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The Structure of the Adduct of $Ph_3P=N.Ph$ and $MeO_2C.C\equiv C.CO_2Me$

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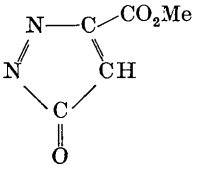
Tetraphenylphosphine imide, $Ph_3P=N.Ph$, forms a 1:1 adduct with acetylenedicarboxylic acid dimethyl ester, $MeO_2C.C\equiv C.CO_2Me$; two types of structure may be proposed for this adduct, one containing a four-membered ring of phosphorus, nitrogen and two carbon atoms, the other being an open chain structure with a $\rangle P=C-C=N-$ unit. The molecular structure of the adduct has been determined by X-ray analysis of the bromo-derivative, prepared from *N-p*-bromophenyl-*PPP*-triphenylphosphine imide, $Ph_3.P=N.C_6H_4.Br$. Crystals of the bromo-derivative are monoclinic, $a=11{\cdot}83$, $b=9{\cdot}24$, $c=25{\cdot}43$ Å, $\beta=104°\ 15'$, $Z=4$, space group $P2_1/c$. The intensities of all reflexions with $d\geq 1$ Å were measured with a scintillation counter and Mo $K\alpha$ radiation, and visual estimates of Cu $K\alpha$ Weissenberg films were made for higher order reflexions. The bromine atom is in a pseudo-special position, and the structure was solved by determining the x and z coordinates from the b-axis projection, and then deducing the y parameters by trials with various models. The parameters were then refined by three-dimensional F_o and (F_o-F_c) syntheses, differential syntheses, and a cycle of least squares; R for 1940 observed reflexions is 0·21.

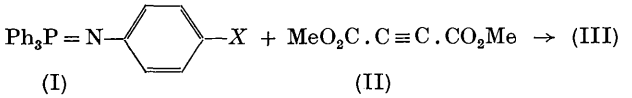
The molecule has the open-chain structure, $Ph_3P=C(CO_2Me).C(CO_2Me)=N.C_6H_4.Br$ and all the dimensions are normal; one distance which is worthy of note, since it does not appear to have been measured previously, is P=C, which is $1{\cdot}70\pm 0{\cdot}03$ Å.

Introduction

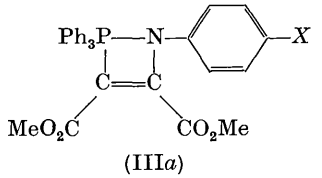
Tetraphenylphosphine imide (I, $X=H$) forms a 1:1 adduct (III) with acetylenedicarboxylic acid dimethyl ester (II). Chemically the adduct is very resistant to oxidative, reductive and hydrolytic attack, but $Ph_3P\rightarrow O$, Ph.NH.Me and



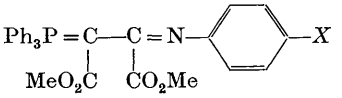
can be isolated as degradation products, indicating that in the formation of the adduct there is no extensive rearrangement. Two possible structures may be suggested for the adduct, (III*a*) with a four-membered ring, and the open-chain formulation (III*b*), and the stability of the compound makes it difficult to distinguish between these by chemical methods. We have therefore undertaken an X-ray investigation of the bromo-derivative (III, $X=Br$), prepared from *N-p*-bromophenyl-*PPP*-triphenylphosphine imide (I, $X=Br$). This analysis shows that the bromo-derivative has structure (III*b*, $X=Br$), and hence the unsubstituted adduct is (III*b*, $X=H$).



(I) (II)



(III*a*)



(III*b*)

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Experimental

Crystals of the bromo-derivative grown from ethyl acetate are colourless needles elongated along *b*. The unit cell dimensions and space group were determined from various rotation, Weissenberg and precession films.

Crystal data

(λ(Cu $K\alpha$) = 1·5418 Å; λ(Mo $K\alpha$) = 0·7107 Å).

Adduct of $Ph_3P{=}N.C_6H_4.Br$ and

$$MeO_2C.C \equiv C.CO_2Me,$$

molecular formula $C_{30}H_{25}O_4NPBr$; $M = 574{\cdot}4$.
Monoclinic,

$$a = 11{\cdot}83 \pm 0{\cdot}02,\ b = 9{\cdot}24 \pm 0{\cdot}02,$$
$$c = 25{\cdot}43 \pm 0{\cdot}04 \text{ Å};\ \beta = 104° 15' \pm 5'.$$

$U = 2694$ Å^3.
$D_m \sim 1{\cdot}4$ g.cm^{-3}, $Z = 4$, $D_x = 1{\cdot}416$ g.cm^{-3}.
Absorption coefficients for X-rays,

$$\lambda = 1{\cdot}5418 \text{ Å},\ \mu = 30 \text{ cm}^{-1},$$
$$\lambda = 0{\cdot}7107 \text{ Å},\ \mu = 18 \text{ cm}^{-1}.$$

$F(000) = 1176$.
Absent spectra: $h0l$ when h is odd, $0k0$ when k is odd.
Space $P2_1/c$ (C_{2h}^5).

