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The Crystal and Molecular Structure of Arsenic Tricyanide

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Arsenic tricyanide forms monoclinic crystals in the space group C_2^3–$C2$ with four molecules in a unit cell of dimensions $a = 9{\cdot}19$, $b = 6{\cdot}90$, $c = 8{\cdot}92$ Å, and $\beta = 101{\cdot}2°$. The molecules are pyramidal with approximate C_{3v} symmetry. One of the cyanides is involved in the formation of a weak bond to the arsenic atom in the adjacent molecule. Infinite, approximately linear, chains AsCN···AsCN··· are present and presumably account for the low volatility of this compound.

Introduction

The tricyanides of phosphorus and arsenic have very low volatilities compared to the trihalides. This suggests that the crystal or molecular structures of these compounds might show interesting features. Accordingly, a study was undertaken of the crystal structure of $P(CN)_3$. This structure proved to be unexpectedly complex crystallographically, and the study of $As(CN)_3$ was undertaken both for its own sake and to throw light on the $P(CN)_3$ problem. The arsenic compound proved to have a simpler structure and is reported here. The relationship between the two structures will be reported later, with the phosphorus structure.

Experimental

Redistilled $AsCl_3$, mixed with freshly prepared AgCN, was sealed in a glass tube under vacuum and heated at 100 °C. for 24 hours (Emerson, 1960). The tube was broken and the excess $AsCl_3$ was distilled off in a vacuum line. The $As(CN)_3$ was then vacuum sublimed at about 200 °C. The product appeared as white needle-like crystals. These crystals were very hygroscopic so single crystals were transferred in a dry box into glass capillaries which were then sealed with Apiezon wax.

A crystal of the order of 0·2 mm. in diameter was selected for intensity measurements and multiple film Weissenberg photographs were taken with Cu $K\alpha$ radiation of the 0, 1st, 2nd, and 3rd layers for rotation around the needle axis. A second set of 0 layer photographs was taken with Mo $K\alpha$ radiation to check the assumption that absorption corrections could be ignored for a crystal of this size. Precession photographs of four zones were taken using Mo $K\alpha$ radiation. The relative intensities of 402 independent reflections were estimated by visual comparison with a standard intensity strip. Lorentz and polarization corrections were applied with the aid of programs available for this purpose on the Univac Scientific 1103 computer (Rossman, Jacobson, Hirshfeld & Lipscomb, 1959).

Unit cell and space group

The needle axis of the crystals proved to be the b axis of a monoclinic cell with dimensions

$$a = 9{\cdot}19 \pm 0{\cdot}06,\ b = 6{\cdot}90 \pm 0{\cdot}04,\ c = 8{\cdot}92 \pm 0{\cdot}06\ \text{Å};\quad \beta = 101{\cdot}2 \pm 0{\cdot}5°.$$

Cell dimensions were determined by measurements on Weissenberg and rotation photographs taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The only systematic extinctions were for reflections with $h+k$ odd, and the space group could therefore be C_2^3–$C2$, C_s^3–Cm, or C_{2h}^3–$C2/m$. No density measurements were made on $As(CN)_3$, but by comparison of this unit cell with the apparently related unit cell for $P(CN)_3$, for which the density had been measured, it was decided that there were four molecules per unit cell. The calculated density is 1·831 g.cm.$^{-3}$.

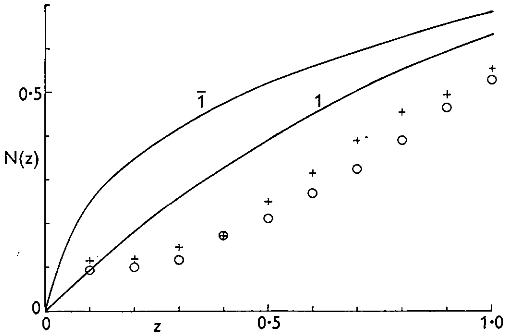

Fig. 1. Statistical distribution of $As(CN)_3$ intensities. Theoretical curves for centric and acentric cases are labelled $\bar{1}$ and 1 respectively. ○: calculated points from hkl data. +: calculated points from $h0l$ data.

