845. *The Crystal Structure of 9-Phenyl-9-arsafluorene (Monoclinic Form).*

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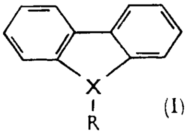
(Appendix on its Preparation, by D. M. Heinekey and I. T. Millar.)

The compound crystallises in two forms, (i) monoclinic ($a = 18{\cdot}67$, $b = 5{\cdot}79$, $c = 13{\cdot}93$ Å, $\beta = 102°$) with space group $P2_1$ and two molecules in the asymmetric unit, and (ii) orthorhombic ($a = 8{\cdot}04$, $b = 6{\cdot}02$, $c = 30{\cdot}2$ Å) with space group $P2_12_12_1$.

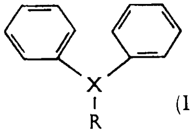
A partial three-dimensional *X*-ray crystal-structure analysis of the monoclinic form has shown that the molecule consists of a planar arsafluorene group with As–C = 1·98 Å and angle C–As–C 88°; the arsenic atom has a pyramidal configuration with As–C(phenyl) = 2·02 Å and the angle C(phenyl)–As–C 98°. The molecule is symmetrical about a plane which passes through the As–C(phenyl) bond and which is perpendicular to the planes of the arsafluorene and the phenyl groups; the angle between the normals to the phenyl ring and the tricyclic planar arsafluorene system is 80°. For the carbon–carbon bonds the lengths are not significantly different from those in fluorene and benzene.

Crystallographic data are reported for 9-phenyl-9-arsafluorene oxide dihydrate.

Derivatives of fluorene in which the CH_2 group has been replaced by a group V atom (I) have been subjected to extensive chemical investigation. Resolution of the 9-*p*-carboxyphenyl-2-methoxy-9-arsafluorene indicated[1] that either the arsafluorene was not planar or the group R (in this example, *p*-carboxyphenyl) did not lie in the plane of the arsafluorene. Failure[2] to resolve the 9-*p*-carboxyphenyl-9-arsafluorene into optically active isomers supported the latter interpretation. Thermochemical measurements[3] on the hypothetical conversion of (I) into (II) show that the five-membered ring is associated with strain when X is C or N but with stabilisation when X is P.



(I)



(II)

Preliminary investigation showed that 9-phenyl-9-phosphafluorene, and its oxide, decomposed in the *X*-ray beam. We have examined the arsenic compound to establish its stereochemistry and particularly the relationship between the phenyl group and the arsafluorene group.

Methods and Results

In the original sample there were needles and equant crystals. Recrystallisation from ethanol gave only equant crystals. Examination under the microscope showed that the different crystals represented polymorphic forms, not just variations in habit; the needles melted at 81° and were weakly birefringent, while the equant crystals melted at 86° and were strongly birefringent. The weakly birefringent form was metastable with respect to the other one. Both forms were examined by *X*-ray diffraction, to determine the unit cell dimensions and space groups.

Crystal Data.—$C_{18}H_{13}As$, $M = 304{\cdot}2$.

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[1] Campbell and Poller, *J.*, 1956, 1195.

[2] Campbell, *J.*, 1950, 3109; 1952, 4448.

[3] Bedford, Heinekey, Millar, and Mortimer, *J.*, 1962, 2932.

Needle form: Monoclinic, $a = 18{\cdot}67 \pm 0{\cdot}04$, $b = 5{\cdot}79 \pm 0{\cdot}01$, $c = 13{\cdot}93 \pm 0{\cdot}03$ Å, $\beta = 102 \pm 1°$, $U = 1473$ Å^3, $D_m = 1{\cdot}40$ (by flotation), $Z = 4$, $D_c = 1{\cdot}37$, $F(000) = 616$. Space group $P2_1(C_2{}^2$, No. 4) determined by structure analysis. Cu-K_α radiation, single-crystal oscillation, and Weissenberg photographs, absorption coefficient $\mu = 33$ cm.$^{-1}$, no absorption correction applied. No molecular symmetry required, two molecules in the asymmetric unit.

Equant form: Orthorhombic, $a = 8{\cdot}04 \pm 0{\cdot}05$, $b = 6{\cdot}02 \pm 0{\cdot}02$, $c = 30{\cdot}2 \pm 0{\cdot}2$ Å, $U = 1460$ Å^3, $D_m = 1{\cdot}40$, $Z = 4$, $D_c = 1{\cdot}38$. Space group $P2_12_12_1(D_2{}^4$, No. 19). No molecular symmetry required.

Space-group Determination of Monoclinic Form.—We chose to investigate the monoclinic form for which the systematic absences were consistent with the space groups $P2_1/m$ or $P2_1$. If the space group were $P2_1/m$ the results would be more accurate than those which are possible in the non-centrosymmetric structure with space group $P2_12_12_1$. If it were $P2_1$, however, there would be two molecules in the asymmetric unit, so that the heavy atoms would not give rise to false symmetry in the early stages of structure determination, and comparison of the two molecules would give a check on the correctness of the structure.

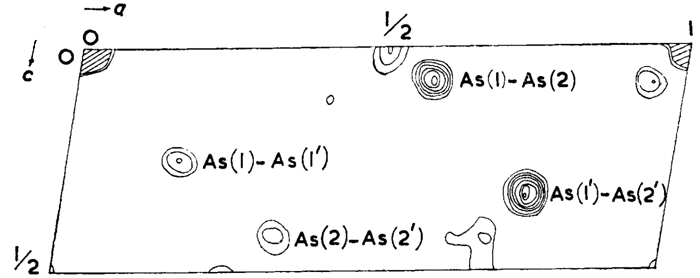

FIG. 1. Patterson projection down [010]. Contours at equal arbitrary intervals.

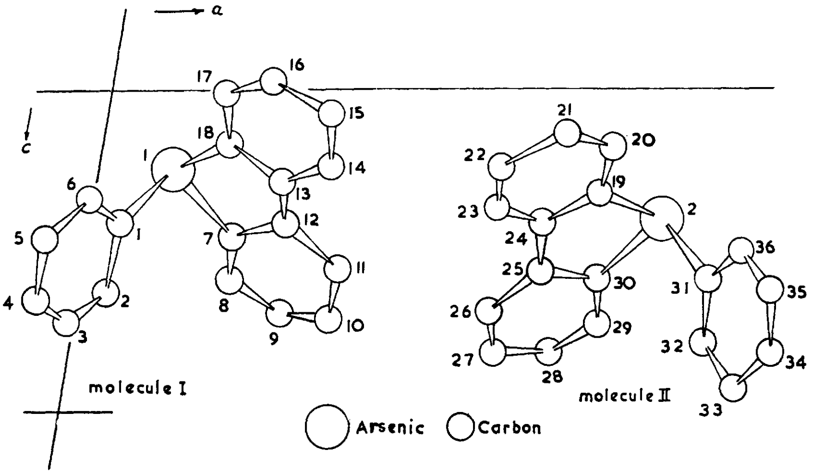

FIG. 2. The two molecules of the asymmetric unit as seen projected down [010].

A Patterson projection down the *b*-axis enabled us to distinguish between the possible space groups. For $P2_1/m$ there would be one large peak in addition to the origin but for $P2_1$ there would be two pairs of peaks, one twice the height of the other, in addition to the one at the origin. The projection and its interpretation are shown in Fig. 1, and clearly indicate that the space group is $P2_1$ with one arsenic atom, As(1) at $x/a = 0{\cdot}092$, $z/c = 0{\cdot}125$, and the other As(2), at $x/a = 0{\cdot}675$, $z/c = 0{\cdot}208$. Structure factors for $F(h0l)$ were calculated with the atoms in these positions and a satisfactory value of R, 0·35, was obtained.

Structure Determination.—There were 36 carbon atoms to be located in addition to the two arsenic atoms, so it was necessary to use three-dimensional data to give a reasonable ratio of

TABLE 1.

