trans ester **12b** and the *trans,cis* ester **13b** in a ratio of 1:5.25.

Registry No.—**4**, 13350-94-2; **5**, 13368-63-3; **6**, 13368-64-4; **9a**, 13368-65-5; **10a**, 13368-66-6; **10b**, 13368-67-7; **11a**, 13368-68-8; **11b**, 13368-69-9; **12a**, 13368-70-2; **12b**, 13368-71-3; **13a**, 13368-72-4; **13b**, 13428-14-3; **14a**, 13368-94-6; **14b**, 13428-15-4; **15a**, 13368-76-8; **15b**, 13396-39-9; **17**, 13368-77-9; **22a**, 1461-97-8; **24b**, 13368-79-1; **25a**, 111-16-0.

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The Crystal and Molecular Structure of 2,6-Diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde ($C_{25}H_{20}OS$)

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The structure of 2,6-diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde ($C_{25}H_{20}OS$) has been solved by an X-ray diffraction study. The crystals are monoclinic with lattice parameters, a = 11.00, b = 11.06, c = 16.86 A, β = 96.5°, and Z = 4. The space group is $P2_1/n$ with one molecule in the asymmetric unit. The crystal structure was solved from the Patterson function by location of the sulfur atom and by five subsequent Fouriers. Anisotropic full matrix least-squares refinement using 906 reflections has reduced the R to 10.3%. The thiopyran ring is nonplanar. One of the sulfur–carbon distances of 1.74 A indicates a partial double bond. Other bond distances and angles are normal.

A yellow crystalline compound ($C_{25}H_{20}OS$) was synthesized by Latif, *et al.*,[1] by the treatment of benzaldehyde with sodium polysulfide in aqueous ethyl alcohol at reflux temperature. The presence of three Ph–C groups, a sulfide linkage, and a ketone group were found by them. Later Cremer and Subbaratnam[2] prepared the same compound under similar conditions and by chemical, nmr, mass spectral, and ultraviolet studies suggested a number of possible five- and six-membered ring structures which were consistent with the data. An X-ray study on this compound was undertaken by us to determine the structure unequivocally and add to the knowledge of sulfur heterocyclic compounds. When we first obtained the crystals,[3] only the molecular formula was known for certain. The X-ray study[4] showed the compound to be 2,6-diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde. Cremer and Subbaratnam[4] found this structure consistent with their spectroscopic and chemical studies.

Experimental Section

A crystal of approximate dimensions 0.1 × 0.2 × 1.0 mm was selected and used for collection of the data. 2,6-Diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde, $C_{25}H_{20}OS$, has a molecular weight of 368.3. It is monoclinic with lattice parameters, a = 11.00 ± 0.01, b = 11.06 ± 0.01, c = 16.86 ± 0.01 A, and β = 96.5° ± 10′. The systematic absences were confined to $k \neq 2n$ for the $0k0$ reflections and $h + l = 2n$ for the $h0l$ zone; thus the space group is $P2_1/n$: V = 2038.5 A^3, d_o = 1.145 ± 0.005 g cm^{-3}, Z = 4, d_c = 1.199 g cm^{-3}. The absorption coefficient for Cu Kα radiation is μ = 14.4 cm^{-1}. Total number of electrons in the unit cell is $F(000)$ = 776.

Multiple film Weissenberg photographs were taken with Cu Kα radiation for k = 0 to 8 for oscillation of the crystal around the b axis. Intensities of 906 independent reflections were measured visually by comparing with a standard intensity strip. The data were corrected for Lorentz and polarization factors using a data reduction program[5] which also gives a Wilson plot for pre-

TABLE I

ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS

Atom	x/a	y/b	z/c
S(1)	0.2322(4)[a]	0.0575(4)	0.1817(3)
C(2)	0.3726(14)	−0.0344(15)	0.2139(10)
C(3)	0.3572(21)	−0.0905(19)	0.2978(13)
C(4)	0.2500(17)	−0.1198(15)	0.3210(10)
C(5)	0.1251(15)	−0.1040(17)	0.2767(11)
C(6)	0.1108(13)	−0.0175(15)	0.2176(9)
C(7)	0.3900(16)	−0.1338(16)	0.1506(11)
C(8)	0.4772(17)	−0.0950(18)	0.0969(15)
C(9)	0.5028(17)	−0.1829(20)	0.0356(11)
C(10)	0.4397(20)	−0.2897(21)	0.0288(10)
C(11)	0.3592(16)	−0.3189(15)	0.0834(13)
C(12)	0.3316(14)	−0.2397(14)	0.1479(11)
C(13)	0.4772(14)	−0.1203(16)	0.3454(10)
C(14)	0.5436(19)	−0.0035(22)	0.3794(10)
C(15)	0.6746(20)	−0.0166(25)	0.3983(15)
C(16)	0.7379(23)	0.0939(27)	0.4311(16)
C(17)	0.6749(25)	0.2011(27)	0.4436(12)
C(18)	0.5441(25)	0.2051(25)	0.4221(16)
C(19)	0.4820(19)	0.1029(27)	0.3902(12)
C(20)	0.0192(17)	−0.1800(19)	0.2926(13)
C(21)	0.0341(13)	−0.2576(13)	0.3472(9)
C(22)	0.9874(15)	0.0324(15)	0.1826(11)
C(23)	0.9056(16)	0.0711(16)	0.2388(12)
C(24)	0.7868(19)	0.1224(19)	0.2108(13)
C(25)	0.7536(19)	0.1317(17)	0.1297(14)
C(26)	0.8342(19)	0.1017(21)	0.0766(14)
C(27)	0.9533(18)	0.0492(17)	0.0966(13)

[a] The number in parenthesis is the standard deviation and refers to the least significant digits.