Although it was realized that this was not a suitable compound the statistical distribution of the intensities was calculated (Howells, Phillips & Rogers, 1950). The results, shown in Fig. 1 for the $h0l$ and hkl inten-

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Table 1. *Final parameters*

Atom	x/a	y/b	z/c	B
As	0·2904 ± 0·0004	0·0000 ± 0·0033	0·2616 ± 0·0004	2·63 ± 0·05
C_1	0·229 ± 0·004	0·210 ± 0·007	0·362 ± 0·005	4·9 ± 0·9
C_2	0·113 ± 0·004	− 0·123 ± 0·007	0·255 ± 0·005	5·7 ± 1·1
C_3	0·213 ± 0·004	0·135 ± 0·008	0·070 ± 0·005	6·0 ± 1·1
N_1	0·188 ± 0·004	0·327 ± 0·007	0·443 ± 0·004	7·1 ± 1·0
N_2	0·008 ± 0·004	− 0·213 ± 0·007	0·245 ± 0·004	7·0 ± 1·0
N_3	0·183 ± 0·003	0·196 ± 0·006	− 0·051 ± 0·004	5·4 ± 0·8

sities were interpreted as indicating the space group C_s^3–Cm. This was incorrect and considerably delayed the solution. The correct space group, as indicated by the solved structure, was C_2^3–$C2$.

Determination of an incorrect structure in *Cm*

Almost all of the calculations described below were made on a Univac Scientific 1103 Computer using methods and programs which have been previously described (Rossman, Jacobson, Hirshfeld & Lipscomb, 1959).

The locations of the arsenic atoms were readily found from a Patterson projection along the *b* axis, and a Fourier projection was prepared with the phases determined by the arsenic atoms. This gave indications of several possibilities for the cyanide groups, but these were ambiguous since the arsenic atoms alone have $C2/m$ symmetry. At this point least squares (Hughes, 1941) were used for testing the various possibilities and for refining the likely ones. The arsenic alone gave a reliability factor,

$$R = \Sigma||kF_o| - |F_c||/\Sigma|kF_o| = 0{\cdot}37\ .$$

The best of the chemically reasonable cyanide combinations gave $R = 0{\cdot}24$ in five cycles of refinement. At this point the full three dimensional data were introduced and in five more cycles $R = 0{\cdot}19$. This structure in space group *Cm* was more or less reasonable chemically, but the bond angles around the As differed by 15° between the two molecules in the asymmetric unit. Various small changes in the positions of the cyanides were tried to make the two molecules more nearly equivalent, but none of these changes improved matters. One of these attempts also refined to $R = 0{\cdot}19$ but in so doing distorted all the As–C–N bond angles away from linear by 20 to 60°.

It was clear that this structure was not correct although it must have a large element of correctness. It was also felt that all possible reasonable changes had been tried in space group *Cm*, and that if the structure were wrong the space group must also be wrong. The space group *Cm* had been chosen on the basis of the statistical distribution of intensities although it has been pointed out (Hargreaves, 1955; Wilson, 1949) that where a heavy atom dominates the scattering, as happens here, the intensity distribution may be abnormal. The distribution found here did not resemble either of those calculated by Hargreaves, but it also did not look 'normal'. Since $C2/m$ would have refined in *Cm* it was decided to try $C2$.

Determination of the correct structure in *C*2

A trial structure was found, which appeared reasonable in light of the original Fourier synthesis, with two of the three cyanides in positions close to those in the *Cm* structure. A least squares refinement of this structure in projection fell from $R = 0{\cdot}17$ to $R = 0{\cdot}14$ in three cycles. The full three dimensional data were introduced and in four cycles R fell to 0·118. In the least squares program used the function

$$r = \Sigma w_0^4(|kF_o|^2 - |F_c|^2)^2/\Sigma w_0^4|kF_o|^4,$$

the numerator of which is being minimized, gives a better measure of convergence in the later stages; at this point in the calculations $r = 0{\cdot}054$.* In the next cycle of refinement a computer error occurred, and both R and r increased slightly. The error was not immediately recognized, and refinement was continued until all full shifts in the position parameters were less than 0·001 ($R = 0{\cdot}106$, $r = 0{\cdot}056$). When the error was discovered, the refinement was repeated from the point of error until once again all full shifts in the position parameters were less than 0·001 ($R = 0{\cdot}104$, $r = 0{\cdot}052$). These two refinements gave answers which agreed within the standard deviations of the parameters, but did not appear to be converging toward a common result. This seemed somewhat alarming to us, but it was suggested by Dr E. W. Hughes that this probably meant simply that there was a very broad minimum at the solution, and we had accidentally approached it from two different directions. At his suggestion we averaged the parameters obtained from the two refinements

Table 2. *Interatomic distances and angles*

Distance		Angle	
As–C_1	1·85 ± 0·05 Å	C_2–As–C_3	91·5 ± 3·5°
As–C_2	1·82 ± 0·05	C_1–As–C_3	87·6 ± 3·5
As–C_3	1·96 ± 0·05	C_1–As–C_2	91·5 ± 3·5
As–N_1	3·03 ± 0·04	N_2–As–N_3	92·8 ± 2·0
As–N_2	2·95 ± 0·04	N_1–As–N_3	94·9 ± 2·0
As–N_3	3·09 ± 0·04	N_2–As–N_1	91·8 ± 2·0
C_1–N_1	1·19 ± 0·07	As–C_1–N_1	171 ± 8
C_2–N_2	1·13 ± 0·07	As–C_2–N_2	175 ± 8
C_3–N_3	1·14 ± 0·07	As–C_3–N_3	168 ± 8

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* The weighting factor, w_0, was $= 1$ for $|kF_0| \leq 23$, and $23/|kF_0|$ for $|kF_0| > 23$.

