455	-5	-4	121	126	5	-1	49	9	
2	6	96	85	0	-13	346	24	0	-8	250	244	-4	-4	477	487	6	-1	175	145	
-9	7	269	222	-1	-13	226	232	1	-8	328	34	-3	-4	273	259	-11	0	132	142	
4	6	107	123	2	-13	126	117	2	-8	121	127	-2	-4	85	106	-10	0	107	95	
5	6	344	2	-2	-12	118	126	3	-8	259	257	-1	-4	226	238	-9	0	198	205	
-9	7	103	87	-8	-12	428	234	6	-8	40	40	0	-4	545	555	-8	0	313	311	
-8	7	67	96	-4	-12	89	87	5	-8	109	109	1	-6	49	1	-7	0	128	127	
-6	7	353	350	-3	-12	198	198	-5	-8	238	241	3	-6	338	58	-5	0	316	318	
-5	7	203	196	-2	-12	56	53	-9	-7	434	63	4	-6	149	138	-4	0	455	486	
-4	7	456	466	-1	-12	173	179	-9	-7	239	241	5	-4	119	119	-3	0	467	467	
-3	7	417	411	0	-12	205	205	0	-7	156	146	6	-4	192	171	-2	0	133	152	
-2	7	86	94	1	-12	388	29	-5	-7	44	6	7	-4	90	52	-1	0	470	465	
-1	7	419	412	2	-12	254	249	-5	-7	248	261	-11	-3	203	196	0	0	479	466	
0	7	337	340	3	-12	186	173	-2	-7	354	344	-10	-3	83	87	1	0	145	148	
1	7	323	318	-8	-11	168	173	-3	-7	136	123	-9	-3	346	42	2	0	386	375	
2	7	232	233	-7	-11	191	190	-2	-7	501	502	-8	-3	1	39	3	0	251	254	
3	7	88	92	-8	-11	359	29	-1	-7	261	251	-7	-3	524	542	6	0	123	122	
4	7	74	80	-9	-11	135	138	0	-7	248	236	-4	-3	50	62	5	0	289	288	

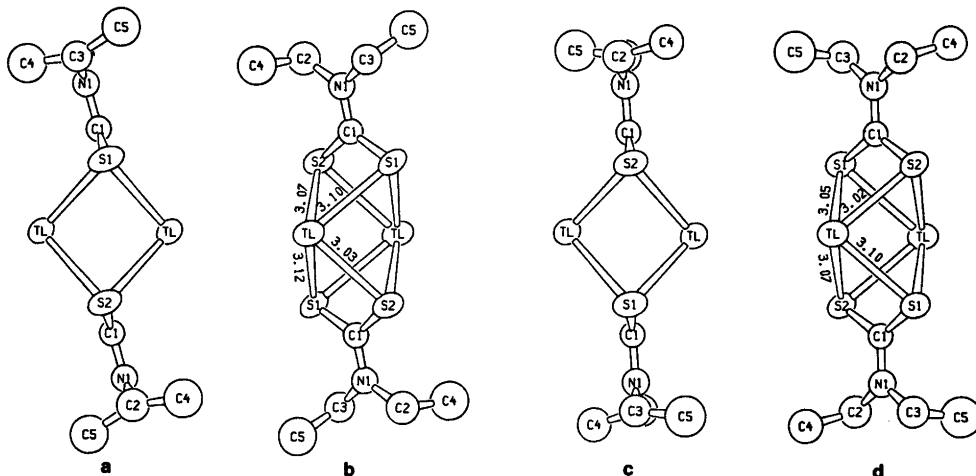


Fig. 1 a-d. The dimeric molecules in thallium(I) diethyldithiocarbamate; a and b show molecule A, c and d molecule B. In a and c the sulfur plane is normal to the paper plane, in b and d it is inclined by 45°.

Table 4. Interatomic distances and angles in the dimeric molecules. Atoms which have been transformed according to the centrosymmetry are denoted by a bar.