Observed structure amplitudes and calculated structure factors ($F_c = A + iB$) × 10.
Reflections too weak to be observed have been omitted.

h	*k*	*l*	$\|F_o\|$	*A*	*B*
0	0	2	1256	−1354	0
0	0	3	373	−344	0
0	0	4	517	−559	0
0	0	5	274	259	0
0	0	9	428	366	0
0	0	10	369	353	0
0	0	12	376	−391	0
1	0	1	354	500	0
1	0	2	406	−406	0
1	0	3	436	−467	0
1	0	4	724	−723	0
1	0	6	606	614	0
1	0	7	643	535	0
1	0	8	296	312	0
1	0	9	292	−239	0
1	0	10	343	−307	0
2	0	0	204	−208	0
2	0	1	1082	−1217	0
2	0	2	960	−977	0
2	0	3	292	−253	0
2	0	4	339	−268	0
2	0	7	252	245	0
2	0	8	299	264	0
2	0	10	317	−352	0
2	0	11	373	−329	0
3	0	2	1189	−1183	0
3	0	3	314	−316	0
3	0	4	215	260	0
3	0	5	643	626	0
3	0	6	58	551	0
3	0	7	285	−259	0
3	0	8	285	−194	0
4	0	0	480	387	0
4	0	1	624	−587	0
4	0	3	565	−488	0
4	0	4	362	−294	0
4	0	5	410	399	0
4	0	6	665	734	0
4	0	8	432	−447	0
4	0	9	373	−396	0
5	0	0	473	−376	0
5	0	1	908	−876	0
5	0	2	192	−192	0
5	0	3	517	534	0
5	0	4	761	746	0
5	0	5	266	276	0
5	0	6	263	−243	0
5	0	9	321	−273	0
6	0	0	339	229	0
6	0	1	222	−185	0
6	0	2	339	−355	0
6	0	3	565	471	0
6	0	4	813	793	0
6	0	5	402	455	0
6	0	6	281	−231	0
6	0	7	624	−649	0
6	0	8	347	−286	0
6	0	9	332	285	0
7	0	0	292	−257	0
7	0	1	495	460	0
7	0	2	843	782	0
7	0	3	306	290	0
7	0	4	281	−277	0
7	0	8	358	−399	0
8	0	0	332	−274	0
8	0	2	769	654	0
8	0	3	717	634	0
8	0	4	410	−377	0
8	0	5	606	−601	0
8	0	6	543	−444	0
8	0	8	369	317	0
9	0	0	321	242	0
9	0	1	373	301	0
9	0	2	317	−316	0
9	0	3	306	−283	0
9	0	4	321	280	0
9	0	6	351	−390	0
9	0	7	332	−314	0
10	0	0	351	358	0
10	0	1	624	611	0
10	0	2	543	442	0
10	0	3	565	−459	0
10	0	4	717	−598	0
10	0	6	332	248	0
11	0	2	339	283	0
11	0	4	332	−213	0
11	0	5	369	−363	0
11	0	7	347	345	0
12	0	0	517	453	0
12	0	2	388	−375	0
12	0	3	365	−221	0
13	0	0	332	261	0
13	0	2	339	−290	0
13	0	3	376	−380	0
14	0	0	565	−571	0
15	0	1	380	−310	0
15	0	2	347	−308	0
−1	0	2	665	703	0
−1	0	3	406	468	0
−1	0	4	406	333	0
−1	0	5	698	−789	0
−1	0	6	270	−309	0
−1	0	8	565	544	0
−1	0	9	643	693	0
−2	0	1	1182	1349	0
−2	0	2	1034	1160	0
−2	0	4	783	−913	0
−2	0	5	517	−492	0
−3	0	1	196	−173	0
−3	0	2	443	−305	0
−3	0	3	226	−134	0
−3	0	4	266	−163	0
−3	0	5	215	201	0
−3	0	6	222	−182	0
−3	0	7	680	−714	0
−3	0	8	289	−290	0
−3	0	10	332	413	0
−3	0	11	384	315	0
−3	0	12	339	−243	0
−4	0	1	255	−235	0
−4	0	2	565	−574	0
−4	0	3	1034	1122	0
−4	0	4	606	625	0
−4	0	5	204	125	0
−4	0	6	222	−600	0
−4	0	7	676	−520	0
−4	0	8	289	223	0
−4	0	10	332	−95	0
−4	0	11	384	36	0
−4	0	12	339	57	0
−5	0	1	278	−250	0
−5	0	2	624	615	0
−5	0	3	584	665	0
−5	0	5	443	−138	0
−5	0	6	237	207	0
−5	0	7	317	271	0
−5	0	8	380	−342	0
−5	0	9	292	−320	0
−5	0	11	347	346	0
−5	0	12	413	478	0
−6	0	1	517	−439	0
−6	0	2	484	−384	0
−6	0	3	351	−368	0
−6	0	4	270	221	0
−6	0	5	938	932	0
−6	0	6	517	550	0
−6	0	7	543	−401	0
−6	0	8	543	−562	0
−6	0	9	325	−300	0
−6	0	10	317	249	0
−6	0	11	347	285	0
−7	0	1	565	−490	0
−7	0	2	476	−438	0
−7	0	4	595	615	0
−7	0	6	432	−323	0
−7	0	9	306	−222	0
−7	0	10	325	−289	0
−8	0	1	296	−199	0
−8	0	3	237	−177	0
−8	0	4	495	−546	0
−8	0	5	391	367	0
−8	0	6	665	669	0
−8	0	7	413	426	0
−8	0	9	517	−480	0
−8	0	10	506	−461	0
−9	0	1	252	182	0
−9	0	2	252	−181	0
−9	0	3	672	−697	0
−9	0	4	351	−323	0
−9	0	5	584	432	0
−9	0	6	584	576	0
−9	0	7	302	256	0
−10	0	1	299	−268	0
−10	0	2	517	−477	0
−10	0	3	325	−234	0
−10	0	7	310	273	0
−10	0	8	476	490	0
−11	0	1	373	295	0
−11	0	2	495	419	0
−11	0	4	573	−494	0
−11	0	5	606	−669	0
−11	0	7	443	400	0
−11	0	8	425	488	0
−12	0	1	517	459	0
−12	0	2	325	208	0
−12	0	3	328	−305	0
−12	0	4	617	−573	0
−14	0	2	584	642	0
−14	0	3	358	365	0
−14	0	5	343	−294	0
−15	0	1	365	379	0
−15	0	2	380	362	0
−16	0	1	465	−494	0
−16	0	2	362	−363	0
−16	0	3	436	466	0
−16	0	4	376	437	0
16	1	1	261	−241	2
16	1	2	261	−327	60
−1	1	1	395	307	110
−1	1	2	1399	1335	624
−1	1	3	671	410	534
−1	1	4	239	−198	29
−1	1	5	485	−372	50
−1	1	6	309	−279	180
−1	1	7	324	170	−169
−1	1	8	202	18	−178
−1	1	11	350	315	84
−1	1	12	284	303	−21
−2	1	1	477	−154	382
−2	1	2	866	423	−634
−2	1	3	921	665	394
−2	1	4	649	458	475
−2	1	5	511	494	−67
−2	1	7	343	−338	27
−2	1	8	436	−459	24
−2	1	10	443	418	−75
−2	1	11	384	415	43
−3	1	1	1429	−1382	50
−3	1	2	507	−426	−123
−3	1	3	772	537	−410
−3	1	4	1059	955	−62
−3	1	5	417	473	47
−3	1	6	470	−498	23
−3	1	7	567	−504	341
−3	1	8	202	−145	−158
−3	1	9	291	24	−317
−4	1	1	724	−660	−208
−4	1	2	384	264	87
−4	1	3	384	−240	−256
−4	1	4	243	56	−157
−4	1	5	198	148	101
−4	1	6	187	183	25
−4	1	7	380	308	−237
−4	1	9	507	−462	−21
−4	1	10	313	−342	−55
−5	1	1	305	187	−162
−5	1	2	537	−375	339
−5	1	3	772	−755	71
−5	1	4	149	−75	−70
−5	1	5	694	743	−225
−5	1	6	567	606	160
−5	1	8	443	−462	107
−5	1	9	299	−382	−91
−5	1	10	239	−13	−214
−6	1	1	511	−433	264
−6	1	2	1115	−952	−61
−6	1	3	473	−329	275
−6	1	4	417	344	13
−6	1	5	273	294	−116
−6	1	6	365	−94	293
−6	1	7	198	75	181
−6	1	8	328	377	9
−7	1	1	376	−214	191
−7	1	2	172	141	−119
−7	1	3	339	−26	−363
−7	1	4	556	−468	−119
−7	1	5	414	−298	241
−7	1	7	653	588	122
−7	1	8	273	274	6
−7	1	9	254	−256	−22
−7	1	10	269	−268	−21
−8	1	1	436	477	−35
−8	1	2	354	314	−135
−8	1	3	824	−790	81
−8	1	4	795	−809	15
−8	1	5	187	73	−175
−8	1	6	295	244	−123
−8	1	7	232	236	104
−8	1	8	202	−91	194
−8	1	10	247	274	−145
−9	1	1	183	109	130
−9	1	2	455	−37	455
−9	1	4	373	218	−333
−9	1	5	295	−77	−283
−9	1	6	335	−352	57
−9	1	7	309	−204	159
−9	1	8	232	233	129
−9	1	9	343	424	−36
−10	1	1	313	301	170
−10	1	2	410	414	−80
−10	1	3	198	182	−96
−10	1	5	410	−424	−68
−10	1	6	436	−449	−18
−10	1	7	288	140	−221
−10	1	8	399	388	54
−11	1	1	485	448	−128
−11	1	2	373	370	27
−11	1	3	269	−25	260
−11	1	6	228	75	−190
−11	1	8	247	−284	24
−12	1	2	224	−124	170
−12	1	3	224	115	163
−12	1	4	250	307	−101
−12	1	5	232	254	−31
−12	1	6	239	−281	23
−12	1	7	410	−461	−25
−13	1	1	316	−333	45
−13	1	2	209	249	−31
−13	1	3	473	554	−29
−13	1	4	339	308	199
−13	1	5	243	−165	178
−14	1	3	273	−187	203
−14	1	5	250	245	−125
−14	1	6	254	264	44
−15	1	1	361	−376	−160
−15	1	2	455	−513	−45
−15	1	4	380	397	19
−15	1	5	258	327	70
0	1	1	284	−81	286
0	1	2	254	139	210
0	1	3	854	815	160
0	1	4	399	330	−96
0	1	5	280	−144	−204
0	1	6	780	−734	2
0	1	7	544	−523	−97
0	1	9	429	349	−72
0	1	10	235	198	149
1	1	0	574	686	226
1	1	1	619	469	349
1	1	2	913	−572	608
1	1	3	924	−778	−285
1	1	4	217	−117	−179
1	1	5	518	34	−505
1	1	6	202	−164	−126
1	1	7	276	−245	176
1	1	9	224	228	17
1	1	10	451	442	−21
1	1	12	284	−306	80
2	1	0	724	−88	668
2	1	1	376	271	223
2	1	2	1417	1066	−850
2	1	3	432	267	178
2	1	4	924	−881	153
2	1	5	585	−626	−45
2	1	6	269	−208	−131
2	1	7	190	194	−130
2	1	8	395	386	97
2	1	9	228	−1	208
3	1	0	597	455	214
3	1	1	1010	−407	842
3	1	2	821	−658	−23
3	1	3	593	−143	−498
3	1	4	466	165	−385
3	1	5	522	−495	43
3	1	6	239	−122	217
3	1	7	235	253	4
3	1	8	526	525	−21
3	1	9	309	325	60
3	1	10	291	−318	−56
3	1	11	361	−318	144
4	1	0	1399	1222	−20
4	1	1	328	−208	−215
4	1	2	280	−268	−27
4	1	3	783	−686	285
4	1	4	343	−295	−195
4	1	5	507	466	−257