Table 3. *Observed and calculated structure factors**

H	K	L	10Fo	10Fc	10A	10B
0	2	0	481	437	435	43-
0	4	0	679	622	621	34-
0	6	0	453	437	436	23
0	8	0	233	220	220	9-
0	2	1	374	344	48-	341
0	0	2	911	1075	1075-	0
0	2	2	1004	986	952-	256
0	4	2	703	642	640-	55-
0	6	2	400	345	345-	0
0	0	3	383	382	382	0
0	2	3	188	180	89	156
0	4	3	231	172	142	97-
0	0	4	896	946	946	0
0	2	4	693	673	654	157-
0	4	4	522	467	464	54
0	6	4	338	314	314	12-
0	0	5	214	246	246-	0
0	2	5	286	245	244-	23-
0	0	6	727	673	673-	0
0	2	6	505	420	419-	35
0	4	6	262	314	314-	16-
0	0	7	171	166	166	0
0	2	7	283	254	244	70-
0	0	8	319	317	317	0
0	2	8	321	292	290	31-
0	0	9	221	204	204-	0
0	2	9	195	168	167-	21-
0	0	10	255	224	224-	0
0	2	10	142	147	147-	2
0	0	11	121	143	143	0
0	0	12	85	92	92	0
1	1	0	212	143	100-	102-
1	3	0	348	364	364-	6
1	1	1	1051	1098	1096-	72-
1	3	1	839	793	790-	63
1	5	1	412	446	446-	3-
1	7	1	276	281	281-	4-
1	1	2	600	680	234	639
1	3	2	469	418	380	175-
1	1	3	841	898	883	164-
1	3	3	546	501	495	78-
1	1	4	386	403	401-	40-
1	3	4	362	314	313-	30-
1	1	5	538	526	523-	58
1	3	5	555	467	466-	37-
1	1	6	302	293	288	52
1	3	6	400	330	330	13-
1	1	7	350	331	331	7-
1	3	7	295	244	243	23-
1	1	8	212	246	246-	3-
1	3	8	300	245	245-	4-
1	1	9	190	185	185-	4-
1	3	9	112	135	134-	18
1	1	10	190	189	189	11
1	3	10	166	156	156	0
2	0	0	1206	1403	1403-	0
2	2	0	753	726	684-	242-
2	4	0	505	513	499-	119
2	6	0	438	363	362-	30-
2	8	0	202	181	180-	15
2	0	1	331	308	308	0
2	2	1	631	487	484	54-
2	0	2	443	497	497	0
2	2	2	820	753	753	8-
2	4	2	567	482	480	46-
2	6	2	290	277	275	32
2	0	3	610	626	626-	0
2	2	3	429	440	422-	124-
2	0	4	231	269	269-	0
2	2	4	629	596	596-	21-
2	0	5	419	418	418	0
2	2	5	474	421	410	94
2	0	6	331	329	329	0
2	2	6	295	264	264	14
2	0	7	257	271	271-	0
2	2	7	388	355	353-	40
2	0	8	88	112	112-	0
2	2	8	166	162	162-	6
2	0	9	240	251	251	0
2	2	9	286	225	224	24
2	0	10	85	86	86	0
2	0	11	145	158	158-	0
3	1	0	682	767	582	499-
3	3	0	557	541	523	140
3	5	0	355	333	333	13
3	7	0	207	186	185	23-
3	1	1	476	452	424	157
3	3	1	715	621	621	2
3	1	2	615	671	638-	209-
3	3	2	453	456	456-	17
3	1	3	319	388	388-	14-
3	3	3	333	297	297-	4
3	5	3	357	259	259-	4-
3	1	4	524	573	572	27-
3	3	4	426	397	393	53
3	1	5	240	215	215	3
3	3	5	276	218	212	50
3	1	6	383	389	385-	57
3	3	6	429	368	367-	24-
3	3	7	142	118	118-	5-
3	1	8	348	286	286	2
3	3	8	283	250	250	14
3	1	10	171	186	186-	4
4	0	0	505	605	605	0
4	2	0	281	270	251	99
4	4	0	369	330	330	3-
4	0	1	720	709	709-	0
4	2	1	715	589	588-	30
4	0	2	412	410	410-	0
4	2	2	80	111	110-	11
4	0	3	686	736	736	0
4	2	3	534	509	509	14-
4	2	4	176	177	175	28
4	0	5	476	476	476-	0
4	2	5	441	413	412-	28-
4	0	7	279	300	300	0
4	2	7	352	324	323	28-
4	0	9	209	218	218-	0
4	2	9	188	202	202-	3-
4	0	11	88	128	128	0
5	1	0	624	667	638-	193
5	3	0	593	577	576-	30
5	5	0	331	318	315-	42-
5	7	0	264	231	231-	6
5	1	1	97	89	84-	30-
5	3	1	164	170	170-	12
5	1	2	562	637	627	111
5	3	2	519	462	457	69-
5	1	4	434	504	500-	64-
5	3	4	379	368	366-	42
5	1	6	326	334	331	42-
5	3	6	283	303	303	9-
5	1	7	52	81	80-	14-