(1) K. A. Latif, M. A. Razzaq, S. K. Adhikari, and M. M. Eunus, *J. Indian Chem. Soc.*, **36**, 209 (1959); K. A. Latif, S. K. Adhikari, and M. M. Eunus, *ibid.*, **36**, 212 (1959).

(2) S. E. Cremer and A. V. Subbaratnam, *Chem. Commun.*, **1**, 33 (1967).

(3) The crystals were produced by S. E. Cremer at the Illinois Institute of Technology. Preliminary studies were made by S. E. Cremer and A. V. Subbaratnam. Because of difficulty in unequivocally assigning the structure from their studies, they suggested to us that an X-ray study be undertaken and provided us with a sample of the material.

(4) M.-U. Haque and C. N. Caughlan, *Chem. Commun.*, **1**, 34 (1967).

(5) All programs used except least-squares refinement were those from the Montana State University Library for Crystallographic Computing for the IBM 1620, written by C. T. Li, G. Svetich, C. N. Caughlan, R. D. Witters, and K. Watenpaugh.

TABLE II

THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS

Atom	$\beta(1,1)$[a]	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
S(1)	0.0071(5)[b]	0.0084(5)	0.0031(2)	0.0003(4)	−0.0003(2)	0.0013(3)
C(2)	0.0055(19)	0.0079(21)	0.0052(9)	0.0031(15)	0.0002(10)	0.0008(10)
C(3)	0.0123(27)	0.0105(27)	0.0055(14)	−0.0020(21)	0.0002(16)	−0.0018(15)
C(4)	0.0108(23)	0.0081(23)	0.0024(8)	0.0020(17)	−0.0008(12)	−0.0030(11)
C(5)	0.0049(21)	0.0075(24)	0.0040(10)	0.0031(18)	0.0003(12)	0.0016(13)
C(6)	0.0080(18)	0.0010(20)	0.0033(8)	−0.0008(14)	0.0012(10)	−0.0007(9)
C(7)	0.0049(21)	0.0102(23)	0.0026(9)	0.0031(17)	−0.0004(12)	0.0009(11)
C(8)	0.0070(22)	0.0091(27)	0.0058(13)	0.0042(18)	0.0008(14)	0.0001(16)
C(9)	0.0084(24)	0.0085(25)	0.0047(10)	0.0018(19)	−0.0029(11)	−0.0001(12)
C(10)	0.0089(24)	0.0154(31)	0.0026(8)	0.0043(22)	0.0004(11)	0.0008(12)
C(11)	0.0059(23)	0.0086(22)	0.0074(12)	0.0034(17)	−0.0031(14)	0.0001(13)
C(12)	0.0066(18)	0.0054(20)	0.0056(10)	0.0016(14)	−0.0021(10)	−0.0004(10)
C(13)	0.0028(19)	0.0111(23)	0.0023(7)	0.0005(17)	−0.0020(10)	0.0013(10)
C(14)	0.0101(30)	0.0125(31)	0.0017(8)	−0.0002(25)	−0.0018(12)	0.0019(12)
C(15)	0.0107(25)	0.0209(39)	0.0083(15)	0.0014(25)	−0.0025(16)	0.0030(19)
C(16)	0.0153(32)	0.0160(45)	0.0117(18)	−0.0055(33)	−0.0046(18)	−0.0013(22)
C(17)	0.0134(32)	0.0136(39)	0.0065(10)	−0.0037(29)	0.0007(14)	−0.0014(16)
C(18)	0.0146(35)	0.0108(35)	0.0087(16)	0.0016(26)	0.0007(19)	0.0003(19)
C(19)	0.0127(26)	0.0023(33)	0.0081(11)	0.0009(26)	0.0013(13)	−0.0030(13)
C(20)	0.0103(22)	0.0081(26)	0.0071(14)	−0.0019(19)	0.0060(14)	−0.0007(14)
C(21)	0.0135(19)	0.0145(21)	0.0063(8)	−0.0006(14)	0.0020(9)	0.0051(10)
C(22)	0.0046(20)	0.0091(22)	0.0062(12)	0.0008(16)	0.0011(16)	−0.0016(13)
C(23)	0.0055(19)	0.0075(21)	0.0082(11)	0.0009(15)	−0.0005(12)	0.0021(12)
C(24)	0.0101(31)	0.0168(28)	0.0056(17)	−0.0012(22)	0.0005(17)	0.0017(16)
C(25)	0.0102(27)	0.0124(23)	0.0064(11)	−0.0007(19)	0.0033(15)	−0.0007(13)
C(26)	0.0107(24)	0.0199(32)	0.0054(11)	−0.0038(23)	−0.0029(14)	0.0049(16)
C(27)	0.0129(27)	0.0111(24)	0.0035(11)	0.0017(19)	−0.0035(13)	−0.0001(13)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. [b] The number in parenthesis is the standard deviation and refers to the least significant digits.