TABLE 1. (*Continued.*)

h	*k*	*l*	$\lvert F_o \rvert$	*A*	*B*
4	1	6	313	286	72
4	1	7	273	89	274
5	1	0	589	147	464
5	1	1	335	−129	−237
5	1	2	735	−233	−642
5	1	3	239	−169	−134
5	1	4	429	−368	184
5	1	5	179	221	37
5	1	6	656	644	227
5	1	7	462	460	51
5	1	9	243	−292	83
6	1	0	443	−314	264
6	1	1	612	−556	137
6	1	2	608	−419	−277
6	1	3	265	219	−172
6	1	4	514	448	69
6	1	5	269	209	190
6	1	6	276	−117	277
6	1	8	209	170	−91
7	1	0	455	340	−248
7	1	1	544	−313	−289
7	1	2	984	−916	49
7	1	3	250	−168	154
7	1	4	447	459	87
7	1	5	563	576	63
7	1	6	217	185	23
7	1	7	354	−349	−108
7	1	8	243	−279	−55
8	1	0	720	−689	15
8	1	1	205	−254	−52
8	1	2	414	338	−206
8	1	3	146	129	133
8	1	6	224	227	−73
8	1	8	384	−331	−144
9	1	0	470	−405	77
9	1	1	574	−505	130
9	1	3	552	558	96
9	1	4	455	450	43
9	1	6	299	−340	−2
10	1	0	305	272	121
10	1	1	202	184	80
10	1	3	305	131	209
10	1	4	247	268	52
10	1	5	209	195	−132
10	1	6	269	−239	20
10	1	7	339	−418	31
11	1	1	406	443	−80
11	1	2	443	451	38
11	1	4	258	−315	83
11	1	5	247	−230	−86
12	1	2	276	227	96
12	1	5	276	−318	51
12	1	6	284	−334	61
13	1	0	485	553	−55
13	1	1	243	255	118
13	1	3	250	−247	22
14	1	0	273	235	137
14	1	1	224	247	108
14	1	3	284	−280	73
14	1	4	284	−298	−5
15	1	0	258	−239	120
15	1	1	232	−161	−18
0	2	2	248	254	−271
0	2	3	361	419	−124
0	2	4	286	171	171
0	2	5	204	−77	173
0	2	7	370	−63	−364
0	2	8	269	−124	−200
0	2	9	300	−243	−35
0	2	10	160	−121	28
0	2	11	259	174	194
0	2	12	197	188	31
0	2	13	174	144	21
−1	2	3	303	−53	313
−1	2	4	240	97	219
−1	2	5	117	96	77
−1	2	6	296	336	−92
−1	2	8	389	−351	93
−1	2	9	407	−376	−151
−1	2	10	201	65	−167
−1	2	11	225	159	−94
−1	2	13	172	−9	185
−2	2	0	99	−42	−124
−2	2	1	276	−299	−28
−2	2	2	627	−738	215
−2	2	3	160	−162	−17
−2	2	4	574	616	22
−2	2	5	537	528	282
−2	2	6	361	−98	342
−2	2	7	304	−179	230
−2	2	8	192	−87	−120
−2	2	9	420	−23	−426
−2	2	11	272	−153	180
−2	2	14	162	167	57
−3	2	0	311	−282	170
−3	2	1	212	−209	129
−3	2	2	222	−111	−221
−3	2	3	545	141	−579
−3	2	4	290	−33	−273
−3	2	5	564	118	619
−3	2	6	467	101	485
−3	2	7	327	318	1
−3	2	8	251	196	−123
−3	2	9	218	−206	63
−3	2	10	327	−310	93
−3	2	11	208	−175	−106
−3	2	13	193	200	9
−4	2	0	382	401	24
−4	2	1	402	135	−397
−4	2	2	435	−51	−407
−4	2	3	576	−654	−172
−4	2	4	511	−574	−125
−4	2	5	398	392	−17
−4	2	6	608	621	69
−4	2	7	304	305	44
−4	2	8	348	−239	288
−4	2	9	167	−40	118
−4	2	10	328	40	−354
−4	2	11	172	−9	−151
−4	2	14	204	42	79
−5	2	0	670	721	105
−5	2	1	410	313	350
−5	2	2	437	−498	84
−5	2	3	479	−441	−211
−5	2	4	472	50	−463
−5	2	5	465	−165	−493
−5	2	6	165	142	−68
−5	2	7	334	134	349
−5	2	8	274	203	177
−5	2	9	341	267	−229
−5	2	11	170	−187	27
−5	2	12	304	−325	−87
−6	2	0	708	−154	810
−6	2	1	210	168	193
−6	2	2	430	429	−170
−6	2	3	305	96	−244
−6	2	4	395	−268	−318
−6	2	5	604	−647	172
−6	2	6	411	−322	121
−6	2	7	304	237	−180
−6	2	8	347	316	62
−6	2	9	252	120	188
−6	2	10	164	81	166
−6	2	12	197	−41	−195
−6	2	13	171	−13	−159
−7	2	0	176	−125	139
−7	2	1	729	812	80
−7	2	2	459	380	271
−7	2	3	305	−227	194
−7	2	4	293	−290	13
−7	2	5	270	−264	−57
−7	2	6	152	19	−169
−7	2	7	217	68	−161
−7	2	8	145	44	80
−7	2	9	310	−127	289
−7	2	10	166	86	168
−7	2	11	195	185	−52
−7	2	13	169	−163	33
−8	2	0	443	469	−148
−8	2	1	309	132	297
−8	2	2	568	−320	367
−8	2	3	283	258	143
−8	2	4	240	98	−178
−8	2	5	270	49	−260
−8	2	6	316	−317	−46
−8	2	7	373	−377	29
−8	2	8	170	−133	25
−8	2	9	219	181	51
−8	2	10	363	338	3
−8	2	11	152	9	149
−8	2	12	213	−154	142
−9	2	0	387	−386	114
−9	2	1	317	−94	299
−9	2	2	356	324	63
−9	2	3	419	422	−24
−9	2	4	153	140	61
−9	2	5	349	−234	214
−9	2	6	354	−296	20
−9	2	7	220	−38	−213
−9	2	8	266	157	−179
−9	2	9	250	225	−111
−9	2	10	171	−177	43
−9	2	11	214	−117	198
−10	2	0	247	−205	136
−10	2	1	424	209	−385
