836. *The Crystal Structure of* trans-*Oxotrichlorobisdiethylphenylphosphinerhenium*(V).

By H. W. W. Ehrlich and P. G. Owston.

The structure of the green isomer of $[ReOCl_3(PEt_2Ph)_2]$ has been determined and its constitution and *trans*-octahedral configuration have been confirmed. The molecule is somewhat distorted from true octahedral symmetry, the chlorine and phosphorus atoms being displaced from their ideal positions and away from the oxygen atom.

Freni and Valenti [1] reported the preparation of rhenium compounds $[ReCl_3L_2]$ (L = triphenylphosphine). Chatt and Rowe,[2] in attempting the preparation of similar compounds with L = diethylphenylphosphine, isolated three compounds coloured, respectively, green, blue, and violet. Analysis, the study of physical properties, and the *X*-ray analysis reported in this paper, have established that the green compound is not the five-co-ordinate complex $[ReCl_3L_2]$, but the *trans*-isomer of the octahedral complex $[ReOCl_3L_2]$. The blue compound is one of the two possible *cis*-isomers $[ReOCl_3L_2]$. The violet compound is still under investigation.

Experimental

Crystal Data.—$C_{20}H_{30}Cl_3OP_2Re$ (M = 641), monoclinic needles elongated parallel to the b axis. $a = 13{\cdot}05 \pm 0{\cdot}02$, $b = 7{\cdot}83 \pm 0{\cdot}01$, $c = 23{\cdot}90 \pm 0{\cdot}03$ Å, $\beta = 91{\cdot}5 \pm 0{\cdot}1°$; U = 2441 Å^3, $D_m = 1{\cdot}77$ g./c.c., $Z = 4$, $D_c = 1{\cdot}74$ g./c.c., $F(000) = 1256$. Cu-K_α radiation (μ = 138 cm.$^{-1}$), Weissenberg photographs. Absent reflections are $h0l$ with l odd, $0k0$ with k odd; space group $P2_1/c$ (C_{2h}^5, No. 14).

The intensities of the $h0l$ and $0kl$ reflections were estimated visually by the multiple film method. Since the crystals used had an approximately circular cross-section with a radius of 0·05 mm., the effect of absorption was small and was ignored.

The calculations were carried out on a Ferranti "Mercury" computer, with the following programmes: (1) Data reduction (J. A. Bland and J. M. Rowe). (2) Structure factors and least squares refinement (J. S. Rollett). (3) Structure factors and least squares refinement for $P2_1/c$ (O. S. Mills). (4) General Fourier programme (O. S. Mills). (5) Distance angle routine (R. A. Sparks). (6) Molecular accuracy (H. W. W. E.).

Structure Determination.—The x- and z-co-ordinates of the rhenium atom were found by examining the $h0l$ section of the weighted reciprocal lattice, and the y-co-ordinate was found from the Patterson projection down [100]. The phases of the rhenium-atom contributions to the structure factors were calculated and used to obtain Fourier maps which showed the positions of the remaining atoms (other than hydrogen). The parameters were refined by difference-Fourier methods. In the calculation of $F(h0l)$, isotropic temperature factors were used for the carbon and oxygen atoms, and anisotropic temperature factors for the heavier atoms; for $F(0kl)$ all the atoms were given isotropic temperature factors, since the overlapping of the atoms prevented a realistic estimate of the anisotropy. The atomic form-factors were calculated from Forsyth and Wells's formulæ,[3] and the possible effect of anomalous dispersion was neglected.

[1] Freni and Valenti, *J. Inorg. Nuclear Chem.*, 1961, **16**, 240.
[2] Chatt and Rowe, *Chem. and Ind.*, 1962, 92.
[3] Forsyth and Wells, *Acta Cryst.*, 1959, **12**, 412.

TABLE 1.

The final atomic co-ordinates and temperature factor coefficients.