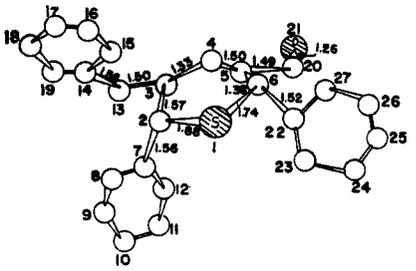

Figure 1.—Molecular structure of 2,6-diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde with pertinent bond distances.

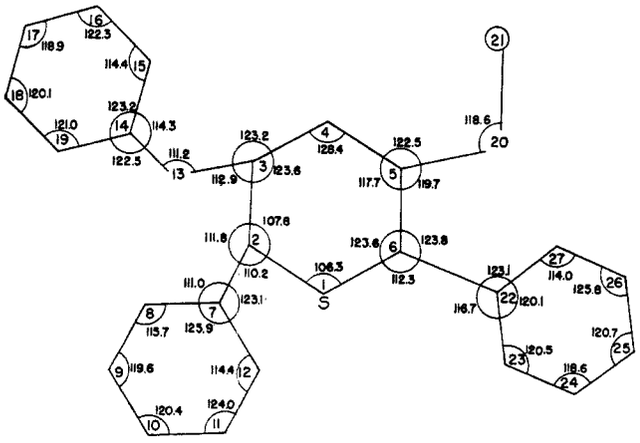

Figure 2.—Bond angles of 2,6-diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde.

liminary scale and temperature factors. No absorption corrections were made.

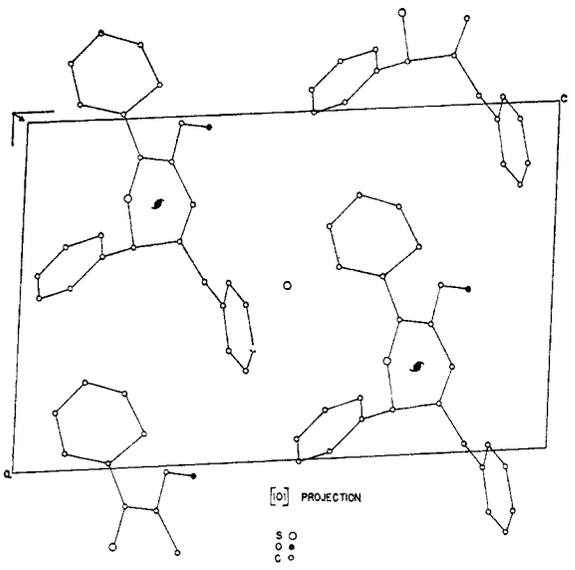

Figure 3.—[101] projection of crystal structure of 2,6-diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde.

Structure Determination

A three dimensional Patterson map was calculated and the sulfur atom position was easily found from the Harker Section. The first Fourier synthesis based on the phases calculated from this sulfur atom position gave two carbon atoms around sulfur. Four more Fourier syntheses located the rest of the structure and gave an R factor of 27%. The interatomic distances and angles calculated from the positions in this Fourier were satisfactory, and refinement was started.