−10	2	2	479	408	−252
−10	2	3	442	153	446
−10	2	4	353	−69	311
−10	2	6	299	73	−201
−10	2	7	347	−3	−362
−10	2	8	247	−284	28
−10	2	9	258	−191	123
−10	2	10	176	171	15
−10	2	11	232	245	−45
−11	2	0	347	−79	−307
−11	2	1	426	−346	−240
−11	2	2	182	−136	88
−11	2	4	421	347	−69
−11	2	5	398	338	−125
−11	2	6	197	99	159
−11	2	7	368	−254	206
−11	2	8	270	−217	−146
−11	2	9	192	41	−180
−11	2	10	153	156	−44
−11	2	12	167	−63	192
−11	2	13	105	−4	85
−12	2	0	316	−285	34
−12	2	1	314	−288	33
−12	2	2	272	−144	−190
−12	2	3	392	309	−258
−12	2	4	299	270	52
−12	2	5	373	−93	374
−12	2	6	247	−116	223
12	2	7	281	16	−238
−12	2	8	300	157	−206
−12	2	9	176	−121	−87
−12	2	10	197	−214	−11
−12	2	11	170	8	135
−13	2	0	162	−131	142
−13	2	1	160	−6	−121
−13	2	2	329	−82	−285
−13	2	4	290	−199	125
−13	2	6	307	313	−25
−13	2	7	172	186	28
−13	2	9	195	−195	−4
−13	2	10	171	−176	−109
−13	2	11	166	41	−120
−13	2	12	179	190	−6
−13	2	13	138	64	128
−14	2	0	225	234	61
−14	2	2	282	−250	−63
−14	2	3	168	−138	119
−14	2	5	288	221	−83
−14	2	6	196	13	199
−14	2	7	195	−94	186
−14	2	10	167	−24	−193
−15	2	0	231	68	167
−15	2	1	303	−252	138
−15	2	3	194	59	−198
−15	2	4	194	−16	−189
−15	2	10	160	−176	50
−15	2	11	185	−166	52
−16	2	0	197	33	166
−16	2	2	232	185	−126
−16	2	4	304	−280	−25
−16	2	6	175	140	−8
−16	2	7	169	155	−104
−16	2	9	201	−24	170
−17	2	0	169	194	−52
−17	2	1	170	119	89
−17	2	3	191	−148	116
−17	2	5	208	3	−190
−17	2	8	133	−30	167
−18	2	0	201	−7	191
−18	2	3	163	168	−19
−18	2	4	162	94	−121
−18	2	5	184	−140	−20
−18	2	6	242	−281	29
−18	2	8	239	246	−7
−19	2	2	175	210	−6
−19	2	5	144	−145	55
−20	2	3	130	21	155
−20	2	5	155	113	−96
1	2	1	136	−303	43
1	2	2	430	79	567
1	2	3	321	259	−125
1	2	4	360	428	−23
1	2	5	384	36	369
1	2	6	503	−531	−30
1	2	7	431	−472	30
1	2	8	246	−46	−229
1	2	9	347	240	−262
1	2	10	162	154	39
1	2	11	192	97	201
1	2	12	197	−93	157
2	2	1	158	170	−72
2	2	2	229	280	176
2	2	3	568	−133	747
2	2	5	517	431	−303
2	2	6	104	−2	−132
2	2	7	340	−314	−102
2	2	8	292	−300	53
2	2	10	326	343	65
2	2	11	195	164	71
3	2	1	245	142	206
3	2	2	544	635	67
3	2	3	526	545	32
3	2	4	314	−278	223
3	2	5	555	−618	64
3	2	6	426	−235	−384
3	2	7	360	126	−312
3	2	8	280	257	31
3	2	9	225	142	145
3	2	10	256	−2	244
4	2	1	449	−145	462
4	2	2	341	−45	389
4	2	3	353	354	−229
4	2	4	546	318	−577
4	2	6	443	−482	198
4	2	7	205	−162	137
4	2	8	396	425	177
4	2	9	298	242	−100
5	2	1	423	432	−82
5	2	3	304	−321	67
5	2	4	359	−392	41
5	2	5	451	−141	−458
5	2	6	242	126	−223
5	2	7	244	35	223
5	2	8	240	109	203
6	2	2	427	340	−348
6	2	3	311	−132	−249
6	2	4	368	−393	−171
6	2	5	311	−160	241
6	2	7	329	347	−109
7	2	1	485	−482	88
7	2	2	378	−331	−131
7	2	3	227	24	−251
7	2	4	409	−74	−358
7	2	6	144	8	136
7	2	7	180	−114	156
8	2	1	298	−172	−192
8	2	2	353	−356	−93
8	2	3	325	−316	134
8	2	5	278	285	−102
8	2	6	247	188	143
8	2	7	162	30	241
9	2	1	429	−276	−346
9	2	2	352	65	−330
9	2	4	272	−111	243
9	2	5	285	75	290
9	2	6	160	144	122
10	2	1	503	−566	22
10	2	2	137	−164	−73
10	2	3	276	239	−139
10	2	5	230	104	223
10	2	6	206	−116	235
11	2	1	282	−12	−281
11	2	3	250	185	221
11	2	4	219	219	175
11	2	5	281	260	−22
11	2	6	172	26	−183
12	2	1	105	74	−104
12	2	2	366	429	−73
12	2	3	355	291	210
12	2	4	258	−187	110
12	2	7	213	−9	−245
13	2	1	164	−40	181
13	2	2	270	177	224
13	2	3	227	250	66
13	2	6	247	−278	18
13	2	7	208	−132	−51
14	2	1	260	192	122
14	2	2	175	−42	136
14	2	3	197	−163	77
15	2	1	214	195	−46
15	2	2	197	168	−65
15	2	5	188	−169	−48
16	2	1	196	−87	169
17	2	1	148	93	−5
17	2	2	223	−172	114
17	2	3	136	−142	−49
18	2	2	170	38	−181
18	2	3	114	−146	36
0	3	1	357	−55	−499
0	3	2	390	−96	−350
0	3	3	336	−307	69
0	3	4	299	−160	245
0	3	5	275	160	197
0	3	6	293	240	56
0	3	7	156	162	−43
0	3	8	246	−164	94
0	3	9	195	−171	0