5	1	8	214	225	225-	8-
5	3	8	178	187	187-	2
6	2	0	133	81	79-	19-
6	0	1	557	572	572	0
6	2	1	620	509	509	3
6	2	2	102	87	87-	7-
6	0	3	534	531	531-	0
6	2	3	465	403	403-	20
6	0	4	131	142	142	0
6	0	5	326	347	347	0
6	2	5	286	302	302	9-
6	0	6	119	134	134-	0
6	0	7	214	218	218-	0
6	2	7	221	211	211-	12
6	0	8	83	102	102	0
6	2	8	97	94	94	0
6	0	9	147	131	131	0
7	1	0	474	465	454	101-
7	3	0	462	399	399	14
7	5	0	269	275	275	6
7	1	1	107	114	114-	8
7	3	1	190	125	116-	46-
7	1	2	424	418	418-	20
7	3	2	340	303	303-	8-
7	1	3	157	148	148	1
7	3	3	185	127	127	8
7	1	4	262	310	309	28
7	3	4	247	226	226	15-
7	1	5	126	139	139-	8-
7	3	5	200	148	148-	0
7	1	6	178	197	195-	31
7	3	6	181	169	169-	2-
7	1	7	124	139	138	15
8	0	0	200	180	180-	0
8	2	0	245	159	157-	23-
8	0	1	302	320	320-	0
8	2	1	305	297	296-	22-
8	0	2	131	135	135	0
8	2	2	269	222	221	16
8	0	3	228	271	271	0
8	2	3	257	210	210	12
8	0	4	147	168	168-	0
8	2	4	217	180	180-	3-
8	0	5	131	159	159-	0
8	2	5	135	147	147-	4
8	0	6	155	169	169	0
8	2	6	116	138	137	15
8	0	7	83	93	93	0
9	1	0	228	216	216-	8-
9	3	0	276	230	230-	1-
9	1	1	247	206	206	4-
9	3	1	181	199	198	15
9	1	2	166	178	178	7
9	3	2	166	158	158	9
9	1	3	190	199	199-	3
9	3	3	176	171	171-	2
9	1	4	121	118	115-	28-
9	3	4	80	100	100-	9
9	1	5	142	165	165	5
10	0	0	286	242	242	0
10	2	0	190	189	189	4-
10	0	1	83	109	109	0
10	2	1	128	122	122	9
10	0	2	224	203	203-	0
10	2	2	183	191	191-	9
10	0	3	66	81	81-	0
10	2	3	66	65	64-	13-
10	0	4	140	167	167	0
10	0	6	126	142	142-	0
11	1	0	33	66	66	3-
11	1	1	176	186	186-	11
12	0	0	128	159	159-	0
12	0	2	124	135	135	0
1-	1	1	1087	1356	1350	123
1-	3	1	744	649	646	60-
1-	5	1	512	511	511	1-
1-	7	1	312	294	294	3
1-	1	2	176	141	39	136
1-	3	2	247	209	187	93
1-	1	3	872	1002	968-	257
1-	3	3	639	672	671-	43
1-	1	4	317	314	180	257-
1-	3	4	185	118	98-	66
1-	1	5	653	663	659	75-
1-	3	5	691	613	611	48
1-	1	6	128	124	120-	31
1-	3	6	138	73	73-	2
1-	1	7	495	497	497-	9-
1-	3	7	357	321	320-	20
1-	1	8	183	151	129	79-
1-	3	8	116	105	105	9
1-	1	9	288	283	283	5-
1-	3	9	290	245	245	13-
1-	1	10	157	129	129-	7-
1-	1	11	162	169	169-	1-
2-	0	1	221	208	208-	0
2-	2	1	624	590	467-	361-
2-	0	2	314	303	303	0
2-	2	2	1223	1158	1156	70
2-	4	2	577	554	553	27-
2-	6	2	328	318	318	5-
2-	8	2	226	203	203	0
2-	0	3	59	36	36	0
2-	2	3	367	344	335	79-
2-	0	4	617	709	709-	0
2-	2	4	667	733	733-	26
2-	2	5	147	102	58-	84-
2-	0	6	538	518	518	0
2-	2	6	569	578	576	53
2-	2	7	133	64	15-	62
2-	0	8	331	362	362-	0
2-	2	8	417	366	366-	14-
2-	0	9	124	75	75	0
2-	0	10	202	256	256	0
2-	2	10	283	222	222	7
2-	0	12	121	131	131-	0
3-	1	1	712	888	842-	282-
3-	3	1	438	398	398-	8-
3-	1	2	510	563	563-	19-
3-	3	2	410	379	356-	131-
3-	1	3	500	554	549	77-
3-	3	3	703	698	697	39
3-	5	3	357	348	348	3-
3-	7	3	235	217	217	10-
3-	1	4	293	305	297	68-
3-	3	4	350	277	276	27
3-	1	5	491	521	520-	28-
3-	3	5	567	552	550-	42-
3-	1	6	205	190	183-	52
3-	3	6	140	114	113-	13-
3-	1	7	472	458	454	64
3-	3	7	355	329	329	5-
3-	1	9	286	278	278-	11-
3-	3	9	364	285	285-	5
3-	1	10	85	34	1	34
3-	1	11	183	194	194	8
4-	0	1	553	662	662	0