The intensities of all reflexions with 2θ(Mo $K\alpha$) $\leq 41°$ (corresponding to a minimum interplanar spacing $d = 1{\cdot}01$ Å) were measured on a G.E. XRD 5 Spectrogoniometer with Single Crystal Orienter, using a scintillation counter, Mo $K\alpha$ radiation (zirconium filter and pulse height analyser), and the moving-crystal moving-counter technique (Furnas, 1957). All the intensities were corrected for background. The intensities of higher order reflexions (to a minimum $d = 0{\cdot}77$ Å) were recorded with Cu $K\alpha$ radiation on Weissenberg films of the $h0l$–$h4l$ zones, and estimated visually. Lorentz and polarization factors were applied, and the structure amplitudes derived. The crystal used for all the intensity measurements was mounted along *b*, and had cross-section 0·1 × 0·1 mm, so that absorption corrections were not considered necessary. 1702 reflexions were observed with the counter equipment, 75% of the total number in the range $0 < 2\theta$(Mo $K\alpha$) $\leq 41°$; 238 additional higher order reflexions were estimated from the Cu $K\alpha$ Weissenberg films.

Structure analysis

The most significant feature of the three-dimensional Patterson function was a set of three peaks at $00\frac{1}{2}$, $0\frac{1}{2}0$, and $0\frac{1}{2}\frac{1}{2}$, corresponding to Br–Br vectors; there are thus three possible positions for the bromine atom: $0\frac{1}{4}0$, $00\frac{1}{4}$, and $0\frac{1}{4}\frac{1}{4}$, which have the same vector distribution. Even if it was possible to distinguish between these three positions, the analysis could not proceed by the heavy-atom method, since the bromine atom contributes to only one quarter of the reflexions. The next highest peaks in the Patterson function could be interpreted as Br–P vectors, so that the phosphorus atom position could be determined relative to the bromine atom, but the three alternative positions for the Br atoms could still not be distinguished. A choice should be possible on the basis of the P–P vectors, but these were not clearly resolved. In an attempt to resolve the ambiguity, the projection along the *b* axis was examined first.

[010] *projection*

The ambiguity of bromine atom position reduces in this projection to a trivial choice of origin, so that it was possible to calculate immediately a Fourier series with all signs positive (based on Br only). The resulting electron-density map could be interpreted only on the basis of a structure of type (III*b*), since the Br and P atoms of one molecule were too far apart to permit the four-membered ring formulation. Coordinates were determined for all the atoms in the molecule, although some were uncertain: one of the phenyl groups was end-on and overlapped the phosphorus atom, and one of the methoxycarbonyl groups was poorly resolved as a result of overlap, so that coordinates for these atoms (including phosphorus) could not be accurately, or even reliably, established. Structure factors were calculated using the scattering factors of *International Tables for X-ray Crystallography* (1962) with $B = 4{\cdot}5$ Å^2 for all atoms, and the x and z parameters were then refined by several cycles of Fourier and difference syntheses. $R(h0l)$ was then 0·24, but some of the atomic positions, particularly for the methoxycarbonyl groups, were still not well established.

Three-dimensional analysis

Using the x and z coordinates from the $h0l$ refinement, and assuming normal bond distances, it was now possible to deduce y coordinates (relative to y_{Br}) for some of the atoms: Br(1), C(3), C(6), and N(33) had all about the same y parameter (the numbering of the atoms is shown in Fig. 1); y_P was determined from the three-dimensional Patterson function (but not very precisely since the Br–P peaks were situated close to mirror planes and hence were not separately resolved); two possible sets of y parameters were then deduced for the three phenyl groups and C(28), according to whether, with $y_P \sim (y_{Br} - 0{\cdot}1)$, the ring C(21)–C(26) was above or below the phosphorus atom, with the other groups situated accordingly. Taking account of the three possible bromine positions there were therefore six possible sets of parameters for these 24 atoms. Structure factors were calculated for all six structures. The three structures with C(21)–C(26) below the phosphorus atom could be discarded since they gave very poor agreement between F_o and F_c for low order $0k0$ reflexions; the other three structures

Table 1. *Measured and calculated structure factors*

Unobserved reflexions, which are listed as 0·0, have threshold values in the range $F_o = 8$–18