TABLE 1. (*Continued*)

h	*k*	*l*	$\lvert F_o \rvert$	*A*	*B*
0	3	11	226	38	−231
0	3	12	203	133	−107
0	3	13	186	95	175
−1	3	2	203	−191	−138
−1	3	3	434	−359	−140
−1	3	4	370	206	−340
−1	3	5	284	188	−186
−1	3	6	266	2	276
−1	3	7	447	8	423
−1	3	9	245	62	−199
−2	3	0	470	87	498
−2	3	1	302	33	305
−2	3	2	374	−195	−219
−2	3	3	592	−128	−567
−2	3	4	389	20	−330
−2	3	5	305	−162	295
−2	3	6	291	−81	235
−2	3	7	274	236	104
−2	3	8	308	323	−123
−2	3	10	202	−159	122
−2	3	11	154	−161	−13
−2	3	12	177	−39	−150
−2	3	13	247	150	−184
−3	3	0	226	59	235
−3	3	1	376	322	90
−3	3	2	300	218	−140
−3	3	3	143	−30	−89
−3	3	4	468	−406	163
−3	3	5	352	−301	−228
−3	3	6	207	113	−185
−3	3	7	169	138	61
−3	3	8	238	−56	211
−3	3	9	342	−39	353
−3	3	11	154	−31	−176
−4	3	0	309	278	−22
−4	3	1	311	173	190
−4	3	2	499	−48	423
−4	3	3	323	−248	157
−4	3	4	394	−163	−325
−4	3	5	466	164	−450
−4	3	6	175	−114	−154
−4	3	7	298	−93	256
−4	3	8	353	−70	345
−5	3	0	329	−114	279
−5	3	1	507	−139	463
−5	3	2	390	231	224
−5	3	3	379	310	−225
−5	3	4	217	125	−121
−5	3	5	245	−205	43
−5	3	6	208	−220	−60
−5	3	7	326	123	−335
−5	3	8	213	149	−146
−5	3	9	197	157	124
−5	3	10	241	−66	230
−5	3	11	226	−69	184
−6	3	1	297	256	−119
−6	3	2	358	338	−102
−6	3	3	384	27	424
−6	3	4	332	−167	255
−6	3	6	407	−38	−369
−6	3	7	420	37	−436
−6	3	8	160	176	−56
−6	3	9	199	−22	192
−6	3	10	178	−26	183
−6	3	11	180	169	−56
−7	3	0	547	121	−519
−7	3	1	195	−73	−191
−7	3	2	347	−10	322
−7	3	3	417	5	446
−7	3	4	290	242	159
−7	3	5	236	10	−209
−7	3	6	192	−155	−86
−7	3	7	154	−82	160
−7	3	8	194	−77	−164
−7	3	9	148	78	−154
−7	3	10	273	237	−110
−7	3	12	233	−68	241
−8	3	0	307	−275	−110
−8	3	1	252	−255	32
−8	3	2	120	161	4
−8	3	3	250	245	−11
−8	3	4	109	118	111
−8	3	5	300	121	301
−8	3	6	141	−106	69
−8	3	7	379	−370	−90
−8	3	8	197	−108	−123
−8	3	9	241	28	−245
−8	3	11	239	−38	273
−9	3	0	254	−253	73
−9	3	1	488	−29	−537
−9	3	2	355	86	−324
−9	3	4	426	−160	342
−9	3	5	335	65	310
−9	3	7	256	77	−238
−9	3	9	255	−186	159
−9	3	10	180	−142	−56
−9	3	11	203	80	−127
−9	3	12	196	143	45
−10	3	0	351	130	−304
−10	3	1	324	−66	−325
−10	3	2	294	−241	−17
−10	3	3	199	−86	153
−10	3	4	154	63	139
−10	3	5	276	277	−82
−10	3	6	195	182	70
−10	3	7	218	−71	130
−10	3	8	241	−226	99
−10	3	9	226	−154	−135
−10	3	10	239	47	−255
−10	3	12	192	−30	143
−11	3	1	343	−341	83
−11	3	2	159	−64	−142
−11	3	3	318	108	−310
−11	3	4	193	33	−151
−11	3	5	176	−41	144
−11	3	6	345	−179	283
−11	3	7	203	77	168
−11	3	8	260	225	−140
−11	3	9	153	50	−173
−12	3	0	217	7	190
−12	3	2	393	175	−295
−12	3	4	199	−153	8
−12	3	5	118	96	164
−12	3	6	242	213	−29
−12	3	7	153	170	−101
−12	3	9	178	−175	136
−12	3	12	124	23	−152
−13	3	0	120	153	51
−13	3	1	150	91	−118
−13	3	3	314	−235	198
−13	3	4	177	−110	−152
−13	3	5	272	110	−287
−13	3	6	180	99	−85
−13	3	7	180	−69	161
−13	3	8	225	28	192
−14	3	0	154	74	140
−14	3	1	179	40	209
−14	3	2	179	−81	150
−14	3	3	179	−68	−178
−14	3	4	180	−31	−179
−14	3	8	148	175	3
−15	3	0	178	21	165
−15	3	4	225	−169	141
−15	3	5	224	−187	78
−15	3	7	218	95	−186
−15	3	9	178	−39	205
−16	3	2	221	141	148
−16	3	3	221	−1	209
−16	3	5	145	29	−163
−16	3	8	153	−57	151
−18	3	7	194	10	−218
1	3	1	353	−344	163
1	3	2	345	−42	−308
1	3	3	485	154	−492
1	3	4	209	105	165
1	3	5	529	−41	524
1	3	6	386	−10	358
1	3	7	271	248	−150
1	3	8	351	−105	−295
1	3	9	197	−126	−124
2	3	1	269	−243	13
2	3	2	361	−287	172
2	3	3	181	111	−49
2	3	4	289	284	38
2	3	5	263	207	27
2	3	6	145	−101	143
2	3	8	224	−8	−251
3	3	1	617	296	−520
3	3	2	344	182	−230
3	3	3	426	27	379
3	3	4	519	148	443
3	3	6	308	169	−245
3	3	8	363	−320	−104
4	3	1	68	−19	66
4	3	2	332	298	−61
4	3	3	160	150	43
4	3	4	106	21	99
4	3	5	350	−166	361
4	3	6	272	−262	−22
4	3	7	401	58	−416
4	3	8	248	188	−199
4	3	10	261	−31	295
5	3	1	399	−22	367
5	3	2	569	−11	542
5	3	3	120	19	95
5	3	4	259	253	−25
5	3	5	299	111	−258
5	3	6	259	−265	−56
5	3	7	360	−290	96
5	3	8	199	−101	−152
5	3	9	225	209	−120
5	3	10	179	192	112
6	3	1	262	223	−47
6	3	2	226	112	159
6	3	3	301	−27	279
6	3	4	210	−209	47
6	3	5	303	−177	−207
6	3	6	250	10	−260
6	3	7	247	210	−105
6	3	8	203	19	158
6	3	9	180	−75	177
7	3	1	316	51	252
7	3	2	378	318	−87
7	3	3	245	39	−199
7	3	4	221	−178	−20
7	3	5	290	−264	61
7	3	6	173	−179	−26
7	3	7	200	31	−193
7	3	9	260	51	257
8	3	1	324	−133	272
8	3	2	153	−23	191
8	3	3	192	−80	−180
8	3	4	375	−142	−311
8	3	7	224	100	155
8	3	8	180	106	156
9	3	1	299	234	−181
9	3	2	146	−130	−156
9	3	3	344	−378	54
9	3	5	381	183	−353
9	3	6	203	103	−93
9	3	7	179	74	198
10	3	1	209	−40	−190
10	3	2	393	193	−359
10	3	3	305	74	−278
10	3	5	223	74	193
11	3	1	185	−211	−74
11	3	2	248	−208	−24
11	3	3	220	0	−190
11	3	4	223	142	−144
11	3	6	244	−62	289
12	3	1	425	−69	−392
12	3	3	242	−156	212
12	3	4	226	−92	225
13	3	1	242	−186	−128
13	3	2	179	27	−201
13	3	4	179	23	272
13	3	5	150	17	180
15	3	2	118	56	146
0	0	6	124	162	0
0	0	14	214	198	0
0	1	8	140	195	−50
0	1	11	171	−83	121
0	2	0	902	−745	−34
0	2	1	502	−495	−88
0	4	0	138	124	−30
0	4	2	214	−64	204
0	4	3	183	−171	36
0	4	4	312	−45	−258
0	4	5	409	−62	−433
0	4	7	251	51	286
0	4	8	253	−46	258
0	4	9	177	51	−31
0	5	1	339	−4	344
0	5	2	332	−27	363
0	5	4	179	−81	−212