Atom	x	y	z	B	β_{11}	β_{13}	β_{33}
Re	0·2587	0·1097	0·3885	3·50	0·00647	−0·00024	0·00194
Cl(1)	0·1185	−0·073	0·4129	3·77	0·00474	0·00225	0·00265
Cl(2)	0·3786	−0·102	0·4297	3·80	0·00765	−0·00154	0·00190
Cl(3)	0·4111	0·272	0·3663	4·60	0·00986	0·00022	0·00241
P(1)	0·2780	−0·070	0·3055	3·00	0·00688	−0·00008	0·00196
P(2)	0·2646	0·212	0·4868	3·16	0·00485	−0·00129	0·00255
O	0·1820	0·249	0·3614	3·46	0·00673	−0·00016	0·00199
C(1)	0·1933	0·000	0·2515	3·00	0·00628	0·00015	0·00186
C(2)	0·2210	0·128	0·2168	3·66	0·00766	0·00019	0·00226
C(3)	0·1400	0·184	0·1765	4·02	0·00838	0·00020	0·00248
C(4)	0·0490	0·122	0·1680	3·80	0·00795	0·00019	0·00235
C(5)	0·0270	−0·019	0·2075	3·73	0·00780	0·00019	0·00230
C(6)	0·0936	−0·067	0·2480	3·66	0·00766	0·00019	0·00226
C(7)	0·4086	−0·074	0·2700	3·60	0·00628	0·00015	0·00186
C(8)	0·4970	−0·124	0·3034	3·60	0·00732	0·00018	0·00216
C(9)	0·2860	−0·301	0·3108	3·60	0·00628	0·00015	0·00186
C(10)	0·2650	−0·413	0·2645	3·66	0·00732	0·00018	0·00216
C(11)	0·2427	0·048	0·5380	3·80	0·00628	0·00015	0·00186
C(12)	0·1445	0·005	0·5530	3·90	0·00732	0·00018	0·00216
C(13)	0·1320	−0·123	0·5900	4·00	0·00837	0·00020	0·00247
C(14)	0·2100	−0·200	0·6170	3·90	0·00817	0·00020	0·00241
C(15)	0·3200	−0·170	0·6000	3·85	0·00732	0·00018	0·00216
C(16)	0·3339	−0·041	0·5650	3·80	0·00628	0·00015	0·00186
C(17)	0·3803	0·330	0·5093	3·80	0·00795	0·00019	0·00235
C(18)	0·3930	0·420	0·5655	3·80	0·00795	0·00019	0·00235
C(19)	0·1580	0·358	0·4936	3·80	0·00795	0·00019	0·00235
C(20)	0·1910	0·537	0·4700	3·80	0·00795	0·00019	0·00235

The temperature factor expressions used were $\exp(-B\sin^2\theta/\lambda^2)$ for $F(0kl)$ and $\exp(-h^2\beta_{11} - hl\beta_{13} - l^2\beta_{33})$ for $F(h0l)$.

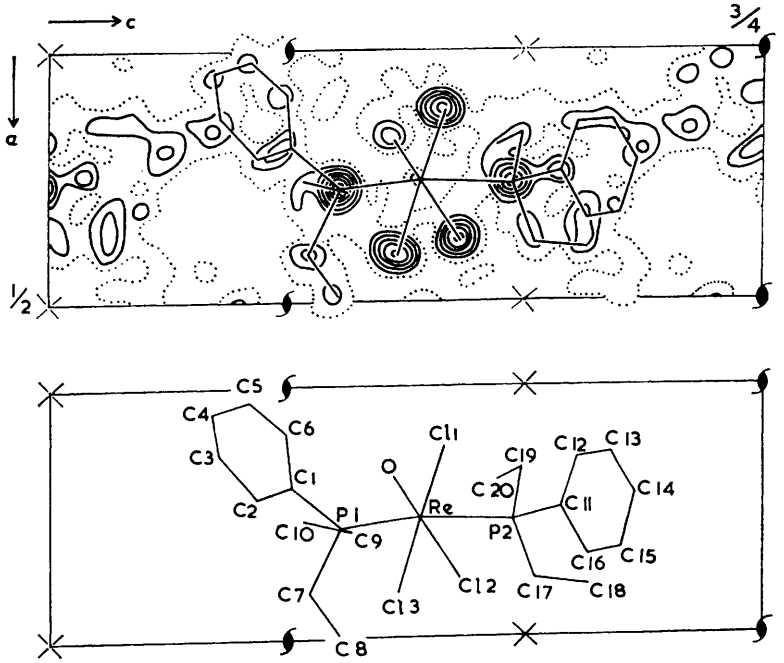
TABLE 2.

Bond lengths and angles.