h	k	l	F OBS	F CALC
0	0	2	28.0	- 35.6
0	0	4	24.9	- 17.0
0	0	6	192.9	-213.9
0	0	8	132.2	120.4
0	0	10	0.0	11.2
0	0	12	33.1	10.9
0	0	14	21.0	- 14.4
0	0	16	51.2	59.2
0	0	18	29.6	- 19.7
0	0	20	20.5	19.4
0	0	22	28.8	- 25.7
0	0	24	0.0	2.0
1	0	-26	13.8	- 14.9
1	0	-24	19.5	- 21.2
1	0	-22	0.0	- 4.6
1	0	-20	27.3	27.6
1	0	-18	36.8	45.3
1	0	-16	17.0	13.0
1	0	-14	47.1	- 53.1
1	0	-12	60.5	62.6
1	0	-10	62.1	- 55.0
1	0	- 8	79.6	74.4
1	0	- 6	125.8	-135.9
1	0	- 4	152.6	186.4
1	0	0	17.1	14.8
1	0	2	172.5	-191.4
1	0	4	13.3	- 13.2
1	0	6	44.4	32.8
1	0	8	147.8	153.3
1	0	10	109.6	-113.1
1	0	12	14.0	- 19.7
1	0	14	33.1	- 31.0
1	0	16	45.8	45.8
1	0	18	41.1	- 40.6
1	0	20	0.0	- 9.4
1	0	22	16.3	- 16.8
1	0	24	14.8	16.7
2	0	-30	26.5	15.6
2	0	-28	14.6	- 8.7
2	0	-26	16.3	- 17.2
2	0	-24	26.7	29.1
2	0	-22	15.8	18.0
2	0	-20	0.0	6.3
2	0	-18	38.2	- 41.9
2	0	-16	14.4	11.0
2	0	-14	21.2	- 19.0
2	0	-12	61.9	68.6
2	0	-10	26.0	- 17.2
2	0	- 8	69.9	78.9
2	0	- 6	226.0	-234.6
2	0	- 4	98.9	105.3
2	0	- 2	60.5	- 70.7
2	0	0	31.0	27.6
2	0	2	120.2	-127.9
2	0	4	140.9	127.0
2	0	6	66.6	- 69.9
2	0	8	10.8	5.9
2	0	10	140.7	-154.2
2	0	12	50.8	51.1
2	0	14	33.5	- 22.3
2	0	16	0.0	- 4.4
2	0	18	32.2	- 36.2
2	0	20	17.5	18.4
2	0	22	0.0	13.6
2	0	24	0.0	28.0
3	0	-24	0.0	10.0
3	0	-22	14.6	10.3
3	0	-20	24.6	- 26.9
3	0	-18	13.8	- 6.3
3	0	-16	66.2	74.9
3	0	-14	0.0	9.0
3	0	-12	24.1	29.8
3	0	-10	89.7	-101.3
3	0	- 8	36.8	43.6
3	0	- 6	101.4	- 98.9
3	0	- 4	37.5	47.8
3	0	- 2	234.2	-271.6
3	0	0	109.6	121.9
3	0	2	15.0	8.4
3	0	4	225.1	237.0
3	0	6	64.6	- 50.7
3	0	8	19.7	20.9
3	0	10	36.1	- 37.9
3	0	12	65.4	68.6
3	0	14	37.4	- 36.1
3	0	16	43.0	38.8
3	0	18	12.7	- 3.5
3	0	20	18.9	15.1
3	0	22	12.1	- 12.0
3	0	24	28.5	- 27.3
3	0	28	21.0	18.8
4	0	-24	13.1	- 15.4
4	0	-22	36.4	- 32.1
4	0	-20	0.0	- 4.5
4	0	-18	17.1	22.2
4	0	-16	22.0	27.9
4	0	-14	42.6	- 43.1
4	0	-12	8.2	- 5.4
4	0	-10	22.9	- 57.1
4	0	- 8	56.3	52.9
4	0	- 6	31.5	- 43.6
4	0	- 4	19.6	- 38.6
4	0	- 2	0.0	10.2
4	0	0	77.5	77.0
4	0	2	95.6	- 89.9
4	0	4	18.7	- 31.4
4	0	6	203.5	-192.0
4	0	8	128.3	129.6
4	0	10	7.2	9.1
4	0	12	51.7	39.1
4	0	14	56.6	- 54.7
4	0	16	39.6	23.0
4	0	18	0.0	16.0
4	0	20	9.7	- 18.5
4	0	22	21.6	- 21.9
4	0	24	30.5	18.2
4	0	26	20.7	17.6
5	0	-24	0.0	- 7.2
5	0	-22	0.0	- 2.3
5	0	-20	24.6	24.2
5	0	-18	12.4	- 13.6
5	0	-16	38.9	- 44.3
5	0	-14	22.2	- 23.1
5	0	-12	34.5	39.6
5	0	-10	62.7	- 58.1
5	0	- 8	38.0	42.4
5	0	- 6	97.3	- 98.6
5	0	- 4	109.4	108.5
5	0	- 2	105.7	-110.0
5	0	0	47.5	35.0
5	0	2	169.2	-177.4
5	0	4	79.4	77.1
5	0	6	17.0	18.6
5	0	8	81.8	76.8
5	0	10	83.9	- 66.6
5	0	12	0.0	- 1.9
5	0	14	7.0	- 3.9
5	0	16	19.7	12.1
5	0	18	17.5	- 10.6
5	0	20	16.1	5.0
5	0	24	32.9	18.7
6	0	-28	29.4	- 17.4
6	0	-22	29.9	27.1
6	0	-20	20.5	- 29.3
6	0	-18	18.7	- 30.5
6	0	-14	41.4	44.8