TABLE III

PRINCIPAL AXIS AND MEAN SQUARE DISPLACEMENT

	Direction cosines referred to crystal axes			Mean square displacement, A²		Direction cosines referred to crystal axes			Mean square displacement, A²
	a axis	*b* axis	*c* axis			*a* axis	*b* axis	*c* axis	
S1	−0.1890	0.7521	0.6312	0.0623	C15	0.8390	−0.2202	0.4975	0.0475
	−0.8417	−0.4893	0.2279	0.0468		−0.1860	0.6634	0.7247	0.1579
	0.5229	−0.4480	0.7251	0.0314		−0.4607	−0.7389	0.4916	0.1148
C2	0.8137	−0.5540	0.1759	0.0201	C16	−0.4697	0.0743	0.8796	0.2047
	0.0672	0.2427	0.9677	0.0759		0.4491	−0.8262	0.3399	0.1202
	−0.5758	−0.7983	0.1764	0.0605		0.7482	0.5172	0.4154	0.0452
C3	0.4467	0.7382	0.5052	0.0483	C17	0.6727	0.6641	0.3259	0.0571
	0.0722	−0.5504	0.8317	0.0900		0.5434	−0.6965	0.4685	0.1077
	−0.9121	0.3515	0.2106	0.0810		−0.4947	0.1517	0.8557	0.0934
C4	−0.6529	−0.6051	0.4554	0.0890	C18	−0.0941	0.0159	0.9954	0.1253
	0.7514	−0.5236	0.4013	0.0507		0.9140	0.3625	0.1821	0.0917
	0.0859	0.5974	0.7973	0.0126		0.3676	−0.9255	0.0902	0.0632
C5	0.7823	−0.5601	0.2722	0.0160	C19	−0.0850	0.9661	0.2433	0.0063
	0.3046	0.6401	0.7052	0.0691		0.0364	−0.2491	0.9677	0.1216
	−0.5427	−0.5092	0.6678	0.047		0.9910	0.0897	0.0984	0.0775
C6	0.0927	0.9849	0.1457	0.0049	C20	0.5421	−0.1344	0.8294	0.1403
	0.7410	−0.1473	0.6550	0.0541		0.0574	0.9885	0.1394	0.0525
	−0.6562	−0.0525	0.7526	0.0406		−0.8656	−0.0307	0.4997	0.0157
C7	0.3948	0.9086	0.1361	0.0718	C21	−0.0197	0.7233	0.6902	0.1378
	−0.4167	0.0828	0.9052	0.0420		0.9521	−0.1340	0.2746	0.0845
	0.7977	−0.3802	0.4679	0.0170		−0.2249	−0.6895	0.6884	0.0402
C8	0.7934	−0.6076	0.0347	0.0223	C22	0.0946	−0.4373	0.8943	0.0891
	−0.0303	−0.1292	0.9911	0.0830		0.1571	0.8846	0.4390	0.0561
	0.6072	0.7720	0.1874	0.0762		−0.9940	0.1005	0.0423	0.0377
C9	−0.6161	−0.1858	0.7653	0.0992	C23	−0.0582	0.2194	0.9738	0.1150
	0.1332	0.9377	0.3208	0.0536		−0.5369	−0.8381	0.0953	0.0504
	0.7655	−0.2696	0.5842	0.0255		0.8306	−0.4955	0.2537	0.0364
C10	0.4335	0.8963	0.0932	0.1086	C24	−0.9305	−0.1826	0.3174	0.0492
	−0.8206	0.3655	0.4392	0.0434		0.1620	0.7153	0.6796	0.1069
	0.4286	−0.2451	0.8695	0.0345		0.4050	−0.6461	0.6468	0.0872
C11	−0.3781	−0.1284	0.9167	0.1273	C25	−0.8971	−0.0168	0.4413	0.0474
	0.3725	0.8766	0.3044	0.061		0.4824	−0.2699	0.8332	0.1023
	0.8295	−0.4274	0.3593	0.0145		0.1344	0.9550	0.2641	0.0749
C12	−0.4269	−0.1391	0.8935	0.0964	C26	−0.3569	0.7685	0.5309	0.1708
	0.5198	0.7533	0.4027	0.0379		−0.6706	−0.6412	0.3729	0.0656
	0.7292	−0.6050	0.3195	0.0235		0.6442	−0.1993	0.7383	0.0362
C13	0.7828	−0.1341	0.6076	0.0027	C27	−0.8157	−0.2217	0.5342	0.1128
	−0.0824	0.9315	0.3541	0.0730		−0.0983	0.9733	0.2069	0.0675
	−0.5918	−0.3594	0.7214	0.0466		0.5958	−0.1038	0.7963	0.0249
C14	0.4085	−0.2270	0.8840	0.0129					
	−0.4366	0.8147	0.3815	0.0873					
	−0.8156	−0.5591	0.1488	0.0676					

Two cycles of least-squares refinement using Busing, Levy, and Martin's[6] least-squares program refining only the positional parameters reduced the R to 22.0%. Two more cycles of refinement varying both positional and isotropic thermal parameters reduced the R to 15.2%. The final three cycles refined positional and anisotropic thermal parameters and level scale factors and reduced the R factor to 10.3%. The Hughes weighting scheme[7] was used throughout the refinement.

Results and Discussion

The final coordinates and anisotropic thermal parameters with their standard deviations are listed in Tables I and II. The direction cosines of the principal axes of thermal vibration along with their mean square displacement, calculated from the anisotropic thermal parameters, are given in Table III. The final set of structure factors based on the final atomic positions are given in Chart I. The interatomic distances and angles with their standard deviations are listed in Tables IV and V. Figure 1 shows the structure with pertinent bond distances, Figure 2 shows the bond angles, and Figure 3 shows the [101] projection which indicates the packing.

Examination of the bond distances and angles show no marked deviations from the expected values of these bonds and angles. Since no other thiopyran structure has been studied by X-ray diffraction technique to our knowledge, it is not possible to compare bond distances and angles. The average C–C bond is 1.53 A and the average C=C bond is 1.35 A in the thiopyran ring. The C–C bonds in all the three phenyl rings average to 1.42 A, which is slightly larger than accepted values

(6) W. R. Busing, K. D. Martin, and H. A. Levy, Least-Squares Program, U. S. Atomic Energy Commission Publication No. ORNL-TM-305, 1962.

(7) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941), *i.e.*, $\sqrt{w} = 4F_{o,\min}/F_o$ when $F_o > 4F_{o,\min}$; $\sqrt{w} = 1.0$ when $F_o < 4F_{o,\min}$.