observations to parameters. We numbered the atoms according to the scheme in Fig. 2. A Patterson projection down the *a* axis gave the As(1)-As(2) separation parallel to *b* and confirmed the *z* co-ordinates. In this space group one *y* co-ordinate may be chosen arbitrarily, so we made *y*/*b* for As(1) = 0·00, and the Patterson projection showed *y*/*b* for As(2) to be 0·425. Structure factors were calculated for all *hkl* reflections and *R* was 0·29. A three-dimensional Fourier synthesis with phases from the arsenic atoms revealed only one clearly recognisable phenyl group [C(1)–C(6)] attached to As(1). With these six carbon atoms and the two arsenic atoms the *R* value was reduced to 0·27. A three-dimensional difference Fourier synthesis was computed; about 50 peaks were observed, some of which corresponded to chemically reasonable positions. The validity of the location of carbon atoms was tested by carrying out two or three cycles of least-squares refinement and noting whether the temperature factor steadily increased (a sign of an incorrectly placed atom) or fell. Some of the atoms chosen originally were found to be incorrect, but, with the aid of the correct ones and a model, more atomic positions were chosen and tested. This process continued until all the atoms were correct by the temperature-factor criterion and the model showed the independent molecules with the same stereochemistry.

Refinement by least squares, with allowance for anisotropic motion for arsenic and isotropic motion for carbon, reduced R to 0·10; the origin for the y co-ordinates was adjusted to be half-way between the arsenic atoms. The final observed and calculated structure amplitudes and phases are shown in Table 1. A three-dimensional difference Fourier synthesis showed no peaks greater than $\pm 0{\cdot}5$ e/Å^3 (compared with a standard deviation of ± 1 e/Å^3), indicating that the structure was correct. No evidence for the positions of the hydrogen atoms was given by this synthesis.

TABLE 2.

Atomic parameters.

	x/a	y/b	z/c	$\sigma(x)$ (10^{-2}Å)	$\sigma(y)$ (10^{-2}Å)	$\sigma(z)$ (10^{-2}Å)	X' (Å)	Y (Å)	Z' (Å)	U (10^{-3}Å^2)	$\sigma(U)$ (10^{-3}Å^2)
As(1)	0·0932	−0·1973	0·1265	$0{\cdot}4_5$	$0{\cdot}6_5$	$0{\cdot}4_5$	1·374	−1·142	1·723		
As(2)	0·6782	0·1971	0·2042	0·4	0·6	0·4	12·070	1·142	2·783		
C(1)	0·0426	−0·0025	0·2093	4	4	4	0·19	−0·02	2·85	33	9
C(2)	0·0432	−0·0651	0·3209	5	5	5	−0·12	−0·38	4·37	69	15
C(3)	0·0038	0·0910	0·3678	4	4	3	−0·99	0·53	5·01	29	10
C(4)	−0·0375	0·2813	0·3320	3	4	3	−1·66	1·63	4·52	36	10
C(5)	−0·0433	0·3283	0·2355	4	6	4	−1·49	1·90	3·21	65	13
C(6)	0·0004	0·1843	0·1717	4	5	4	−0·49	1·07	2·34	45	10
C(7)	0·1778	−0·2764	0·2317	3	4	3	2·65	−1·60	3·16	25	8
C(8)	0·1865	−0·4725	0·3002	5	6	5	2·61	−2·74	4·09	65	13
C(9)	0·2535	−0·5172	0·3548	4	4	4	3·70	−2·99	4·83	35	10
C(10)	0·3124	−0·3536	0·3632	4	6	4	4·78	−2·05	4·95	64	14
C(11)	0·3108	−0·1783	0·2833	3	4	3	4·98	−1·03	3·86	27	8
C(12)	0·2382	−0·1369	0·2119	4	5	4	3·83	−0·79	2·89	60	12
C(13)	0·2253	0·0513	0·1468	4	4	4	3·78	0·30	2·00	38	11
C(14)	0·2772	0·2264	0·1214	4	6	4	4·83	1·31	1·65	73	14
C(15)	0·2652	0·3752	0·0400	4	5	4	4·84	2·17	0·54	55	12
C(16)	0·1894	0·3875	−0·0090	4	5	4	3·56	2·24	−0·12	57	13
C(17)	0·1368	0·2173	0·0063	5	8	5	2·54	1·26	0·09	96	18
C(18)	0·1532	0·0358	0·0856	4	5	4	2·61	0·21	1·17	48	11
C(19)	0·5994	0·4291	0·1645	4	5	4	10·71	2·48	2·74	53	12
C(20)	0·6036	0·6169	0·0925	4	5	4	11·00	3·57	1·26	49	12
C(21)	0·5468	0·7549	0·0721	4	6	4	10·00	4·37	0·98	59	13
C(22)	0·4769	0·7399	0·1240	4	5	4	8·55	4·28	1·69	53	11
C(23)	0·4819	0·5671	0·1865	4	4	4	8·46	3·28	2·54	42	11
C(24)	0·5383	0·4114	0·2095	3	4	3	9·45	2·38	2·85	26	9
C(25)	0·5498	0·2183	0·2867	3	4	3	9·44	1·26	3·91	32	9
C(26)	0·4976	0·1353	0·3489	4	4	4	8·28	0·78	4·75	38	10
C(27)	0·5126	−0·0397	0·4142	4	5	4	8·37	−0·23	5·64	55	13
C(28)	0·5829	−0·1824	0·4130	4	5	4	9·69	−1·06	5·63	51	12
C(29)	0·6284	−0·1032	0·3698	5	6	5	10·66	−0·60	5·04	82	17
C(30)	0·6159	0·0652	0·2970	3	4	3	10·64	0·38	4·05	27	9
C(31)	0·7482	0·4127	0·2979	4	4	4	13·11	2·39	4·06	33	10
C(32)	0·7571	0·3725	0·3983	4	5	4	12·98	2·16	5·43	51	11
C(33)	0·8032	0·5395	0·4689	4	5	4	13·64	3·12	6·39	53	13
C(34)	0·8368	0·7221	0·4131	4	6	4	14·43	4·18	5·63	56	12
C(35)	0·8229	0·7324	0·3160	5	7	5	14·45	4·24	4·31	90	17
C(36)	0·7789	0·5858	0·2531	4	4	4	13·81	3·39	3·45	38	11

Results.—The structure is shown in Figs. 2, 3, and 4. Table 2 shows the fractional co-ordinates, the corresponding standard deviations in Å, the co-ordinates, X', Y, and Z', in Å referred to orthogonal axes parallel to the crystallographic a, b, and c^* axes; also shown are the values of U, the mean square amplitudes of vibration, and their standard deviations. For the arsenic atoms the anisotropic vibration parameters (with standard deviations in parentheses) in Å^2 were:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
As(1)	42(3)	63(5)	45(3)	3(2)	−11(2)	4(2)
As(2)	30(2)	41(4)	45(2)	0(2)	−5(2)	10(2)

No physical significance should be attached to these results because, as the larger values for the standard deviation of U_{22} (which is parallel to b^*) indicates, our observations did not cover a sphere of reciprocal space.