Atoms	Bond length (Å)	Atoms	Bond length (Å)	Atoms	Bond length (Å)	Atoms	Bond length (Å)
Re–Cl(1)	2·41	P(1)–C(1)	1·75	C(1)–C(2)	1·36	C(11)–C(1)	1·38
Re–Cl(2)	2·47	P(1)–C(7)	1·92	C(2)–C(3)	1·48	C(12)–C(13)	1·35
Re–Cl(3)	2·43	P(1)–C(9)	1·86	C(3)–C(4)	1·29	C(13)–C(14)	1·33
Re–P(1)	2·45	P(2)–C(11)	1·80	C(4)–C(5)	1·49	C(14)–C(15)	1·52
Re–P(2)	2·48	P(2)–C(13)	1·84	C(5)–C(6)	1·34	C(15)–C(16)	1·33
Re–O	1·60	P(2)–C(19)	1·81	C(6)–C(1)	1·40	C(16)–C(11)	1·51
						C(7)–C(8)	1·44
						C(9)–C(10)	1·43
						C(17)–C(18)	1·52
						C(19)–C(20)	1·58

Atoms	Bond angle	Atoms	Bond angle	Atoms	Bond angle	Atoms	Bond angle
O–Re–Cl(1)	92°	Cl(2)–Re–Cl(1)	89·0°	P(1)–Re–Cl(1)	87·1°	Re–P(1)–C(1)	110°
O–Re–Cl(3)	94	Cl(2)–Re–Cl(3)	85·7	P(1)–Re–Cl(3)	91·2	Re–P(1)–C(7)	119
O–Re–P(1)	98	Cl(2)–Re–P(1)	81·9	P(2)–Re–Cl(1)	88·1	Re–P(1)–C(9)	122
O–Re–P(2)	100	Cl(2)–Re–P(2)	80·5	P(2)–Re–Cl(3)	91·9	Re–P(2)–C(11)	114
O–Re–Cl(2)	179	Cl(1)–Re–Cl(3)	174·6	P(1)–Re–P(2)	161·9	Re–P(2)–C(17)	116
						Re–P(2)–C(19)	107

During the refinement the unobserved reflections were ignored unless $|F_c|$ was greater than the minimum observable $|F_o|$, in which case ΔF was taken to be $(F_{\text{min. obs}} - F_c)$. The final values of the discrepancy, R, were 0·081 and 0·104 for the 400 $h0l$ and 244 $0kl$ reflections, respectively. The final atomic parameters are listed in Table 1, the atoms being numbered as in the Figure. The principal bond lengths and angles are given in Table 2, and the observed and calculated structure factors in Table 3.



b-Axis electron-density projection. The rhenium-atom contribution has been subtracted, and the final parameters from Table 1 have been used. Contours at 2·5, 5, 7·5, 10, 15, and 20 eÅ^{-2}.

The assessment of the accuracy of the molecular dimensions is complicated by overlap in the [100] projection, which leads to some uncertainty in the values of $\sigma(y)$. The estimated standard deviations obtained by Cruickshank's method [4] must therefore be used with caution, but they are approximately correct for the heavier atoms; they are 0·015 Å for Re–Cl and Re–P bond lengths, and 0·5° for angles involving Re, Cl, and P.

Discussion

These results confirm the constitution of the compound as *trans*-$[ReOCl_3(PEt_2Ph)_2]$, with approximately octahedral co-ordination round the rhenium atom.

It is distorted from true octahedral symmetry: the atoms Cl(1), Cl(3), P(1), and P(2) are all displaced away from the oxygen atom, and lie 0·11, 0·11, 0·34, and 0·41 Å, respectively, below the plane through the rhenium atom and perpendicular to the Cl(2)–Re–O axis. A similar distortion occurs [5] in $[Re_2OCl_{10}]^{2-}$. The Re–Cl bond lengths are rather longer than those [5,6] in $[Re_2OCl_{10}]^{2-}$ and $[ReCl_6]^{2-}$, which are 2·37 Å long. The Re–P bond lengths are normal, showing no evidence of d_π–d_π double-bonding. The Re–O bond length (1·6 Å) is known less precisely, but appears to be shorter than in $[Re_2OCl_{10}]^{2-}$

[4] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.
[5] Morrow, *Acta Cryst.*, 1962, **15**, 851.
[6] Aminoff, *Z. Krist.*, 1936, **94**, 246.

TABLE 3.