6	0	-12	20.7	30.8
6	0	-10	64.1	67.9
6	0	- 8	23.7	- 23.7
6	0	- 6	7.2	- 8.8
6	0	- 4	7.0	- 5.6
6	0	- 2	71.3	67.3
6	0	0	70.6	- 72.5
6	0	2	76.9	63.0
6	0	4	61.1	- 55.8
6	0	6	69.2	64.6
6	0	8	27.1	- 24.8
6	0	10	32.7	29.8
6	0	12	72.4	50.4
6	0	14	17.3	32.7
6	0	16	33.3	27.1
6	0	18	32.2	- 24.8
6	0	20	19.1	10.8
7	0	-24	13.6	16.9
7	0	-22	13.1	- 18.5
7	0	-20	30.8	- 31.5
7	0	-18	0.0	- 3.2
7	0	-16	36.9	45.8
7	0	-14	17.9	- 19.6
7	0	-12	17.5	- 39.6
7	0	-10	55.5	- 54.9
7	0	- 8	33.7	32.8
7	0	- 6	9.7	27.2
7	0	- 4	88.8	82.4
7	0	- 2	28.6	- 24.9
7	0	0	66.4	36.7
7	0	2	0.0	7.4
7	0	4	69.3	57.1
7	0	6	97.1	- 93.5
7	0	8	12.9	- 4.0
7	0	10	10.1	2.6
7	0	12	74.2	64.8
7	0	14	39.1	38.3
7	0	18	28.3	- 12.9
7	0	20	29.6	20.9
7	0	22	23.9	- 7.8
8	0	-26	20.7	14.0
8	0	-22	19.1	- 17.9
8	0	-20	8.2	12.9
8	0	-16	32.5	35.8
8	0	-14	18.3	- 28.4
8	0	-12	0.0	- 9.9
8	0	-10	0.0	6.8
8	0	- 8	56.5	70.2
8	0	- 6	39.1	- 43.3
8	0	- 4	26.7	25.6
8	0	- 2	29.0	- 31.9
8	0	0	57.5	42.3
8	0	2	34.5	- 22.5
8	0	4	0.0	- 11.8
8	0	6	65.3	- 55.3
8	0	8	30.2	24.8
8	0	10	9.4	6.6
8	0	12	11.1	4.0
8	0	14	43.0	- 35.2
8	0	16	26.7	- 19.8
8	0	22	26.7	19.2
9	0	-28	19.7	14.9
9	0	-24	26.5	- 21.9
9	0	-22	13.8	9.6
9	0	-20	23.9	23.6
9	0	-18	0.0	3.0
9	0	-16	30.0	- 31.8
9	0	-14	0.0	6.4
9	0	-12	47.3	52.8
9	0	-10	32.9	41.1
9	0	- 8	0.0	- 14.9
9	0	- 6	27.3	- 24.7
9	0	- 4	34.1	28.3
9	0	- 2	9.9	- 5.3
9	0	0	48.7	26.6
9	0	2	45.1	- 29.3
9	0	4	40.7	25.3
9	0	6	42.3	- 23.8
9	0	8	0.0	- 2.5
9	0	12	18.5	3.6
9	0	14	19.1	- 16.8
9	0	16	33.1	19.1
10	0	-22	25.7	18.0
10	0	-16	0.0	- 5.1
10	0	-14	29.4	29.6
10	0	-12	0.0	7.3
10	0	-10	73.0	- 76.3
10	0	- 8	7.0	- 27.1
10	0	- 6	16.3	- 9.2
10	0	- 4	32.6	33.5
10	0	- 2	20.0	- 11.2
10	0	0	35.6	12.1
10	0	2	9.7	- 7.3
10	0	4	0.0	- 7.3
10	0	6	23.9	16.7
10	0	8	28.8	- 22.1
10	0	12	12.1	2.9
11	0	-18	21.8	17.5
11	0	-12	35.4	21.5
11	0	-10	11.7	1.7
11	0	- 8	19.7	- 34.6
11	0	- 6	12.7	23.5
11	0	- 4	8.0	26.0
11	0	- 2	38.6	- 40.3
11	0	0	19.1	3.0
11	0	4	19.3	7.8
11	0	6	30.6	- 24.5
11	0	8	20.0	4.2
12	0	0	17.9	6.4
11	0	14	19.8	- 8.5
12	0	-20	17.7	- 12.6
12	0	-18	11.3	8.1
12	0	-16	23.9	19.2
12	0	-14	23.5	- 17.1
12	0	-12	18.6	- 14.3
12	0	-10	10.8	22.3
12	0	- 8	10.6	8.9
12	0	- 6	10.5	- 32.5
12	0	0	42.1	35.0
12	0	2	22.0	10.8
12	0	8	49.3	24.0
13	0	-20	14.0	13.0
13	0	-12	17.3	16.6
13	0	-10	13.2	13.5
13	0	- 8	9.2	- 12.7
13	0	- 6	20.5	- 26.8
13	0	2	23.2	- 17.1
13	0	4	21.4	5.2
14	0	-14	23.9	16.6
14	0	-10	23.7	- 21.1
14	0	- 8	18.1	- 17.7
14	0	- 4	34.3	29.2
14	0	2	20.9	- 10.7
0	1	1	114.9	-125.4
0	1	3	113.7	-126.0
0	1	5	154.8	160.4
0	1	7	75.8	- 66.5
0	1	9	15.8	- 8.3
0	1	11	35.2	- 38.3
0	1	13	33.5	30.9
0	1	15	20.8	22.6
0	1	17	20.9	- 20.3
0	1	19	0.0	- 3.8
0	1	21	20.9	- 19.8
0	1	23	34.1	34.5
1	1	-29	40.0	- 24.9
1	1	-27	32.4	34.2
1	1	-23	15.9	14.2