The bond lengths and angles were calculated together with their estimated standard

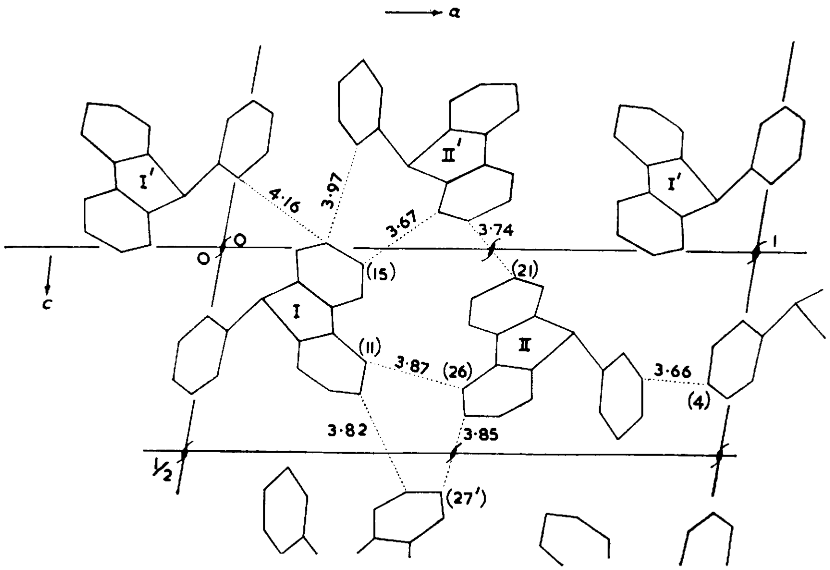

FIG. 3. Projection of the structure along [010]. The numbers are distances in Å between the atoms joined by the dotted lines. Molecules I' and II' are related to I and II, respectively, by screw axes.

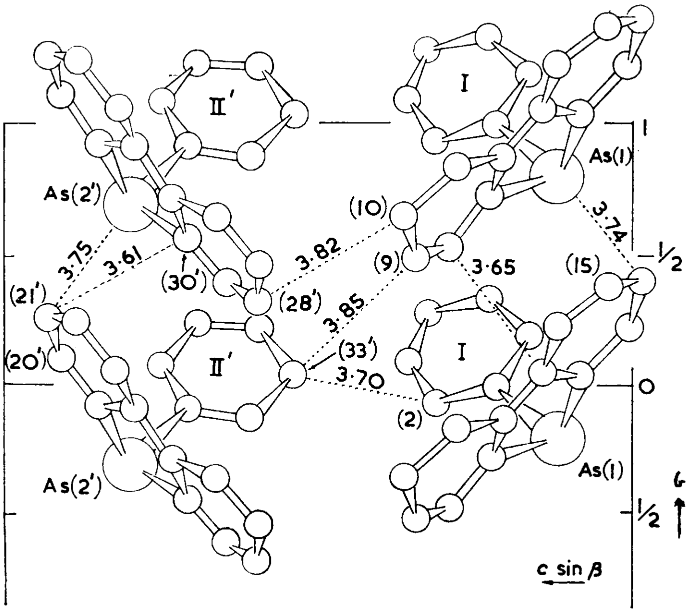

FIG. 4. Projection of half the structure down [100], showing molecules for which most atoms have $x/a < 0{\cdot}5$. The numbers are distances in Å between atoms joined by dotted lines.

deviations which were ±0·04 Å for As–C bonds, ±0·05—0·06 Å for carbon–carbon bonds, and 1° for C–As–C angles and 3—4° for C–C–C angles. The two molecules were identical within experimental error and each had a plane of symmetry; for molecule I, this passes through C(1), C(4), As(1), and between C(13) and C(12), while for molecule II the plane passes through C(34), C(31), As(2), and between C(24) and C(25). This repetition of measurement has been used to determine the dimensions of a mean molecule as shown in Fig. 5.

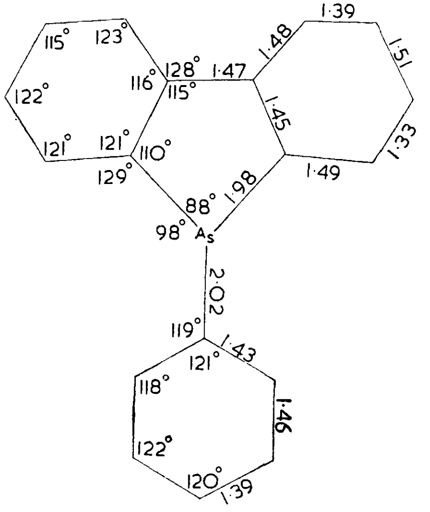

FIG. 5. Dimensions of the mean molecule; standard deviations are ±0·03 Å for C–C bond lengths, ±0·02 Å for As–C bond lengths, ±2° for C–C–C angles, and ±1° for As–C–C and C–As–C angles.

Planes were calculated for the carbon atoms of the fluorene groups, of the constituent six-membered rings, and of the phenyl groups. In each case the arsenic atom was not included in the calculation, but its distance from the plane of the carbon atoms was found.

For molecule I the plane through the fluorene group is given by

$$0{\cdot}414X' - 0{\cdot}637Y - 0{\cdot}651Z' - 0{\cdot}160 = 0.$$

As(1) lies 0·01 Å from this plane and the largest deviation of a carbon atom is 0·13 Å for C(9), the constituent six-membered rings have an angle of 3° between their normals. For molecule II the plane through the fluorene group is given by

$$-0{\cdot}309X' - 0{\cdot}617Y - 0{\cdot}724Z' + 6{\cdot}491 = 0.$$

As(2) lies 0·04 Å from this plane and the largest deviation for a carbon atom is 0·08 Å for C(29), the angle between the normals to the constituent six-membered rings is zero.

The plane of the phenyl group C(1)–C(6) is

$$-0{\cdot}762X' - 0{\cdot}592Y - 0{\cdot}264Z' + 0{\cdot}868 = 0,$$

with a maximum deviation of 0·03 Å for C(5) and As(1) at 0·04 Å from this plane. The plane of the phenyl group C(31)–C(36) is

$$0{\cdot}813X' - 0{\cdot}583Y - 0{\cdot}009Z' + 9{\cdot}225 = 0,$$

with a maximum deviation of 0·02 Å for C(33) and As(2) at 0·1 Å from this plane.

The angle between the normal to the fluorene group and the normal to the phenyl group is 77° for molecule I and 83° for molecule II.

As a check the planes of the five-membered heterocyclic rings were calculated, including the arsenic atoms weighted suitably. The largest deviation of any carbon atom from the appropriate plane was 0·09 Å which is twice the mean standard deviation in the co-ordinates of this atom, C(12); for molecule II the largest deviation was only 0·03 Å.

All the interatomic distances of less than 4·5 Å were calculated. No unreasonably short intermolecular distances were found; the shortest ones for each kind of intermolecular contact are shown in Figs. 3 and 4. Within the molecules the distances between the *ortho*-carbon atoms of the phenyl groups, atoms (2), (6), (32), and (36), and the nearest atoms in the fluorene rings, (7), (18), (30), and (19), respectively, lay in the range 3·25—3·44 Å.