Atoms	Distances (Å) in dimer A	Distances (Å) in dimer B
Tl— $\bar{\text{Tl}}$	3.619(1)	3.602(1)
Tl—S1	3.115(3)	3.047(3)
Tl— $\bar{\text{S1}}$	3.101(3)	3.104(3)
Tl—S2	3.034(3)	3.020(3)
Tl— $\bar{\text{S2}}$	3.073(3)	3.069(3)
S1—S2	2.954(4)	2.954(4)
S1—C1	1.71(1)	1.70(1)
S2—C1	1.72(1)	1.72(1)
C1—N1	1.32(1)	1.35(1)
N1—C2	1.51(2)	1.49(2)
N1—C3	1.48(2)	1.50(2)
C2—C4	1.50(2)	1.54(2)
C3—C5	1.56(2)	1.51(2)

Atoms	Angles (°) in dimer A	Angles (°) in dimer B
S1—C1—S2	118.6(4)	119.5(3)
S1—C1—N1	120.9(5)	121.3(5)
S2—C1—N1	120.4(5)	119.2(5)
C1—N1—C2	122.3(9)	123.5(9)
C1—N1—C3	122.4(8)	121.8(9)
C2—N1—C3	115.3(9)	114.6(9)
N1—C2—C4	110.1(11)	112.3(10)
N1—C3—C5	111.6(10)	108.5(11)

terminal carbons. Scattering factors published by Hanson *et al.*⁶ were used to calculate F_c . Atomic coordinates, isotropic temperature factors and interlayer scale factors were refined by full matrix least squares minimizing $\sum \omega(|F_o| - |F_c|)^2$. The weight of a reflection, ω , was σ_F^{-2} where $\sigma_F = \sigma_T k / (4LpI)^{1/2}$ (k is the absolute scale factor, L the Lorentz and p the polarization factor). The discrepancy index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.126. With anisotropic temperature factors for thallium and sulfur R decreased to 0.059. Corrections for anomalous dispersion by thallium⁷ decreased R further to 0.057. The remaining four carbon atoms were located in a difference synthesis. The refinement was continued to $R = 0.037$ ($R_w = 0.050$). The shifts in the last cycle were less than one tenth of the estimated standard deviations. The difference synthesis showed no significant maxima.

The final atomic parameters are given in Table 2 and the observed and calculated structure amplitudes in Table 3.

DESCRIPTION OF THE STRUCTURE

General features. The crystal is built from centrosymmetrical dimeric molecules, $[\text{TlS}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$. The two molecules in the unit cell are independent and have their centres

Table 5. Least squares planes through central parts of ligands defined by the equation $Ax + By + Cz + D = 0$ where x, y, z are triclinic fractional coordinates. The distances of the defining points from the planes are shown. Unit weights were used for the first plane in each ligand, weights based on the estimated standard deviations of the coordinates for the second plane.

a. Plane parameters.

	A	B	C	D
Ligand A	4.933398	-0.564609	-5.741099	0.570082
	4.999688	-0.588242	-5.731134	0.549958
Ligand B	-1.650597	-0.683955	-5.412206	4.037951
	-1.482710	-1.009860	-5.414187	4.115935

b. Distance (Å).

	S1	S2	C1	N1	C2	C3
Ligand A	0.005	0.015	-0.020	-0.021	0.005	0.017
	0.001(3)	0.002(3)	-0.023(9)	-0.017(8)	0.010(13)	0.030(11)
Ligand B	0.045	-0.043	0.002	-0.011	0.055	-0.048
	0.006(3)	-0.004(3)	0.003(9)	-0.007(8)	0.093(12)	-0.076(12)

at 0,0,0 (A) and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (B). Each molecule is linked by Tl—S bonds to two neighbours of its own kind so that two independent chains are formed. The chains run in the *c*-direction and are separated by the alkyl groups of the ligands.

The dimers. The dimeric molecules are similar to those found in the methyl,³ propyl,¹ and isopropyl² homologues. Dimers have also been found in solutions.⁴ The ethyl compound is the first case where there are two independent molecules in the structure. The molecules A and B are very similar; Fig. 1 and Table 4. The central parallelograms of sulfur atoms have corner angles 88.4°(A) and 89.1°(B). The short edges, *i.e.* the S—S bite in the ligands, are 2.95

Å in both dimers. The long edges are 4.02 Å (A) and 3.97 Å (B). Since the Tl—S bonds are in the close range 3.02 to 3.12 Å, the Tl—Tl vectors are normal to the sulfur planes (within 2°). The angles and distances in the dithiocarbamate ligands are in good agreement with the values in other dithiocarbamates. The SSCNCC groups are planar as usual. The fit of the least squares plane is somewhat better in A than in B; Table 5.