Observed and calculated structure factors.

l	$\lvert F_o\rvert$	F_c
	0 0 l	
2	93	85
4	211	−223
6	171	−178
8	163	166
10	196	202
12	56	−65
14	97	−104
16	80	86
18	72	66
20	11*	12
22	78	−80
24	37	−36
26	52	45
28	35	31
30	16	−13
	1 0 l	
−30	58	−50
−28	54	−46
−26	13*	15
−24	104	105
−22	37	−38
−20	60	−53
−18	59	−54
−16	12*	9
−14	12*	10
−12	130	−130
−10	142	−154
−8	131	138
−6	196	201
−4	12	−13
−2	358	−392
0	44	−30
2	308	328
4	72	75
6	173	−198
8	146	−142
10	164	164
12	222	217
14	90	−89
16	108	−108
18	47	47
20	85	90
22	69	65
24	46	−48
26	39	−42
28	33	36
30	13	18
	2 0 l	
−30	32	34
−28	30	−35
−26	73	−71
−24	33	33
−22	98	83
−20	14*	−13
−18	71	−71
−16	64	−67
−14	112	114
−12	73	83
−10	154	−168
−8	192	−208
−6	93	102
−4	88	84
−2	12	3
0	416	−462
2	211	−200
4	245	243
6	89	86
8	199	−197
10	209	−203
12	105	116
14	214	216
16	42	−28
18	135	−141
20	45	−37
22	82	90
24	68	66
26	52	−50
28	32	34
30	18	22
	3 0 l	
−30	32	41
−28	52	47
−26	12*	−8
−24	96	−96
−22	31	31
−20	102	113
−18	53	50
−16	91	−98
−14	47	−52
−12	198	200
−10	153	156
−8	108	−112
−6	133	−126
−4	51	−35
−2	210	215
0	22	17
2	182	−199
4	12	−19
6	81	94
8	58	54
10	76	−79
12	240	−233
14	58	54
16	159	159
18	14*	17
20	131	−134
22	107	−108
24	32	41
26	45	38
28	31	−32
30	22	−22
	4 0 l	
−28	10*	−2
−26	58	60
−24	14*	−15
−22	107	−109
−20	14*	9
−18	113	111
−16	48	53
−14	157	−156
−12	222	−232
−10	177	190
−8	209	228
−6	12	2
−4	111	−117
−2	98	−73
0	152	164
2	88	−57
4	114	−112
6	74	35
8	118	114
10	197	179
12	80	−74
14	200	−199
16	13*	−14
18	111	109
20	62	66
22	78	−71
24	64	−60
26	60	58
28	46	47
	5 0 l	
−28	19	−16
−26	11*	6
−24	59	56
−22	45	−47
−20	126	−123
−18	32	−34
−16	114	121
−14	130	142
−12	190	−177
−10	244	−241
−8	117	127
−6	160	176
−4	9*	−7
−2	210	−201
0	33	−27
2	206	230
4	51	78
6	121	−125
8	70	−80
10	22	14
12	156	143
14	29	26
16	97	−103
18	14*	15
20	69	48
22	84	70
24	37	−35
26	47	−42
28	55	48
	6 0 l	
−28	8*	2
−26	29	−30
−24	13*	11
−22	84	73
−20	25	26
−18	84	−81
−16	40	−45
−14	96	97
−12	167	165
−10	74	−70
−8	228	−224
−6	57	69
−4	110	116
−2	64	65
0	256	−249
2	118	−109
4	170	180
6	78	92
8	106	−101
10	164	−156
12	30	−27
14	109	108
16	14*	14
18	73	−71
20	14*	−21
22	42	38
24	40	40
26	61	−56
28	42	−45
	7 0 l	
−26	10*	−4
−24	56	−57
−22	25	27
−20	93	83
−18	38	32
−16	57	−52
−14	62	−56
−12	66	78
−10	140	141
−8	75	−97
−6	113	−122
−4	11*	8
−2	226	235
0	123	123
2	227	−221
4	141	−134
6	135	131
8	159	177
10	13*	12
12	130	−127
14	14*	−16
16	84	83
18	15*	−16
20	75	−65
22	23	−18
24	28	34
26	41	36
	8 0 l	
−26	49	52
−24	11*	6
−22	79	−74
−20	14	−17
−18	38	35
−16	25	31
−14	29	−27
−12	67	−63
−10	42	47
−8	85	86
−6	46	−51
−4	103	−97
−2	23	−29
0	210	215
2	195	184
4	117	−114
6	142	−133