4-	2	1	658	648	648	20-
4-	0	2	297	401	401-	0
4-	2	2	438	487	485-	45-
4-	0	3	538	626	626-	0
4-	2	3	467	508	497-	103
4-	0	4	495	557	557	0
4-	2	4	390	390	386	56-
4-	4	4	414	384	381	45
4-	6	4	238	229	228	18-
4-	0	5	395	413	413	0
4-	2	5	295	277	276	19
4-	0	6	388	396	396-	0
4-	2	6	426	410	408-	38-
4-	0	7	264	263	263-	0
4-	2	7	235	180	179-	17
4-	0	8	357	369	369	0
4-	2	8	297	269	268	17
4-	0	9	85	115	115	0
4-	2	9	135	98	98	8-
4-	0	10	202	233	233-	0
4-	2	10	238	208	208-	0
4-	0	12	121	139	139	0
5-	1	1	386	363	356	72
5-	3	1	112	79	77	17
5-	1	2	624	680	663	153
5-	3	2	505	489	487	44-
5-	1	3	212	256	231-	110
5-	3	3	455	373	370-	51-
5-	1	4	491	514	512-	42
5-	3	4	565	406	404-	39
5-	1	5	283	327	326	22-
5-	3	5	343	263	263	12
5-	1	6	321	357	356	24
5-	3	6	293	273	268	53-
5-	1	7	300	310	309-	24-
5-	3	7	238	210	210-	1-
5-	1	8	219	233	231-	28-
5-	3	8	209	169	169-	12
5-	1	9	200	215	215	3-
5-	3	9	247	204	204	4-
5-	1	10	135	117	114	27-
5-	3	10	90	107	107	0
5-	1	11	140	164	164-	2
6-	0	1	419	539	539-	0
6-	2	1	534	615	608-	95
6-	2	2	195	142	141	18
6-	0	3	481	612	612	0
6-	2	3	474	508	508	6-
6-	0	4	162	126	126-	0
6-	2	4	207	202	194-	55
6-	0	5	383	453	453-	0
6-	2	5	395	383	383-	3-
6-	0	6	212	167	167	0
6-	2	6	193	212	212	11
6-	0	7	302	327	327	0
6-	2	7	279	291	290	25-
6-	0	8	193	230	230-	0
6-	2	8	162	147	147-	7-
6-	0	9	171	203	203-	0
6-	2	9	195	187	187-	4-
6-	0	10	121	136	136	0
6-	2	10	142	145	145	10-
6-	0	12	109	104	104-	0
7-	3	1	207	105	104	16
7-	1	2	457	499	499-	7-
7-	3	2	383	391	391-	15-
7-	1	4	372	458	454	57-
7-	3	4	312	345	345	14
7-	1	5	112	84	83-	13
7-	1	6	314	356	355-	19-
7-	3	6	290	284	283-	21
7-	1	7	142	112	111	15
7-	1	8	267	259	259	7-
7-	3	8	214	210	210	9
7-	1	9	42	101	101-	1-
7-	3	9	107	84	83-	11
7-	1	10	155	161	160-	15
8-	0	1	326	324	324	0
8-	2	1	453	377	374	48-
8-	0	2	88	44	44	0
8-	2	2	173	142	142	11
8-	0	3	319	417	417-	0
8-	2	3	307	339	336-	42-
8-	2	4	121	62	44-	44-
8-	0	5	252	353	353	0
8-	2	5	300	305	305	6
8-	0	7	228	281	281-	0
8-	2	7	262	254	254-	4
8-	0	8	59	69	69	0
8-	0	9	150	199	199	0
8-	2	9	195	188	188	10
8-	0	11	62	120	120-	0
9-	1	1	262	191	191-	12-
9-	3	1	200	167	167-	11
9-	1	2	295	261	261	16
9-	3	2	288	253	253	7
9-	1	3	181	159	158	20
9-	3	3	133	119	118	16-
9-	1	4	255	282	281-	19-
9-	3	4	212	238	238-	2-
9-	1	5	126	97	96-	10-
9-	3	5	121	94	94-	4-
9-	1	6	205	243	241	32
9-	3	6	247	222	222	12-
9-	1	8	176	197	197-	3
10-	0	1	145	132	132-	0
10-	2	1	190	174	173-	15
10-	0	2	243	197	197-	0
10-	2	2	205	181	181-	13
10-	0	3	226	203	203	0
10-	2	3	202	178	176	29
10-	0	4	233	203	203	0
10-	2	4	162	129	129	0
10-	0	5	202	194	194-	0
10-	2	5	176	182	182-	3-
10-	0	6	112	109	109-	0
10-	2	6	152	111	111-	10
10-	0	7	138	170	170	0
10-	2	7	147	165	165	1
10-	0	9	121	135	135-	0
11-	1	1	176	200	200	0
11-	3	1	140	147	147	8-
11-	1	2	112	99	98-	15
11-	3	2	85	90	90-	4-
11-	1	3	176	179	179-	6
11-	3	3	152	145	145-	8
11-	1	4	114	129	129	9
11-	1	5	121	151	151	3-
11-	1	6	80	123	123-	2-
12-	0	2	119	163	163	0
12-	0	4	133	161	161-	0
12-	0	6	62	116	116	0