The linkage. Each dimer is linked to two identical neighbours, Fig. 2. The Tl—S networks of the two chains are strikingly similar, Fig. 3. The intramolecular Tl—S bonds are in the range 3.71 to 3.89 Å. Although rather long, these

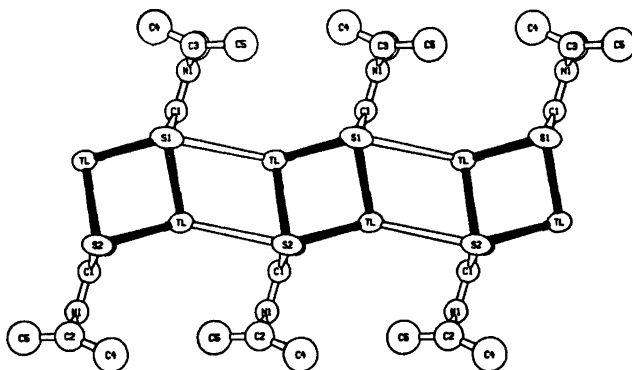


Fig. 2. Chains A. All the thallium atoms are situated in the paper plane.

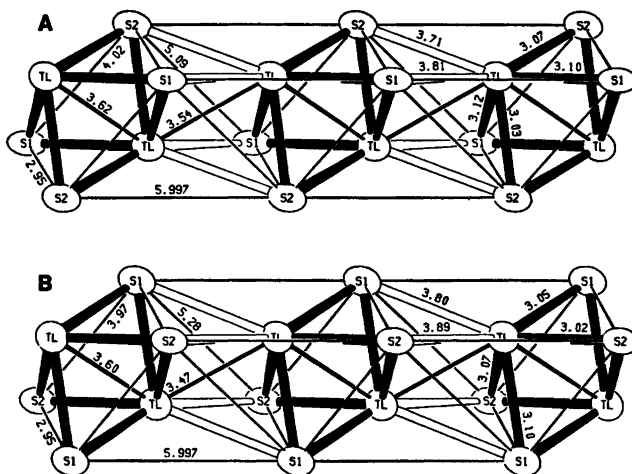


Fig. 3. The thallium sulfur arrangement within the chains of molecules; chain A above and chain B below. Tl—S bonds in the molecules are black.

Table 6. Interatomic distances in Å shorter than 4 Å between atoms in different dimers. The relation of the second atom to the coordinates x, y, z of Table 2 is shown. Distances between atoms in different chains are set in italics.

Distances from atoms in dimer A			Distances from atoms in dimer B				
Atom 1	Atom 2	Dist.	Atom 1	Atom 2	Dist.		
Tl(A)	C1(A)	3.462	-x, -y, -z + 1	Tl(B)	C1(B)	3.466	$x, y, z - 1$
Tl(A)	Tl(A)	3.536	-x, -y, -z + 1	Tl(B)	Tl(B)	3.474	-x + 1, -y + 1, -z
S1(A)	C2(B)	<i>3.598</i>	x, y, z	C2(B)	S1(A)	<i>3.598</i>	x, y, z
C4(A)	S2(B)	<i>3.641</i>	-x + 1, -y, -z + 1	S2(B)	C4(A)	<i>3.641</i>	-x + 1, -y, -z + 1
Tl(A)	S2(A)	3.710	-x, -y, -z + 1	Tl(B)	N1(B)	3.738	$x, y, z - 1$
S2(A)	C4(B)	<i>3.739</i>	-x, -y, -z + 1	C4(B)	S2(A)	<i>3.739</i>	-x, -y, -z + 1
C2(A)	S2(B)	<i>3.766</i>	-x + 1, -y, -z + 1	S2(B)	C2(A)	<i>3.766</i>	-x + 1, -y, -z + 1
Tl(A)	S1(A)	3.806	-x, -y, -z + 1	Tl(B)	S1(B)	3.803	$x, y, z - 1$
C3(A)	S2(B)	<i>3.854</i>	-x + 1, -y, -z + 1	S2(B)	C3(A)	<i>3.854</i>	-x + 1, -y, -z + 1
C4(A)	C5(B)	<i>3.857</i>	-x, -y, -z	C5(B)	C4(A)	<i>3.857</i>	-x, -y, -z
S2(A)	C2(B)	<i>3.865</i>	-x, -y, -z + 1	C5(B)	C5(B)	<i>3.857</i>	-x, -y + 1, -z + 1
C4(A)	S1(B)	<i>3.888</i>	$x, y - 1, z - 1$	C2(B)	S2(A)	<i>3.865</i>	-x, -y, -z + 1
Tl(A)	N1(A)	3.907	-x, -y, -z + 1	Tl(B)	S2(B)	3.888	$x, y, z - 1$
C2(A)	C5(B)	<i>3.968</i>	-x, -y, -z + 1	S1(B)	C4(A)	<i>3.888</i>	$x, y + 1, z + 1$
				Tl(B)	C4(B)	3.890	$x, y, z - 1$
				C5(B)	C2(A)	<i>3.968</i>	-x, -y, -z + 1