8	32	20
10	202	198
12	28	29
14	91	−92
16	15*	11
18	96	101
20	14*	21
22	34	−34
24	44	−45
26	28	31
	9 0 l	
−24	68	72
−22	12*	13
−20	86	−79
−18	41	−40
−16	20	10
−14	21	27
−12	57	−57
−10	79	−86
−8	54	60
−6	66	61
−4	48	−49
−2	110	−107
0	121	−125
2	95	92
4	113	96
6	105	−121
8	111	−122
10	14	−24
12	121	118
14	15*	10
16	128	−116
18	14*	−8
20	87	78
22	55	59
24	21	−22
	10 0 l	
−24	11	−16
−22	73	64
−20	43	38
−18	68	−68
−16	37	−32
−14	35	34
−12	86	84
−10	35	−30
−8	95	−93
−6	20	17
−4	85	75
−2	33	45
0	81	−76
2	134	−140
4	69	62
6	32	17
8	35	−34
10	92	−100
12	15*	−22
14	120	100
16	14*	16
18	110	−101
20	49	−51
22	18	19
24	39	48
	11 0 l	
−22	22	−20
−20	67	74
−18	32	27
−16	37	−30
−14	60	−63
−12	64	45
−10	134	130
−8	15*	17
−6	82	−89
−4	14*	−9
−2	81	69
0	67	63
2	50	−42
4	29	−18
6	76	77
8	86	79
10	37	−43
12	84	−77
14	14*	−20
16	107	85
18	18	14
20	50	−49
22	48	−57
	12 0 l	
−20	24	−12
−18	53	46
−16	38	42
−14	42	−43
−12	120	−107
−10	14*	−6
−8	122	116
−6	20	15
−4	86	−74
−2	71	−74
0	74	54
2	95	94
4	38	−31
6	43	−32
8	66	64
10	76	62
12	13*	11
14	68	−56
16	11*	−16
18	61	52
20	40	35
	13 0 l	
−18	14	−10
−16	39	40
−14	46	43
−12	12*	−19
−10	117	−106
−8	23	−25
−6	93	86
−4	34	34
−2	66	−58
0	84	−90
2	65	60
4	65	55
6	71	−55
8	79	−70
10	13*	8
12	61	54
14	31	33
16	51	−47
18	7*	−4
	14 0 l	
−16	14	−11
−14	27	25
−12	52	47
−10	11*	23
−8	80	−74
−6	13*	8
−4	60	56
−2	37	32
0	72	−59
2	89	−89
4	51	39
6	81	67
8	12	−21
10	72	−75
12	37	−38
14	36	28
16	18	19
	15 0 l	
−14	16	−22
−12	8*	8
−10	37	39
−8	10*	0
−6	58	−52
−4	11*	5
−2	64	61
0	67	63
2	29	−31
4	74	−69
6	24	19
8	62	70
10	8*	16
12	27	−28
	16 0 l	
−6	8*	−9
−4	46	−41
−2	9*	2
0	43	36
2	52	49
4	23	−27
6	20	−47
	0 1 l	
1	337	−292
2	215	188
3	116	106
4	120	105
5	278	287
6	288	−302
7	101	83
8	29	−32
9	122	−139
10	200	197
11	61	−67
12	95	96
13	121	124
14	37	−34
15	33	27
16	65	−56
17	56	−57
18	11*	11
19	41	−42
20	71	70
21	23	18
22	27	26
23	71	65
24	11*	−8
25	20	−22
26	16	−13
27	46	−39
28	21	16
29	7*	9
30	26	26
	0 2 l	
0	93	87
1	159	−136
2	30	−23
3	236	−200
4	80	53
5	126	117
6	195	−164
7	202	201
8	117	−85
9	59	−54
10	9*	4
11	170	−190
12	9*	0
13	77	−79
14	52	−51
15	112	117
16	11*	−9
17	110	107
18	11*	8
19	106	−101
20	11*	18
21	76	−76
22	22	−34
23	15	14
24	10*	3
25	44	44
26	24	22
27	8*	6
28	7*	5
29	49	−42
30	4*	−1
	0 3 l	
1	70	69
2	16	24
3	25	−28
4	31	41
5	118	−126
6	185	−185
7	9*	10
8	91	−85
9	111	113
10	96	78
11	32	22
12	113	122
13	66	−64
14	44	−44
15	34	−33
16	141	−150
17	27	24
18	16	−27
19	32	35
20	83	92
21	35	−34
22	11*	12
23	51	−42
24	45	−43
25	9*	5
26	37	−32
27	21	19
28	26	23
29	5*	2
	0 4 l	
0	184	−171
1	34	33
2	20	−23
3	40	−45
4	136	142
5	65	51
6	128	114
7	76	74
8	58	−50
9	58	−55