1	1	-21	23.5	- 21.5
1	1	-20	46.0	26.0
1	1	-19	45.7	- 24.7
1	1	-18	0.0	7.5
1	1	-17	40.2	- 15.9
1	1	-16	0.0	4.3
1	1	-14	0.0	0.8
1	1	-13	77.7	- 90.5
1	1	-12	23.9	- 24.8
1	1	-11	18.9	- 16.6
1	1	-10	18.5	- 11.9
1	1	- 9	19.3	- 11.6
1	1	- 8	79.1	- 74.4
1	1	- 7	175.4	188.0
1	1	- 6	116.1	-103.1
1	1	- 5	64.7	- 73.7
1	1	- 4	94.8	-107.3
1	1	- 3	31.3	- 39.9
1	1	- 2	34.5	- 31.7
1	1	- 1	37.4	- 30.4
1	1	0	34.5	- 42.5
1	1	1	21.6	- 12.3
1	1	2	28.6	- 24.9
1	1	3	17.5	18.2
1	1	4	54.9	- 53.7
1	1	5	8.6	- 1.9
1	1	6	35.6	- 41.8
1	1	7	50.2	45.6
1	1	8	32.7	- 33.9
1	1	9	33.5	- 38.3
1	1	10	53.8	- 60.8
1	1	11	49.2	49.0
1	1	12	0.0	- 2.1
1	1	13	41.6	- 37.0
1	1	14	23.9	27.5
1	1	15	0.0	9.1
1	1	16	9.2	- 6.9
1	1	17	33.8	- 33.7
1	1	18	10.9	- 11.2
1	1	19	38.6	- 32.0
1	1	20	26.3	- 19.1
1	1	21	17.7	- 12.5
1	1	22	9.5	8.7
1	1	23	0.0	6.4
1	1	25	32.5	- 24.1
1	1	27	22.8	15.0
2	1	-29	23.2	- 14.5
2	1	-27	31.1	27.8
2	1	-23	0.0	2.6
2	1	-22	0.0	5.6
2	1	-21	44.2	- 43.1
2	1	-20	0.0	- 3.1
2	1	-19	43.2	48.2
2	1	-18	13.1	- 2.3
2	1	-17	31.1	- 23.9
2	1	-16	25.7	25.5
2	1	-15	48.7	44.2
2	1	-14	21.0	23.9
2	1	-13	83.2	- 91.9
2	1	-12	19.5	- 24.0
2	1	-11	37.7	33.5
2	1	-10	0.0	3.2
2	1	- 9	68.3	- 68.4
2	1	- 8	0.0	11.6
2	1	- 7	48.1	56.4
2	1	- 6	103.9	-105.5
2	1	- 5	24.6	17.4
2	1	- 4	76.1	91.2
2	1	- 3	57.0	- 62.4
2	1	- 2	13.1	25.1
2	1	- 1	69.9	- 65.4
2	1	0	39.7	45.1
2	1	1	26.9	- 17.9
2	1	2	164.5	-176.5
2	1	3	46.0	- 46.0
2	1	4	88.0	- 77.9
2	1	5	50.4	- 54.1
2	1	6	42.5	39.0
2	1	7	23.0	24.8
2	1	8	10.6	22.8
2	1	9	56.5	59.1
2	1	10	45.6	44.2
2	1	11	36.1	36.2
2	1	12	37.2	34.4
2	1	13	38.4	- 47.1
2	1	14	27.4	24.4
2	1	15	0.0	- 2.7
2	1	16	0.0	10.8
2	1	17	13.6	- 6.1
2	1	18	0.0	- 4.7
2	1	19	21.8	18.1
2	1	20	15.0	12.6
2	1	21	24.9	- 24.6
2	1	22	0.0	4.2
2	1	27	17.7	10.6
3	1	-29	18.9	5.5
3	1	-26	19.5	12.2
3	1	-25	19.1	- 16.4
3	1	-23	0.0	5.2
3	1	-22	0.0	- 8.2
3	1	-21	16.1	- 11.3
3	1	-20	27.3	- 27.1
3	1	-19	61.6	66.8
3	1	-18	0.0	7.8
3	1	-17	29.8	- 31.0
3	1	-16	0.0	- 7.3
3	1	-15	0.0	- 4.9
3	1	-14	53.1	- 53.7
3	1	-13	62.5	- 65.5
3	1	-12	8.0	4.6
3	1	-11	59.6	67.9
3	1	-10	12.4	- 4.7
3	1	- 9	9.5	2.8
3	1	- 8	26.5	26.2
3	1	- 7	55.7	61.2
3	1	- 6	0.0	2.3
3	1	- 5	56.6	- 66.7
3	1	- 4	97.5	-100.9
3	1	- 3	41.1	48.8
3	1	- 2	71.8	72.4
3	1	- 1	51.0	- 53.7
3	1	0	36.2	- 31.3
3	1	1	8.8	13.8
3	1	2	38.4	51.9
3	1	3	8.8	0.0
3	1	4	71.7	74.1
3	1	5	35.6	39.6
3	1	6	49.4	39.7
3	1	7	44.5	35.9
3	1	8	40.7	- 35.6
3	1	9	37.5	- 39.8
3	1	10	15.9	- 23.6
3	1	11	13.8	1.5
3	1	12	15.4	- 8.3
3	1	13	29.4	- 24.7
3	1	14	20.5	12.2
3	1	15	60.3	60.1
3	1	16	8.3	8.2
3	1	17	23.9	- 22.0
3	1	18	14.6	4.6
3	1	19	24.9	20.2
3	1	20	0.0	3.9
3	1	21	32.7	- 31.8
4	1	-30	21.6	- 10.4
4	1	-25	17.1	- 19.8
4	1	-23	20.7	27.8
4	1	-22	28.5	- 35.7
4	1	-21	7.8	15.6
4	1	-20	9.2	14.7