Table 7. Distances of coordination. The relation of the sulfur atoms to the coordinates x, y, z of Table 2 is shown.

Dimer A			Dimer B		
Atom	Dist. (Å)		Atom	Dist. (Å)	
S2	3.034(3)	x, y, z	S2	3.020(3)	x, y, z
S2	3.073(3)	-x, -y, -z	S1	3.047(3)	x, y, z
S1	3.101(3)	-x, -y, -z	S2	3.069(3)	-x + 1, -y + 1, -z + 1
S1	3.115(3)	x, y, z	S1	3.104(3)	-x + 1, -y + 1, -z + 1
S2	3.710(3)	-x, -y, -z + 1	S1	3.803(3)	$x, y, z, -1$
S1	3.806(3)	-x, -y, -z + 1	S2	3.888(3)	$x, y, z - 1$

bonds are strong enough to maintain the similarity of the chains under the influence of the packing forces in the crystal.

The interatomic distances between different molecules are listed in Table 6. The Tl—C1 distance, 3.46 Å (A) and 3.47 Å (B), are substantially smaller than the sum of the van der Waals radii given by Bondi,⁸ 3.73 Å (Tl: 1.96 Å; aromatic C: 1.77 Å). The Tl—C contacts are evidently compressed by the Tl—S bonds; Fig. 2. The shorter Tl—S distances in chains A, average 3.76 Å *vs.* 3.85 Å in B, are possible because of the larger angle between the ligand and the central sulfur plane in A, 16.2° *vs.* 5.1° in B; Fig. 1 *a* and *c*.

The coordination. The Tl—S distances are listed in Table 7. The metal coordination is trigonal prismatic, Fig. 3. Two of the quad-

angular faces are shared with neighbours. The largest face is left unshared with the bulk of the ligands outside.

The metal coordination number is seven in the corresponding methyl compound,⁹ six and five in the propyl compound,¹ and five in the isopropyl compound.² The consistency of the series⁹ is confirmed by the coordination number six in the ethyl compound. The decrease in the number of coordinated atoms with the bulk of the ligands is associated with the increasing difficulty of obtaining molecular packings which are suitable for coordination.

The metal atom arrangement. The thallium atoms form planar zigzag chains, Table 8. The Tl—Tl distances in the molecules are similar to those found in the isopropyl compound,² 3.58 Å. The longer distances in the methyl¹ and

Table 8. Distances and angles in metal atom chains.

	Distances (Å)		Angle (°)
Chain A	3.536(1)	3.619(1)	113.87(5)
Chain B	3.474(1)	3.603(1)	115.84(5)

propyl² compounds, 3.85 and 4.00 Å, show that these molecules are deformed in the crystal structures.

The structure of the dimeric molecule suggests that the thallium atoms are held in contact, 3.6 Å apart, by the bridging sulfur atoms.² Shorter Tl—Tl distances occur between the molecules in the ethyl compound, 3.47 Å. The radius of Tl⁺, which is a highly polarizable ion,¹⁰ apparently depends not only on the bonding conditions but also on the direction.