TABLE 3. (*Continued.*)

l	$\lvert F_o \rvert$	F_c	*l*	$\lvert F_o \rvert$	F_c	*l*	$\lvert F_o \rvert$	F_c	*l*	$\lvert F_o \rvert$	F_c	*l*	$\lvert F_o \rvert$	F_c	*l*	$\lvert F_o \rvert$	F_c
10	130	−134	3	139	−117		0 6 *l*		23	17	−17	21	6 *	1		0 9 *l*	
11	21	−19	4	32	−40	0	110	−119	24	5 *	13	22	4 *	−9	1	46	−42
12	26	19	5	147	−137	1	84	79							2	8 *	14
13	36	30	6	10 *	6	2	11 *	−4		0 7 *l*					3	8 *	2
14	81	90	7	10 *	−22	3	71	64	1	16	22		0 8 *l*		4	8 *	−2
15	50	46	8	58	57	4	76	79	2	78	−80	0	35	33	5	39	40
16	11 *	−9	9	86	96	5	50	−50	3	19	15	1	15	17	6	8 *	7
17	42	48	10	11 *	1	6	41	52	4	11 *	−15	2	10 *	6	7	8 *	−13
18	76	−91	11	29	34	7	102	−105	5	27	34	3	18	22	8	7 *	−11
19	25	−30	12	50	−54	8	25	−27	6	73	85	4	42	−50	9	40	−40
20	11 *	−3	13	82	−94	9	11 *	−2	7	11 *	11	5	15	−14	10	12	−15
21	18	−11	14	11 *	−2	10	37	−36	8	27	24	6	27	−21	11	6 *	−10
22	72	60	15	11 *	−13	11	65	68	9	11 *	11	7	38	−32	12	6 *	−8
23	17	15	16	35	34	12	22	20	10	60	−65	8	39	41	13	22	25
24	20	22	17	38	35	13	11 *	8	11	34	29	9	14	14			
25	25	21	18	11 *	16	14	19	16	12	63	−66	10	9 *	11		0 10 *l*	
26	48	−46	19	24	22	15	52	−57	13	10 *	14	11	50	48			
27	14	17	20	10 *	1	16	11 *	−16	14	26	24	12	25	−25	0	27	35
28	25	−23	21	29	−23	17	40	−50	15	10 *	7	13	22	20	1	15	−19
			22	9 *	−8	18	10 *	−5	16	59	51	14	21	−19	2	18	7
	0 5 *l*		23	43	−40	19	9 *	5	17	9 *	−13	15	28	−26	3	11	−16
			24	21	24	20	22	5	18	8 *	4	16	7 *	5	4	9	−22
1	139	125	25	15	15	21	23	16	19	7 *	−2	17	19	−21			
2	44	−42	26	5 *	3	22	21	18	20	30	−24	18	30	32			

* Unobserved reflection; the value quoted for $\lvert F_o \rvert$ is the minimum observable.

(1·86 Å), in which Re–O double-bonding occurs; this may indicate some triple-bonding, for which suitable orbitals are available. The other bond lengths show no significant variation from normal.

All contacts between molecules involve the bulky groups in the tertiary phosphine ligands. Two of the contacts with the molecules in the next cell along the *b*-axis, Cl(1)–C′(20) (3·47 Å) and C(15)–C′(18) (3·45 Å) are the shortest. There are no close contacts involving the oxygen atoms, and all other intermolecular distances are longer than 3·6 Å.

We thank Dr. J. Chatt, F.R.S., and Dr. G. A. Rowe for valuable discussions. We are indebted to the authors of the computer programmes, and to Dr. B. Richards who supervised the calculations.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, HEAVY ORGANIC CHEMICALS DIVISION,
AKERS RESEARCH LABORATORY, THE FRYTHE,
WELWYN, HERTS.

[*Received, September 28th*, 1962.]