4	1	-19	19.3	18.8
4	1	-18	16.6	19.3
4	1	-17	57.8	- 83.1
4	1	-16	0.0	- 3.1
4	1	-15	32.4	38.0
4	1	-14	0.0	- 2.8
4	1	-13	19.3	- 26.3
4	1	-12	17.1	19.4
4	1	-11	58.0	63.9
4	1	-10	19.1	21.5
4	1	- 9	92.1	-104.6
4	1	- 8	26.3	- 25.7
4	1	- 7	12.7	23.7
4	1	- 6	45.1	- 48.4
4	1	- 5	6.9	- 9.7
4	1	- 4	19.3	27.5
4	1	- 3	52.6	65.4
4	1	- 2	38.2	- 37.3
4	1	- 1	66.7	- 80.2
4	1	0	48.7	- 51.5
4	1	1	20.0	21.0
4	1	2	19.7	- 28.0
4	1	3	24.3	- 18.7
4	1	4	0.0	9.4
4	1	5	19.7	22.2
4	1	6	0.0	- 7.9
4	1	7	2.0	0.0
4	1	8	25.1	- 19.2
4	1	9	37.7	- 40.3
4	1	10	39.3	35.4
4	1	11	39.3	35.4
4	1	12	21.6	23.5
4	1	13	0.0	5.8
4	1	14	0.0	5.8
4	1	15	8.3	2.5
4	1	16	0.0	5.4
4	1	17	0.0	5.4
4	1	18	8.8	5.8
4	1	19	14.8	12.9
4	1	20	0.0	2.8
4	1	21	41.6	- 40.3
4	1	22	0.0	5.5
4	1	25	38.0	- 21.6
5	1	-29	23.2	- 15.5
5	1	-23	40.0	36.8
5	1	-22	0.0	- 0.5
5	1	-21	37.0	- 39.3
5	1	-20	14.2	13.6
5	1	-19	0.0	5.4
5	1	-18	8.8	5.8
5	1	-17	15.0	- 15.4
5	1	-16	0.0	2.7
5	1	-15	63.3	- 77.2
5	1	-14	0.0	- 0.7
5	1	-13	59.1	- 60.1
5	1	-12	11.3	13.7
5	1	-11	6.0	0.7
5	1	-10	27.6	31.4
5	1	- 9	17.7	- 20.8
5	1	- 8	14.4	24.6
5	1	- 7	49.9	60.0
5	1	- 6	48.9	47.8
5	1	- 5	28.3	- 29.7
5	1	- 4	35.2	48.8
5	1	- 3	42.8	- 42.7
5	1	- 2	19.5	- 19.0
5	1	- 1	46.9	- 50.5
5	1	0	20.7	21.5
5	1	1	70.1	73.9
5	1	2	70.1	64.8
5	1	3	19.5	19.5
5	1	4	7.8	21.9
5	1	5	47.9	- 49.2
5	1	6	7.0	- 18.8
5	1	7	25.5	- 32.0
5	1	8	25.1	- 21.6
5	1	9	8.8	9.0
5	1	10	18.5	8.4
5	1	11	35.6	39.1
5	1	12	0.0	16.8
5	1	13	30.8	- 27.1
5	1	14	0.0	3.1
5	1	15	0.0	1.4
5	1	16	0.0	2.7
5	1	17	0.0	2.2
5	1	18	11.1	6.4
5	1	19	0.0	2.2
6	1	-23	0.0	2.2
6	1	-22	17.3	13.2
6	1	-21	17.7	- 24.3
6	1	-20	0.0	5.8
6	1	-19	30.8	37.1
6	1	-18	9.2	- 2.8
6	1	-17	23.9	- 16.1
6	1	-16	0.0	5.8
6	1	-15	26.3	26.1
6	1	-14	0.0	1.4
6	1	-13	37.0	- 45.3
6	1	-12	0.0	- 1.1
6	1	-11	42.1	- 41.5
6	1	-10	24.4	- 20.7
6	1	- 9	13.4	- 11.7
6	1	- 8	12.4	16.3
6	1	- 7	57.2	72.6
6	1	- 6	62.1	67.8
6	1	- 5	87.0	-101.9
6	1	- 4	9.0	- 16.7
6	1	- 3	54.3	59.2
6	1	- 2	0.0	- 3.3
6	1	- 1	10.1	- 10.7
6	1	0	9.5	8.7
6	1	1	0.0	11.2
6	1	2	16.8	14.5
6	1	3	7.1	- 10.7
6	1	4	7.4	9.6
6	1	5	14.2	- 18.7
6	1	6	8.8	7.7
6	1	7	0.0	- 2.1
6	1	8	42.6	47.4
6	1	9	9.4	19.5
6	1	10	34.4	35.9
6	1	11	6.9	5.7
6	1	12	27.8	- 23.1
6	1	13	43.8	- 45.2
6	1	14	0.0	- 17.0
6	1	15	0.0	- 7.9
6	1	16	14.6	- 13.2
6	1	17	0.0	11.9
6	1	19	35.2	29.6
6	1	22	20.0	- 1.0
7	1	-27	19.7	14.8
7	1	-25	23.5	- 21.0
7	1	-22	17.7	- 15.3
7	1	-21	8.2	7.4
7	1	-20	15.9	- 14.3
7	1	-19	44.2	45.6
7	1	-18	7.6	- 7.3
7	1	-17	19.5	- 24.3
7	1	-16	0.0	5.0
7	1	-15	7.2	0.0
7	1	-14	9.9	14.3
7	1	-13	27.3	- 32.7
7	1	-12	0.0	- 7.4
7	1	-11	58.1	64.0
7	1	-10	0.0	9.8
7	1	- 9	15.6	- 18.6
7	1	- 8	40.0	48.9
7	1	- 7	26.3	20.3
7	1	- 6	20.0	- 24.5
7	1	- 5	47.5	- 53.8
7	1	- 4	0.0	0.8
7	1	- 3	18.9	24.2
7	1