* Based on the last least-squares cycle with isotropic temperature factors.

and ran through a least squares cycle with these average parameters. The calculated full shifts were smaller for this cycle than for either of the two extreme sets of parameters refined separately.

A bond distance calculation at this point indicated that one of the nitrogen atoms was significantly closer to an adjacent arsenic atom than would have been expected from the normal van der Waals radii for these atoms. It was felt that this might lead to significant anisotropic vibrations, and accordingly twelve cycles of anisotropic refinement were carried out, six with anisotropic arsenic atoms only, and six with all atoms anisotropic. At this point $R=0{\cdot}097$ and $r=0{\cdot}036$; the refinement was not carried any further. In spite of the apparent improvement in R and r values the position parameters at this point were essentially the same as those obtained in the purely isotropic refinement, and their standard deviations had only decreased by 5%.

The final position parameters and isotropic temperature factors are shown in Table 1.

The uncertainties shown are the standard deviations estimated from the elements of the inverse matrix in the usual way. Since a diagonal approximation was used in the direct matrix these error estimates are only approximate. In addition there is a complication in the uncertainties of the y/b parameters. Since there is no symmetry element which serves as a reference point in the b direction one of the atoms must be chosen to do so and its y/b parameter then should not be treated as an adjustable parameter. This option was not possible in the computer program used and the As y/b value was treated as a variable although it was not. The uncertainty calculated reflects this effect and is not significant. The uncertainties in the y/b parameters for the light atoms represent the uncertainty in the position of that atom with respect to all the other atoms, and since an individual light atom represents only a small portion of the scattering matter this is a reasonable measure of the uncertainty.

The structure is shown and the atoms are labelled in Fig. 2. The intramolecular bond lengths and bond angles are given in Table 2. The observed and calculated structure factors are given in Table 3.

Three short intermolecular distances occur in the structure. The N_2 atom of one molecule is 2·85 Å from the As atom, 3·01 Å from the C_1 atom, and 3·06 Å from the C_3 atom in the adjacent molecule. All the other intermolecular distances are greater than 3·5 Å.

The anisotropic thermal motions of the C and N atoms appear to be large, but the standard deviations in the temperature parameters are so large (they varied from 25 to 100% of the value of the parameter) that no meaningful conclusions could be drawn. The anisotropic motion of the arsenic atom could be determined, however. Values of the experimental parameters are given in Table 4. Following the method described by Rossman & Lipscomb (1958) the principal axes of the ellipsoid of vibration were determined. The results are given in Table 5. φ, ψ, and ω are the direction cosines with respect to the orthogonal axes a^*, b, and c. The errors were crudely estimated by varying β_4 and β_5 by the standard deviations given and seeing the change in the calculated results. The values of B in the directions toward the atoms C_1, C_2, and C_3 are $2{\cdot}8\pm0{\cdot}6$, $1{\cdot}1\pm0{\cdot}3$, and $4{\cdot}1\pm0{\cdot}4$ respectively. There is a significantly smaller vibration in the direction of the short intermolecular distance.