The Tl—Tl distances in the dithiocarbamates are not much longer than the interatomic distances in metallic thallium, 3.408 Å.¹¹ Short distances are observed in other compounds e.g. Tl₂Ti₄O₉ (3.25 Å),¹² Tl₄(OCH₃) (3.84 Å),¹³ Tl⁺Tl⁺S₂ (3.40 Å),¹⁴ Tl₂VS₄ (3.75 Å),¹⁵ and TlX₄(NH₃)₂CS (4.13 Å)¹⁶ (X = H₂PO₄⁻, ClO₃⁻, ClO₄⁻, NO₃⁻). The Tl—Tl distances in the sulfur containing compounds are not related to the number of Tl—S—Tl bridges.

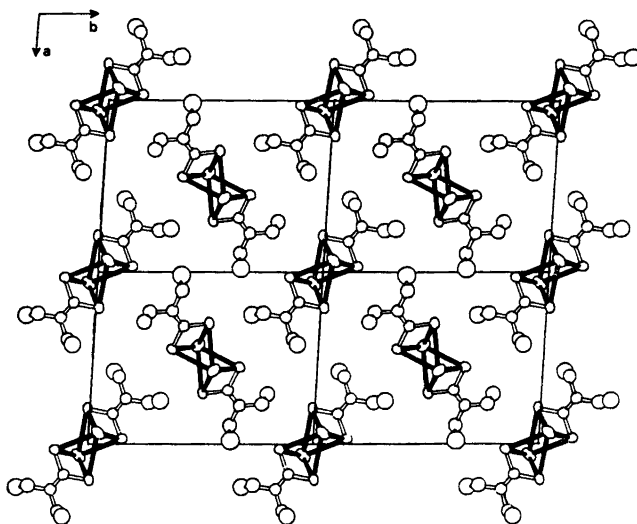
Table 9. Minimum distances used in the calculation of the packing surface. No tests were made for Tl—S distances. C_M represents methyl and methylene carbon atoms.

Atoms	Dist. (Å)	Atoms	Dist. (Å)
Tl—Tl	3.41	S—C _M	3.52
Tl—N	3.25	N—N	3.10
Tl—C	3.40	N—C	3.25
Tl—C _M	3.49	N—C _M	3.33
S—S	3.48	C—C	3.40
S—N	3.29	C—C _M	3.48
S—C	3.44	C _M —C _M	3.57

The packing of the chains. The packing of the flat chains running in the *c*-direction is shown in Fig. 4. Distances between atoms in different chains are shown in Table 6. The absence of metal-ligand interactions between the chains results in the parquet-like packing which is also found in some long chain hydrocarbons.¹⁷

THE RELATION BETWEEN THE METAL COORDINATION AND MOLECULAR PACKING

When molecules consisting of metal atoms and ligands form a crystal, the metal atoms may increase their coordination numbers by employ-

**Fig. 4.** Projection of the arrangement of the chains on a plane normal to *c*. The figure shows nine chains of molecules A (*z*=0) and four chains of molecules B (*z*=½).

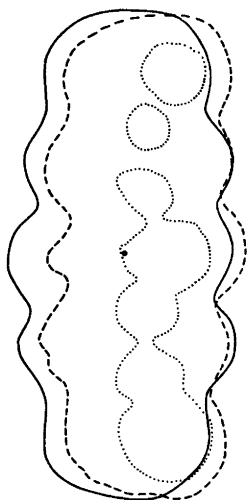


Fig. 5. The surface of parallel packing at three levels corresponding to 0.0 Å (full line), 3.2 Å (broken line) and 6.4 Å (dotted line) above the paper plane. The calculation was performed with molecule B in the orientation shown in Fig. 1c with the molecular centre in the paper plane.

ing donor atoms from suitably oriented molecules in the vicinity. The fundamental importance of the packing characteristics of the molecules for the coordination geometry in the crystal will be illustrated by a molecular packing program related to PACK.²

The program simulates the packing of two parallel molecules. One of the molecules is kept stationary. The other one is translated in small steps keeping the parallel orientation. The positions in scan are marked as allowed if all the interatomic distances exceed minimum values, otherwise as forbidden. This hard spheres approach is justified by the rapid increase in the repulsion between two atoms when their separation drops below a certain value.