Table 1. (*cont.*)

H	K	L	F OBS	F CALC
0	2	8	85.6	74.5
0	2	9	38.0	- 34.3
0	2	10	98.2	- 93.2
0	2	11	49.2	40.9
0	2	12	21.2	21.8
0	2	13	22.2	- 26.2
0	2	14	39.7	- 40.7
0	2	15	19.5	- 12.0
0	2	16	17.9	17.8
0	2	17	9.4	6.4
0	2	18	20.2	21.2
0	2	19	13.1	21.2
0	2	20	0.0	0.6
0	2	21	0.0	- 1.4
0	2	22	0.0	- 9.3
0	2	23	0.0	- 5.6
1	2	-28	24.8	18.4
1	2	-23	0.0	- 9.2
1	2	-22	26.9	- 24.3
1	2	-21	22.8	- 25.9
1	2	-20	32.2	29.7
1	2	-19	0.0	- 2.6
1	2	-18	21.4	- 17.6
1	2	-17	16.8	28.3
1	2	-16	24.6	- 26.8
1	2	-15	8.8	2.2
1	2	-14	36.1	- 34.4
1	2	-13	32.7	- 29.4
1	2	-12	75.7	83.0
1	2	-11	17.9	13.6
1	2	-10	44.2	- 47.0
1	2	- 9	0.0	3.0
1	2	- 8	61.1	- 55.6
1	2	- 7	34.9	44.4
1	2	- 6	108.8	-133.7
1	2	- 5	129.9	-131.3
1	2	- 4	175.4	199.0
1	2	- 3	84.1	- 81.4
1	2	- 2	111.7	-133.4
1	2	- 1	49.9	40.2
1	2	0	84.9	108.0
1	2	1	19.1	19.8
1	2	2	55.1	- 63.6
1	2	3	8.8	- 9.8
1	2	4	139.0	152.1
1	2	5	55.7	- 57.9
1	2	6	63.0	- 75.4
1	2	7	8.8	3.2
1	2	8	34.7	37.4
1	2	9	9.5	3.0
1	2	10	60.7	- 61.8
1	2	11	0.0	4.8
1	2	12	38.6	40.3
1	2	13	0.0	- 4.1
1	2	14	34.3	- 31.1
1	2	15	0.0	- 1.1
1	2	16	69.5	65.6
1	2	17	23.0	12.6
1	2	18	17.9	- 10.6
1	2	19	15.4	- 13.9
1	2	20	18.1	14.6
1	2	21	0.0	- 8.7
1	2	22	7.8	- 9.6
1	2	-23	0.0	- 7.3
2	2	-22	0.0	1.2
2	2	-21	0.0	1.7
2	2	-20	0.0	0.4
2	2	-19	27.8	25.1
2	2	-18	30.2	- 22.3
2	2	-17	12.9	13.2
2	2	-16	29.4	25.8
2	2	-15	13.6	- 23.1
2	2	-14	8.8	8.1
2	2	-13	0.0	2.6
2	2	-12	47.7	51.5
2	2	-11	17.7	23.0
2	2	-10	98.9	-110.2
2	2	- 9	0.0	15.0
2	2	- 8	7.0	16.4
2	2	- 7	17.7	12.0
2	2	- 6	71.7	- 78.9
2	2	- 5	32.7	30.8
2	2	- 4	145.6	171.6
2	2	- 3	37.0	- 27.7
2	2	- 2	19.8	- 19.8
2	2	- 1	16.6	27.2
2	2	0	73.2	81.0
2	2	1	48.5	- 50.9
2	2	2	64.2	- 70.2
2	2	3	28.6	- 31.8
2	2	4	86.0	102.6
2	2	5	17.7	23.6
2	2	6	36.2	- 38.4
2	2	7	63.3	65.7
2	2	8	84.4	81.4
2	2	9	45.5	40.7
2	2	10	17.1	- 22.2
2	2	11	18.1	- 21.5
2	2	12	77.5	75.6
2	2	13	8.8	- 6.7
2	2	14	0.0	- 7.8
2	2	15	0.0	12.4
2	2	16	17.9	14.8
2	2	17	0.0	- 2.1
2	2	18	26.5	- 24.6
2	2	19	0.0	- 2.3
2	2	20	9.4	10.6
2	2	21	0.0	0.8
3	2	-23	0.0	- 3.2
3	2	-22	0.0	3.5
3	2	-21	0.0	12.2
3	2	-20	19.8	- 20.1
3	2	-19	0.0	6.4
3	2	-18	26.8	- 22.8
3	2	-17	20.2	- 14.7
3	2	-16	0.0	5.2
3	2	-15	10.3	- 16.3
3	2	-14	9.9	8.3
3	2	-13	0.0	- 4.3
3	2	-12	33.5	43.2
3	2	-11	60.0	68.9
3	2	-10	75.9	- 80.5
3	2	- 9	67.2	64.6
3	2	- 8	98.3	102.4
3	2	- 7	58.3	- 54.3
3	2	- 6	28.5	- 30.7
3	2	- 5	19.6	- 25.2
3	2	- 4	92.6	102.2
3	2	- 3	0.0	5.6
3	2	- 2	88.8	-104.1
3	2	- 1	34.7	- 47.7
3	2	0	91.5	100.9
3	2	1	29.0	- 28.1
3	2	2	52.4	- 53.4
3	2	3	0.0	0.1
3	2	4	52.0	56.9
3	2	5	18.7	- 14.8
3	2	6	126.4	-139.7
3	2	7	31.1	24.8
3	2	8	37.0	33.5
3	2	9	11.3	- 20.9
3	2	10	64.1	- 59.1
3	2	11	0.0	8.4
3	2	12	53.1	48.9
3	2	13	29.9	31.5
3	2	14	23.0	- 27.9
3	2	15	9.5	- 3.0
3	2	16	0.0	- 0.2
3	2	17	0.0	- 12.9
3	2	18	9.2	- 8.1
3	2	19	0.0	1.9
3	2	20	0.0	6.6
3	2	25	21.8	- 16.5