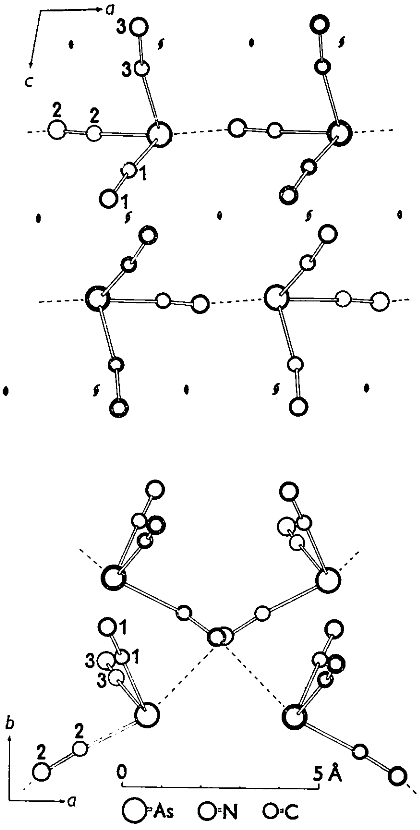

Fig. 2. The crystal structure viewed down the b axis (top) and the c axis (bottom). The strong interaction between molecules is shown as a dotted line.

Table 4. *Anisotropic thermal parameters for* As *atom*

β_1	0·0098 ± 0·0003	β_4	−0·0197 ± 0·0024
β_2	0·0124 ± 0·0003	β_5	−0·0130 ± 0·0034
β_3	0·0082 ± 0·0005	β_6	0·0024 ± 0·0004

Table 5. *Direction and magnitude of the principal axes of the ellipsoid of vibration*

B	φ	ψ	ω
−0·2 ± 0·4	0·57 ± 0·06	0·75 ± 0·01	0·35 ± 0·12
3·0 ± 0·2	−0·37 ± 0·17	−0·15 ± 0·02	0·92 ± 0·08
5·6 ± 0·3	0·74 ± 0·06	−0·65 ± 0·02	0·19 ± 0·13

The possibility of isocyanide groups

In order to test whether the atomic arrangement might be As–N–C in any of the bonds the C atoms in the normal structure were considered as N atoms and the N atoms considered as C atoms, and least squares refinement carried on from the last cycle of the normal isotropic refinement. In the first cycle after the change $R=0{\cdot}114$ and $r=0{\cdot}062$, but in three more cycles $R=0{\cdot}110$ and $r=0{\cdot}054$, i.e., no choice could be made as to the correctness of the model on the basis of the R and r values. However, the temperature factors allow a decision to be made. These are compared in Table 6 with the results for the normal cyanide case. In the cyanide structure the outer atoms (with respect to the As) have larger temperature factors than the inner atoms, and all of the temperature factors are about the same. In the isocyanide structure the inner atoms have the larger temperature factors and they are nearly twice as large as those for the outer atoms; this is unreasonable and therefore the isocyanide seems unlikely.

Table 6. *Temperature factors for the light atoms cyanide versus isocyanide*

As–C–N		As–N–C	
Atom	*B*	Atom	*B*
C_1	4·9	N_1	7·6
C_2	5·7	N_2	8·8
C_3	6·0	N_3	9·9
N_1	7·1	C_1	4·6
N_2	7·0	C_2	4·8
N_3	5·4	C_3	3·5

Discussion

The molecule has approximately the C_{3v} symmetry which is normal for the bonds to an isolated trivalent As atom. The relative lightness of the C and N atoms makes the positions quite uncertain, and as a consequence none of the bond distances or bond angles are very accurate. If we assume that the variations in the distances and angles are not real, and we use both the C and the N atoms to estimate the bond angles at the As (this is equivalent to assuming that the As–C–N groups should be linear), then we would say that the As–C distance is 1·88 Å, the C–N distance is 1·15 Å, and the C–As–C bond angle is 92°. From the covalent radii (Pauling, 1959) one would predict 1·98 for the As–C bond length and 1·15 for the C–N bond length. Since the hybridization at the C atom is *sp* it is reasonable that the distance measured here is shorter than normal, although the data are not good enough to be sure this is significant.

Indeed it is probable that the difference between the As–C_2 and the As–C_3 distances is real, since the difference is over twice the standard deviation and is supported by a similar difference in the As–N_2 and As–N_3 distances of over three times the standard deviation. Since the N_2 atom is involved in a relatively strong external interaction it is tempting to group cyanides 1 and 3 together as normal and to regard cyanide 2 as different both internally and externally. The abnormally short 2·85 Å distance between N_2 and the As in the adjacent molecule indicates an interaction considerably stronger than the normal Van der Waal's interaction. If Pauling's rule (Pauling, 1959) is used a bond order of 0·03 would be estimated for this bond. This is not quite fair since the rule is based on the assumption that the same kinds of orbitals are involved in the weak bonding as in the normal bonds with which it is compared; the bonding in this interaction is presumably between the lone pair of electrons on the CN and an empty *d* orbital on the As. Nevertheless, it does indicate that one or two kilocalories per mole more than the normal van der Waal's forces are involved in holding the crystal together. The other two short intermolecular distances are consequences of this interaction and do not need to be considered separately.