The generated three-dimensional body of forbidden positions defines the *surface of parallel packing*. The parallel case is of particular interest in crystallography but similar packing surfaces may be calculated for other orientations. The set of positions which is inside the packing surfaces of all orientations defines the *surface of closest packing*. This surface cannot be penetrated by another molecule in any orientation.

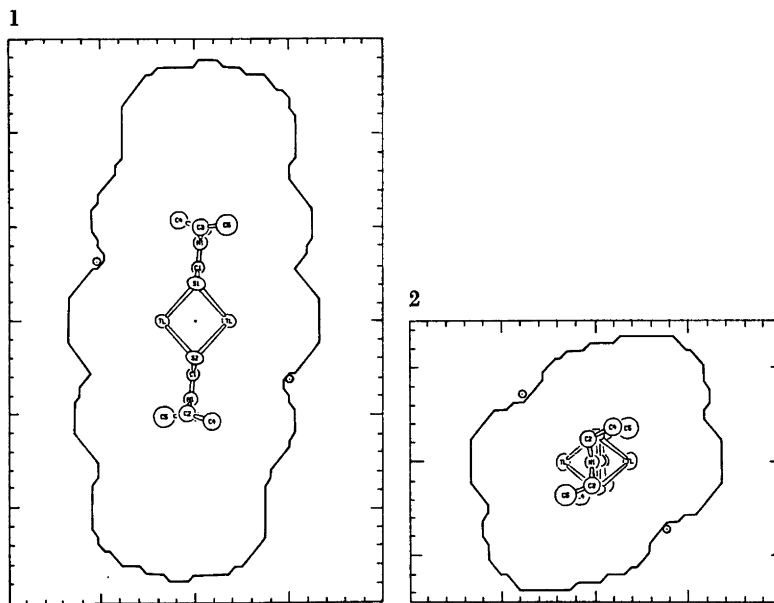


Fig. 6. Two sections of the packing surface of molecule B. The stationary molecule shows the orientation used: thallium atoms in the paper, the paper being normal to the short edge of the sulfur parallelogram in case 1 and to the long edge in case 2. Each thallium atom in the stationary molecule has two sulfur atoms in the moving molecule at equal distance. The minimum distances are obtained at the indicated points. An Ångström scale is shown in the frame.

The surface of parallel packing has been calculated for thallium(I) diethyldithiocarbamate. The molecule B was used as a model in the calculations, Fig. 1. The minimum distances, Table 9, were computed from the van der Waals radii defined by Bondi.⁸ The thallium radius, 1.96 Å, assessed by Bondi with reservation, is rather long considering the observed distances. The radius in the metal,¹¹ 1.71 Å, was then selected as appropriate for minimum distances. The methyl and methylene groups were assigned radii as entities, 1.78 Å, since no hydrogen positions had been determined. The contact distances between carbon atoms in crystals of hydrocarbons^{17,18} are usually around 3.9 Å but the distances may be as short as 3.57 Å if the packing is successful.⁸ No tests were made for Tl—S distances which represent attractions.

Fig. 5 shows the surface obtained at a resolution of 0.4 Å. It is composed of intersecting contact spheres between pairs of atoms. Only surface positions close to the centre may involve Tl—S bonds between the two molecules. Positions close to the ends involve methyl-methyl contacts only.

The thallium coordination geometry varies with the position of the neighbour molecule on the packing surface. The highest possible coordination number is six since Tl—Tl contacts prevent the formation of more than two new Tl—S bonds from each metal atom. There are two planar regions on the surface where two sulfur atoms are at equal distances from the thallium atom, Fig. 6. In case 1 the sulfur atoms belong to the same ligand, in case 2 to different ligands. The shortest distances are obtained at the indicated points. They are equal within the resolution, 3.7 Å in case 1 and 3.6 Å in case 2. The coordination is trigonal prismatic in both cases but the metal atom is situated inside the faces of the prism in case 1 and slightly outside one of the faces in case 2.

Case 1 is observed in the structure of the ethyl compound. The neighbour molecule is found at the indicated point of minimum Tl—S distances. A map with twice as fine a grid also reproduces the actual position within the grid step.

Case 2 is observed in a somewhat deformed version in the methyl compound³ where a

seventh sulfur atom from a third molecule completes the coordination. The metal atom is again well inside the coordination polyhedron.

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