CHART I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

	0 0 L	
2	950	-1066
4	891	-873
6	118	67
8	475	-481
10	237	173
	0 1 L	
3	544	-603
4	1386	1495
5	622	628
7	246	-219
8	169	127
11	207	200
	0 2 L	
2	889	-1010
3	661	-718
5	405	-335
6	270	-184
7	176	133
8	135	-116
9	283	254
10	485	468
15	162	155
	0 3 L	
1	329	333
2	736	-785
3	486	-349
4	539	486
5	604	572
6	566	-560
7	579	-532
10	185	191
11	185	187
12	171	-168
	0 4 L	
1	251	-310
2	119	106
3	159	180
5	265	279
6	119	100
7	265	-261
	0 5 L	
1	193	-263
2	290	-301
3	182	-203
4	145	94
5	411	423
8	170	-128
10	254	249
12	157	-178
	0 6 L	
2	201	209
3	100	-83
4	143	131
5	215	175
6	172	-110
7	344	-376
8	143	94
9	201	128
11	215	196
12	114	-98
13	228	-255
	0 7 L	
2	63	-58
3	223	206
5	99	-39
6	187	241
11	175	-212
12	149	-150
	0 8 L	
2	57	-70
4	240	-218
5	184	161
6	84	45
8	283	225
10	127	-103
	1 0 L	
1	697	-751
3	534	571
5	312	242
7	831	-953
9	327	291
11	178	174
13	223	-214
	1 1 L	
0	156	-152
2	700	-725
3	311	-279
4	881	805
5	441	-422
6	220	-198
	1 7 L	
7	149	-142
	1 1 L	
8	349	-317
10	259	244
11	195	-176
	1 2 L	
0	1092	1150
1	580	584
2	889	-977
4	162	-154
5	68	93
6	391	-341
7	215	-177
8	350	318
9	297	298
10	176	-129
11	121	-115
12	135	-94
14	162	149
	1 3 L	
0	341	347
1	789	-813
2	566	-511
3	303	266
4	303	270
5	303	-256
9	368	369
10	145	-113
	1 4 L	
2	159	-142
3	106	66
4	251	253
5	159	-120
6	292	-306
7	225	-189
8	278	280
	1 5 L	
0	121	132
1	266	-291
2	375	-371
3	338	350
4	72	57
5	254	-250
8	182	122
9	290	281
11	266	-274
	1 6 L	
0	358	-432
1	201	186
2	129	103
3	243	-185
4	243	242
5	300	-293
6	329	-342
7	243	242
8	172	133
	1 7 L	
0	87	-44
1	112	-80
2	162	172
4	137	-101
9	137	128
10	124	-133
11	99	-110
12	112	88
	1 8 L	
0	127	-145
1	127	128
3	84	51
4	226	172
6	99	-85
9	113	-87
	-1 0 L	
1	979	1054
3	1202	-1354
5	1172	-1127
7	639	471
	-1 1 L	
1	233	-240
2	169	-153
3	259	-209
4	492	511
5	311	271
7	376	-359
8	103	-87
9	311	-339
10	116	-96
11	90	99
12	182	194
13	220	-192
	-1 2 L	
1	917	1097
2	391	-384
3	1065	-1233
4	229	-188
5	297	225
6	176	129
7	567	533
8	270	259
9	283	-203
14	176	-183
	-1 3 L	
1	697	-649
2	724	628
3	566	-496
4	566	-525
5	684	713
6	381	325
8	381	-346
10	158	-126
11	381	392
12	236	252
	-1 4 L	
1	146	130
2	292	-256
4	292	-247
6	411	485
7	225	-236
9	225	239
	-1 5 L	
2	193	180
4	266	-304
6	266	245
7	109	80
8	193	-163
10	217	188
	-1 6 L	
1	186	-202
2	257	-263
3	100	-66
5	201	158
6	228	174
8	201	-172
10	172	146
11	129	-109
	-1 7 L	
2	149	-182
3	162	-157
4	223	165
6	112	-80
7	162	157
8	187	-187
9	162	-178
10	198	213
	-1 8 L	
1	71	-18
4	141	92
6	127	-98
7	156	-135
8	184	-210
9	213	215
11	127	-78
	2 0 L	
0	430	391
2	1559	1656
4	342	297
6	237	-258
8	385	383
12	282	-246
14	208	183
	2 1 L	
0	505	-513
1	259	189
2	259	-184
3	311	391
4	466	446
5	336	-286
6	143	82
7	220	-218
12	220	234
	2 2 L	
0	459	-447
1	823	875
2	311	-231
3	539	397
4	189	-130
5	148	-128
6	499	-470
8	94	94
	2 3 L	
0	447	408
2	762	808
3	118	-84
4	513	-497
6	408	-403
8	131	105
9	145	141
10	210	-216
12	185	159
	2 4 L	
0	370	374
1	172	-143
2	79	54
3	92	-63
5	172	-165
6	159	-95
7	278	294
	2 5 L	
0	121	85
1	326	-296
2	84	-49
3	423	-368
4	242	-260
6	109	99
10	205	-199
12	157	159
	2 6 L	
0	215	179
1	129	121
2	143	-106
3	129	-77
4	228	220
5	143	-106
6	157	104
7	201	158
8	243	-226
	2 7 L	
0	87	-52
2	87	-64
3	99	4
4	137	-116
5	175	156
6	124	109
8	261	286
11	112	81
	2 8 L	
0	84	61
4	240	-193
9	127	129
	-2 0 L	
2	831	-897
4	639	-620
6	193	-184
8	594	580
10	237	-192
16	252	-250
	-2 1 L	
1	233	-221
2	544	590
3	674	680
6	298	319
7	259	-220
	-2 7 L	
7	175	-145
	-2 1 L	
8	233	-219
12	233	252
13	103	91
	-2 2 L	
1	324	275
2	283	291
3	135	-106
4	311	-272
5	135	76
6	203	-159
7	485	443
8	539	547
	-2 3 L	
1	210	185
2	539	527
3	236	-223
4	749	-755