DISCUSSION

Our results show that the configuration about the arsenic atom is pyramidal, in agreement with the deductions of Campbell and her co-workers.[1,2] This may be the result of sp^3 hybridisation, with the lone pair occupying the fourth position. As both the orthorhombic and the monoclinic form have enantiomorphous space groups, the molecules might be expected to have no plane of symmetry. In fact, however, each molecule in the monoclinic form has a mirror plane, within experimental error, and the deviations from this follow different patterns in the two molecules, indicating that they are experimental error and not of chemical significance. This mirror plane arises from the orientation of the phenyl group which could, in principle, undergo free rotation about the As–C bond. There are two possible explanations for the observed orientation; it may be a purely steric effect or it may indicate d_π–p_π bonding. In the observed structure the nearest approach of an *ortho*-carbon atom on the phenyl group to an atom of the fluorene group is 3·25 Å; rotation about the As–C bond could reduce this to a minimum of 3·0 Å but would result in a hydrogen–carbon distance of 2·5 Å. However, further rotation to make the plane of the phenyl group coincide with the plane of symmetry would give a compact molecule with no overcrowding. Thus on purely steric grounds two configurations seem equally probable.

In the observed orientation, if the z-direction is taken as the bisector of the five-membered ring, there is fairly good overlap between the d_{z^2} orbital and the π-orbitals of the phenyl group and between the $d_{x^2-y^2}$ orbital and the π-orbitals on the fluorene group. The other sterically stable position would give overlap with only the $d_{x^2-y^2}$ orbital for both organic groups.

The dimensions in the fluorene molecule have been determined by two-dimensional methods;[4] the molecule is planar and the mean bond length in the six-membered rings is 1·40 ± 0·01 Å, compared with our mean value of 1·44 ± 0·02 Å. For benzene a three-dimensional analysis[5] gave a mean bond length of 1·39 ± 0·01 Å which can be compared with our mean value of 1·42 ± 0·03 Å. Although in both organic groups the bond lengths are longer in the arsenic compound, as expected for d_π–p_π bonding, they are not significantly longer and our results cannot be taken as evidence for such bonding.

The As–C–C angle in the five-membered ring is the same as the corresponding one in fluorene[4] but the C–C–C bond angle is 7° larger, so that there may be less strain in the heterocyclic ring than in fluorene.

Few As–C bond lengths have been reported. For trimethylarsine spectroscopic methods[6] gave 1·98 Å and a three-dimensional crystal structure analysis[7] of arsenomethane pentamer gave a mean value of 1·95 ± 0·02 Å, but these represented a range from 1·92 to 1·97 Å, each ±0·05 Å, and similarly our results varied over wide limits, 1·91—2·06 Å. Two-dimensional investigation of the hexameric arsenobenzene[8] gave 1·92—2·01 Å, and of chlorodiphenylarsine[9] gave 1·97 ± 0·04 Å. The largest intermolecular separation is between molecule I and I′ (see Fig. 3), otherwise the structure is efficiently packed and there are several contacts nearly as close as the minimum ones shown in the Figures. The nearest neighbour to an arsenic atom is a carbon atom in the same molecule in the unit cell along the b axis; this contact does not represent the direction of the lone pair.

[4] D. M. Burns and Iball, *Proc. Roy. Soc.*, 1955, *A*, **227**, 200.
[5] Cox, Cruickshank, and Smith, *Proc. Roy. Soc.*, 1958, *A*, **247**, 1.
[6] Siebert, *Z. anorg. Chem.*, 1953, **273**, 161.
[7] J. H. Burns and Waser, *J. Amer. Chem. Soc.*, 1957, **79**, 859.
[8] Hedberg, Hughes, and Waser, *Acta Cryst.*, 1961, **14**, 369.
[9] Trotter, *Canad. J. Chem.*, 1962, **40**, 1590.

EXPERIMENTAL

The compound, and its oxide were prepared by Heinekey and Millar as described in the Appendix to this paper.

All *X*-ray photographs were taken with Cu-K_α radiation. Equi-inclination Weissenberg photographs were taken about the *b* axis for the 0th to 3rd layers inclusive and the zero layer line about the *a* axis. Intensities were estimated visually with the aid of a calibration strip and corrected for Lorentz and polarisation factors on the Leeds University Ferranti Pegasus computer with a programme written by Mr. J. G. F. Smith. No absorption correction was applied; the crystals set about the *b* axis were 1 mm. long 0·06 × 0·27 mm. in cross-section. The values of $F(0kl)$ were used to correlate the layer lines and give a set of 987 independent $F(hkl)$ on an arbitrary scale; the scale factor was one of the parameters of the refinement.

The scattering factors were those of Berghuis *et al.*[10] for arsenic and carbon. Refinement was carried out by the method of least squares on the Pegasus computer with programmes written by Cruickshank *et al.*[11] The function minimised was $R' = w(|F_o| - |F_c|)^2$, where w was taken as 1/24 for $|F_o| < 32$ and as $1/(|F_o| + 0{\cdot}2\,|F_o|^2)$ for $|F_o| > 32$. Three-dimensional Fourier synthesis and calculations of interatomic distances and angles were also carried out on the Pegasus computer; [11] a programme written by Mr. J. G. F. Smith was used to compute the standard deviations in bond lengths and angles.

Crystal Data for 9-*Phenyl*-9-*arsafluorene Oxide Dihydrate.*—$C_{18}H_{17}AsO_3$. *M*, 355·6. Monoclinic, $a = 21{\cdot}4 \pm 0{\cdot}2$, $b = 14{\cdot}00 \pm 0{\cdot}05$, $c = 14{\cdot}0 \pm 0{\cdot}1$ Å, $\beta = 131°$, $U = 3208$ Å^3, $D_m = 1{\cdot}47$, $Z = 8$, $D_c = 1{\cdot}47$. Space group $C2/c$ (C_{2h}^6, No. 15), no molecular symmetry required, or $Cc(C_s^4$, No. 9) with two molecules in the asymmetric unit.

We thank Dr. I. T. Millar for the crystals, Dr. N. H. Hartshorne for help with optical work, Mr. J. G. F. Smith and other colleagues [11] for the use of their programmes, and the Director of the Leeds University Electronic Computing Laboratory for computation facilities. One of us (D. S.) thanks the D.S.I.R. for financial support. Some of the equipment was provided by the Royal Society and Imperial Chemical Industries Limited.

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APPENDIX

9-*Phenyl*-9-*arsafluorene and its derivatives.*

By D. M. HEINEKEY and I. T. MILLAR.

9-*Phenyl*-9-*arsafluorene.*—This compound was prepared by the general method described previously.[3,12]

2,2′-Di-iodobiphenyl (10 g.) in dry ether (150 ml.) was added with stirring during ½ hr. to fine lithium foil (1·5 g.) under nitrogen, and the solution of 2,2′-dilithiobiphenyl was decanted from insoluble material. A solution of dichlorophenylarsine (3·5 g.) in benzene (50 ml.) was added to the solution of 2,2′-dilithiobiphenyl during 20 min. After refluxing for 1 hr., the mixture was hydrolysed with cold, air-free water. The organic layer was separated, the solvents were evaporated, and the residue was distilled, yielding 9-*phenyl*-9-*arsafluorene*, b. p. 182—186°/0·3 mm. (2·3 g., 50%), which after recrystallisation from ethanol had m. p. 86° (Found: C, 70·9; H, 4·05. $C_{18}H_{15}As$ requires C, 71·05; H, 4·3%).

A sample in acetone with hydrogen peroxide deposited 9-*phenyl*-9-*arsafluorene oxide dihydrate*, m. p. 152—153° after recrystallisation from aqueous ethanol (Found: C, 60·65; H, 4·8. $C_{18}H_{19}AsO_3$ requires C, 60·7; H, 4·8%). Another sample, heated in a sealed tube at 100° with an excess of methyl bromide, gave 9-*methyl*-9-*phenyl*-9-*arsafluorenonium bromide monohydrate*, m. p. 164—165° (decomp.) after recrystallisation from ethanol (Found: C, 54·2; H, 3·8. $C_{19}H_{18}AsBr$ requires C, 54·6; H, 4·3%).

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[10] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[11] Cruickshank, Pilling, and (in part) Bujosa, Lovell, and Truter, "Computing Methods and the Phase Problem in *X*-ray Crystal Analysis," Pergamon Press, Oxford, 1961, p. 32.

[12] Heinekey and Millar, *J.*, 1959, 3101.