An interaction very similar to that described here occurs in the cyanogen halides (Heiart & Carpenter, 1956; Geller & Schawlow, 1955). In the cyanogen halides the molecules form long parallel chains in the crystals. In $As(CN)_3$ the pattern is more complicated. The chains occur in the direction of the side centering translation, and lie in layers roughly perpendicular to the *c* axis; the chains in each layer are nearly at right angles to the chains in neighboring layers. In the ClCN crystal, and probably in the BrCN crystal, the *X*–C distance is shorter in the solid than in the gas phase. This would indicate that the rehybridization involved in forming the external bond strengthens the internal bond to the heavy atom, perhaps by introducing some *d* character into the bond. The perhaps significant shortening of the As–C_2 bond in the As–$(CN)_3$ is consistent with this effect in the cyanogen halides.

The question arises with the $As(CN)_3$, if one external cyanide interaction occurs, why not three? If three approximately linear external interactions occurred the resulting structure would be rhombohedral, approximately cubic, with As atoms at each corner of the cube and CN groups along the edges. Using the dimensions found in the real structure to estimate the molecular volume in the proposed structure we find about 200 Å^3/mol. compared to 139 Å^3/mol. in the actual structure. The weak specific interactions would not be enough to make up for the generally poor van der Waal's interactions which would occur in this inefficient packing.

We are grateful to the Numerical Analysis Center of the University of Minnesota for providing the necessary time on the Univac Scientific 1103 Computer, and for their help with the computations. The computer programs used were prepared by the former crystallographic group at the University of Minnesota under the direction of Prof. W. N. Lipscomb; we would like to thank the group, and in particular Dr R. A. Jacobson, for their help. We would like to thank the Eastman Kodak Company and the National Science Foundation for the support on one of us (K. E.).

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The Crystal Structure of Cyclopentadienyl Manganese Tricarbonyl, $C_5H_5Mn(CO)_3$*

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The crystal structure of $C_5H_5Mn(CO)_3$ has been determined and refined by three-dimensional X-ray diffraction technique. The crystals are monoclinic with

$$a = 11{\cdot}99,\ b = 7{\cdot}07,\ c = 10{\cdot}93\ \text{Å (all } \pm 0{\cdot}03\ \text{Å) and } \beta = 117{\cdot}8 \pm 0{\cdot}2^\circ.$$

Positional and anisotropic temperature-factor parameters for all atoms except hydrogen were refined by least-squares methods, and the resulting standard deviations in the positions of the carbon and oxygen atoms are about 0·015 Å.

Within experimental error, a single axis passes through the center of the cyclopentadienyl ring, the manganese atom, and the center of the carbonyl groups. The interatomic distances indicate that the manganese atom forms approximately two electron-pair bonds with the ring and five with the three carbonyl groups.

Introduction

The determination of the crystal structure of cyclopentadienyl manganese tricarbonyl was undertaken as part of a program of structure investigations of sandwich compounds. The work reported here was begun in 1955 and the initial refinement of the positional parameters by least-squares methods was completed in 1957. The resulting molecular dimensions (which have been reported by Pauling, 1960, p. 391) were not particularly satisfactory, as the scatter in presumably equivalent values of interatomic distances suggested uncertainties of about 0·1 Å in the positions of the light atoms. More powerful computing facilities have recently become available to us, and accordingly we have continued the least-squares refinement by introducing anisotropic temperature-factor parameters for all the atoms. The resulting structure is more satisfactory, and both the experimental residuals and the scatter of equivalent interatomic distances lead to estimated standard deviations of approximately 0·015 Å in the positions of the light atoms.

Experimental

A sample of $C_5H_5Mn(CO)_3$ was supplied by Dr G. Wilkinson (see Piper, Cotton & Wilkinson, 1955). Crystals were selected directly from the sample and, because of their volatility, were mounted in lithium borate glass capillaries for photography. These crystals were irregular in shape with a maximum linear dimension of about 0·3 mm.

Two specimens were selected and oriented by means of Laue and oscillation photographs. Intensities were estimated visually from multiple-film Weissenberg photographs made with Cu $K\alpha$ radiation for layer lines 0–4 about the b axis and 0–13 about the [102] axis. The two sets of data were corrected for Lorentz and polarization factors and correlated by means of an averaging process.

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