5	499	-467
6	368	358
7	185	-173
8	118	-115
9	303	287
	-2 4 L	
1	278	305
2	265	-275
3	159	113
5	265	-238
6	225	241
7	186	191
8	211	-207
9	199	-191
	-2 5 L	
1	387	373
2	229	-173
3	229	192
5	242	214
6	338	299
8	170	-128
9	133	-123
10	109	-67
	-2 6 L	
1	129	-154
2	186	-177
3	271	-241
4	143	126
6	186	188
7	243	249
8	215	-225
9	129	-125
10	186	148
12	172	-181
	-2 7 L	
1	137	93
3	211	-199
5	249	236
6	137	-92
8	187	207
9	137	-119
11	175	160
	-2 8 L	
1	127	129
6	283	223
8	170	-162
	3 0 L	
1	490	-517
3	475	-496
5	579	-530
7	460	473
9	237	-204
11	103	-74
13	372	422
15	297	-344
	3 1 L	
0	376	-338
1	713	763
4	143	59
5	285	-275
6	325	323
9	285	-261
10	207	-210
	3 2 L	
0	350	329
1	459	479
2	580	-545
3	229	189
4	270	-219
5	108	-105
6	176	151
7	297	262
8	189	153
	3 3 L	
0	368	349
1	329	297
2	394	363
3	552	-594
4	329	-293
5	368	375
6	276	-275
8	131	71
9	329	-304
10	185	-184
11	329	374
12	185	175
	3 4 L	
0	516	666
1	211	205
2	397	-361
3	292	281
5	172	-117
6	344	344
7	318	-282
8	172	-162
	3 5 L	
0	326	336
1	290	297
2	170	-180
3	242	-298
5	145	93
6	157	-132
8	157	165
9	145	153
	3 6 L	
0	386	384
1	100	-118
2	358	-351
3	157	133
7	172	-136
8	157	-137
10	172	156
	3 7 L	
1	99	62
2	261	-299
3	261	-291
4	223	197
5	211	220
6	124	-109
7	137	-116
	3 8 L	
1	240	-215
2	99	-55
5	240	169
	-3 0 L	
3	163	-145
5	193	-135
7	178	178
	-3 8 L	
7	170	94
	-3 0 L	
9	385	360
13	193	-186
15	312	327
	-3 1 L	
1	325	344
2	311	-238
3	182	-167
4	169	158
5	454	-432
6	116	-130
	-3 6 L	
7	100	74
	-3 1 L	
8	143	-137
10	285	310
11	169	-180
12	233	-205
	-3 2 L	
1	297	-265
2	473	438
3	148	-131
4	391	-373
5	526	529
7	215	-170
11	121	-112
12	242	-259
13	242	-244
	-3 3 L	
1	473	-463
3	486	425
5	276	187
7	210	170
	-3 2 L	
8	338	313
	-3 3 L	
8	250	-199
10	316	332
11	131	-114
	-3 4 L	
1	251	-219
2	318	319
3	265	-255
4	225	-167
5	211	166
8	119	115
	-3 5 L	
3	229	238
4	182	-172
5	338	-413
7	303	318
8	170	-165
11	170	-147
	-3 6 L	
1	186	209
2	215	160
3	271	-266
8	201	239
9	157	-181
10	201	-178
11	143	122
	-3 7 L	
1	162	-122
2	261	302
3	124	99
4	211	-258
5	99	-97
6	137	121
9	124	-102
12	124	129
	-3 8 L	
1	354	368
3	184	-165
6	141	-166
	4 0 L	
0	742	767
2	312	275
4	742	-760
6	549	523
12	282	324
14	312	-348
	4 1 L	
0	259	201
1	349	331
2	635	-664
4	441	362
6	233	254
	4 6 L	
7	286	-301
	4 0 L	
8	223	-224
	4 1 L	
8	259	-218
9	156	-169
10	130	125
11	169	156
	4 2 L	
1	539	-521
2	311	265
4	539	-527
5	311	309
6	94	92
7	162	109
12	176	201
14	203	-197
	4 3 L	
1	158	95
3	368	-352
4	644	695
5	171	131
6	198	-196
7	276	240
	4 2 L	
8	176	-184
	4 3 L	
8	263	-305
9	329	-356
10	289	322
11	289	262
12	198	-184
	4 4 L	
0	211	-210
1	476	-505
2	211	188
3	172	-99
4	119	95
7	332	-390
9	251	237
	4 5 L	
0	399	386
2	350	-360
3	157	113
4	145	82
5	193	-131
7	205	189
9	326	-365
	4 6 L	
0	172	-152
4	243	200
5	215	195
6	129	-118
8	143	125
9	243	207
	4 7 L	
0	162	126
1	198	-210
2	236	-214
3	299	303
4	124	104
5	187	-162
6	198	-188
8	149	174
9	112	112
11	112	-142
	4 8 L	
6	170	-162
7	127	-86
8	156	131
	-4 0 L	
4	372	-347
6	534	507
	-4 1 L	
8	207	-165
	-4 0 L	
10	118	130
12	103	-89
14	312	-294
16	208	187
	-4 1 L	
1	156	-143
2	272	-248
3	349	-340
4	700	718
5	285	294
10	195	174
11	325	356
13	298	-326
	-4 2 L	
1	391	-354
3	229	186
4	338	-280
5	108	92
6	338	264
7	256	-209
8	189	-151
9	148	153
10	148	132
12	135	108
	-4 3 L	
2	78	-37
3	303	-264
4	236	211
8	171	-167
13	118	-86
14	198	185
	-4 4 L	
1	503	-558
2	199	-180
3	305	298
5	146	-106
6	106	89
7	211	-203
9	238	235
11	172	-201
	-4 5 L	
1	278	250
2	133	141
3	254	217
4	350	365
5	266	-253
6	303	-343
7	170	147
9	170	-157
10	145	154
11	121	152
	-4 6 L	
1	386	-418
3	315	286
4	186	163
5	143	139
7	215	-170
9	201	154
	-4 7 L	
2	124	-142
3	162	140
4	124	80
5	211	-184
6	175	-159
8	274	357
	-4 8 L	
2	199	194
4	184	-184
8	113	79
	5 0 L	
1	400	366
3	445	-365
5	267	263
7	475	-509
11	237	246
13	223	-179
	5 1 L	
0	90	-75
1	285	-225
2	311	-290
3	415	409
6	207	225
8	233	-196
9	220	230
10	195	219
11	169	-141
	5 2 L	
2	121	-83
3	485	-380
4	432	-405
5	215	281
6	324	-341
11	229	215
	5 3 L	
0	145	129
1	276	-243
3	105	-87
4	263	269
5	198	-174
6	158	130
8	381	-434
9	341	411
11	145	-134
	5 4 L	
0	318	-274
2	211	221
3	278	265
4	159	160
5	146	-138
8	199	210
	5 5 L	
1	217	-193
3	193	178
6	217	202
7	170	-139
9	157	165
	5 6 L	
0	271	-248
1	114	117
3	143	130
4	143	131
5	228	-208
6	344	-353
	5 7 L	
2	223	195
4	198	-183
7	99	69
9	99	-86
10	175	-214
	5 8 L	
1	141	101
3	84	-67
4	127	103
5	127	-117
	-5 0 L	
1	342	315
3	327	-328
5	193	-181
7	475	438
9	237	-223
13	208	215
15	133	-127
	-5 1 L	
1	220	183
3	325	-339
6	466	482
8	285	-283
9	169	-177
	-5 2 L	
1	162	124
2	445	-419
3	311	-237
4	189	140
7	135	108
9	270	-245
12	203	-203
	-5 3 L	
1	250	-236
2	303	298
3	92	94
4	276	-228
5	341	313
7	236	-224
8	171	139
11	131	123
	-5 4 L	
1	186	-158
2	357	-386
3	132	148
4	199	209
6	159	172
8	186	-226
10	278	304
	-5 5 L	
2	170	-151
3	254	-291
5	290	281
6	278	-304
8	170	178
	-5 6 L	
1	143	-112
2	286	-308
3	129	-117
4	143	140
6	186	169
8	228	-240
	-5 7 L	
2	149	-121
3	112	-115
4	187	190
5	149	155
6	137	-157
7	211	-224
	-5 8 L	
1	141	-63
3	141	124
4	113	139
	6 0 L	
0	163	127
2	505	388
6	267	-235
	6 1 L	
1	195	-166
3	336	382
4	116	-114
7	207	-174
	6 2 L	
0	283	-288
1	338	298
2	108	73
4	176	169
6	283	-277
10	135	127
	6 3 L	
0	131	-134
1	185	-171
2	198	181
4	198	-161
	6 4 L	
0	146	97
1	146	101
2	132	144
4	159	-122
	6 5 L	
0	84	-106
2	133	142
3	193	-156
4	205	-240
5	133	123
7	217	257
	6 6 L	
1	129	143
3	157	160
5	186	-156
8	143	-167
	6 7 L	
3	198	-181
5	187	181
	6 8 L	
1	99	-39
4	127	-116
6	99	120
	-6 0 L	
4	372	-373
6	223	-215
16	148	-136
	-6 1 L	
2	325	307
3	325	306
4	207	158
5	220	-196
6	169	-118
7	207	175
	-6 2 L	
1	189	183
2	270	238
3	135	-89
4	229	-231
11	215	257
	-6 3 L	
4	236	-214
5	158	-143
	-6 2 L	
8	242	247
	-6 3 L	
12	223	249
	-6 4 L	
1	265	281
2	225	-283
3	146	-96
6	225	231
9	199	-233
	-6 5 L	
1	133	117
4	133	-110
5	170	127
6	109	93
	-6 6 L	
1	186	152
3	186	-174
	-6 7 L	
5	87	62
6	149	128
7	149	-137
	-6 8 L	
2	156	-128
	7 0 L	
3	178	141
7	267	272
9	297	-303
	7 1 L	
0	298	-285
2	311	316
4	220	-198
	7 2 L	
1	418	377
2	189	164
4	242	-225
5	297	-300
8	162	-170
	7 3 L	
1	289	328
2	118	122
3	210	-193
6	223	295
7	198	-197
	7 4 L	
3	159	156
4	211	-240
7	199	-220
	7 5 L	
0	133	110
1	193	211
2	266	-252
4	205	-234
	7 6 L	
0	201	194
	7 7 L	
0	149	137
7	175	189
	7 8 L	
5	127	133
	-7 0 L	
1	415	-409
3	312	272
9	193	187
	-7 1 L	
3	220	-243
4	220	263
6	285	-299
	-7 2 L	
1	391	-377
5	162	121
7	121	-116
10	215	-210
	-7 3 L	
1	92	-73
4	118	117
7	131	171
11	198	-196
	-7 5 L	
1	96	-102
3	170	206
	-7 6 L	
1	129	-154
3	215	-169
4	114	108
6	172	-156
	8 0 L	
0	445	455
6	223	181
8	282	-283
	8 1 L	
1	246	265
3	143	-112
9	156	-216
	8 2 L	
0	242	231
1	189	218
3	203	-187
5	148	134
8	176	-188
	8 3 L	
1	131	129
3	289	-281
4	131	122
5	118	124
	8 4 L	
0	199	-213
2	211	233
3	186	-190
	8 5 L	
0	121	123
3	193	-202
	-8 0 L	
2	624	-678
	-8 1 L	
4	156	163
6	195	-208
7	143	-139
	-8 2 L	
2	229	-210
4	162	163
	-8 3 L	
4	276	315
7	210	-278
9	145	176
	-8 4 L	
2	238	-274
4	251	308
	-8 5 L	
1	182	205
3	157	157
4	157	153
	-8 6 L	
1	186	-152
5	143	118
	9 0 L	
1	342	-373
5	252	266
	9 1 L	
0	182	185
2	182	-189
3	169	137
	9 2 L	
0	148	128
2	203	-199
5	148	146
	9 3 L	
0	198	166
2	145	-125
	-9 0 L	
1	342	340
3	282	-288
5	208	221
9	178	-229
	-9 1 L	
2	246	-267
3	143	-129
5	195	236
	-9 2 L	
3	148	-150
5	176	202
	-9 3 L	
1	145	-149
4	131	-149
5	250	292
7	185	-200
	-9 6 L	
1	186	-183
3	129	122

[a] Within each group the columns reading from left to right contain the value of l, $10F_o$, and $10F_c$.

TABLE IV

INTERATOMIC DISTANCES

Atoms	Bond, A
S(1)–C(2)	1.88[a]
S(1)–C(6)	1.74
C(2)–C(3)	1.57
C(2)–C(7)	1.56
C(3)–C(4)	1.33
C(3)–C(13)	1.50
C(4)–C(5)	1.50
C(5)–C(6)	1.38
C(5)–C(20)	1.49
C(6)–C(22)	1.52
C(7)–C(8)	1.46
C(8)–C(9)	1.47
C(9)–C(10)	1.37
C(10)–C(11)	1.39
C(11)–C(12)	1.46
C(12)–C(7)	1.33
C(13)–C(14)	1.56
C(14)–C(15)	1.45
C(15)–C(16)	1.48
C(16)–C(17)	1.40
C(17)–C(18)	1.45
C(18)–C(19)	1.40
C(19)–C(14)	1.38
C(20)–O(21)	1.26
C(22)–C(23)	1.44
C(23)–C(24)	1.45
C(24)–C(25)	1.38
C(25)–C(26)	1.37
C(26)–C(27)	1.44
C(27)–C(22)	1.47

[a] Standard deviations are 0.03–0.06 A.

but the difference is not significant. The S(1)–C(2) bond of 1.88 A is a normal bond, but S(1)–C(6) bond of 1.74 A represents a partial double bond in the heterocyclic ring.[8] The thermal motion of most of the atoms in the molecule indicate considerable anisotropy.

A least-squares plane was calculated for the thiopyran ring and shows it to be quite nonplanar. The maximum deviation from the least-square plane, weighting all atoms as unity, was 0.304 A for C(2), which was below the plane, while sulfur was 0.238 A above the plane. The phenyl rings are all planar and calculation of dihedral angles show phenyl rings at C(2) and C(6) and the benzyl ring at C(3) to have dihedral angles of 91.9, 44.4, and 71.1° to the thiopyran plane, respectively.

(8) International Tables of X-Ray Crystallography, Vol. III, 1962, p 276.

TABLE V

BOND ANGLES

Atoms	Angle, deg
C(2)–S(1)–C(6)	106.3[a]
S(1)–C(2)–C(3)	107.8
S(1)–C(2)–C(7)	110.2
C(3)–C(2)–C(7)	111.8
C(2)–C(3)–C(4)	123.6
C(2)–C(3)–C(13)	112.9
C(4)–C(3)–C(13)	123.2
C(3)–C(4)–C(5)	128.4
C(4)–C(5)–C(6)	117.7
C(4)–C(5)–C(20)	122.5
C(6)–C(5)–C(20)	119.7
S(1)–C(6)–C(5)	123.6
S(1)–C(6)–C(22)	112.3
C(5)–C(6)–C(22)	123.8
C(2)–C(7)–C(8)	111.0
C(2)–C(7)–C(12)	123.1
C(8)–C(7)–C(12)	125.9
C(7)–C(8)–C(9)	115.7
C(8)–C(9)–C(10)	119.6
C(9)–C(10)–C(11)	120.1
C(10)–C(11)–C(12)	124.0
C(11)–C(12)–C(7)	114.4
C(3)–C(13)–C(14)	111.2
C(13)–C(14)–C(15)	114.3
C(13)–C(14)–C(19)	122.5
C(15)–C(14)–C(19)	123.2
C(14)–C(15)–C(16)	114.4
C(15)–C(16)–C(17)	122.3
C(16)–C(17)–C(18)	118.9
C(17)–C(18)–C(19)	120.1
C(18)–C(19)–C(14)	121.0
C(5)–C(20)–O(21)	118.6
C(6)–C(22)–C(23)	116.7
C(6)–C(22)–C(27)	123.1
C(23)–C(22)–C(27)	120.1
C(22)–C(23)–C(24)	120.5
C(23)–C(24)–C(25)	118.6
C(24)–C(25)–C(26)	120.7
C(25)–C(26)–C(27)	125.8
C(26)–C(27)–C(22)	114.0

[a] Standard deviations are ≈1°.

Registry No.—2,6-Diphenyl-3-benzyl-2H-thiopyran-5-carboxaldehyde, 13589-13-4.

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