H	K	L	F OBS	F CALC
4	2	-23	11.7	11.4
4	2	-22	0.0	- 2.9
4	2	-21	12.0	- 14.5
4	2	-20	0.0	0.2
4	2	-19	18.4	- 11.1
4	2	-18	26.5	29.0
4	2	-17	0.0	- 3.7
4	2	-16	28.5	29.0
4	2	-15	25.7	25.0
4	2	-14	16.9	- 29.0
4	2	-13	0.0	0.0
4	2	-12	27.8	24.8
4	2	-11	32.9	- 27.3
4	2	-10	20.9	- 20.0
4	2	- 9	5.7	2.3
4	2	- 8	79.7	83.2
4	2	- 7	0.0	- 0.3
4	2	- 6	62.5	- 75.9
4	2	- 5	15.6	13.2
4	2	- 4	0.0	10.4
4	2	- 3	9.9	- 13.7
4	2	- 2	47.1	- 50.1
4	2	- 1	0.0	8.4
4	2	0	112.2	121.1
4	2	1	20.7	- 23.9
4	2	2	45.0	- 46.8
4	2	3	25.7	- 24.8
4	2	4	68.7	72.7
4	2	5	8.5	3.9
4	2	6	36.1	- 51.8
4	2	7	10.9	17.4
4	2	8	81.2	85.9
4	2	9	18.9	15.9
4	2	10	38.4	- 26.6
4	2	11	17.3	- 13.2
4	2	12	25.3	19.7
4	2	13	19.2	19.2
4	2	14	59.6	- 55.2
4	2	15	0.0	2.8
4	2	16	38.2	33.8
4	2	17	15.0	17.6
4	2	18	0.0	- 3.5
4	2	19	0.0	14.0
4	2	20	0.0	4.0
4	2	21	0.0	2.7
4	2	22	26.3	21.6
4	2	23	28.3	- 19.2
4	2	-26	27.1	- 25.9
4	2	-25	0.0	4.0
4	2	-24	0.0	2.7
4	2	-22	0.0	2.7
4	2	-21	0.0	10.8
4	2	-20	9.5	10.7
4	2	-19	9.2	9.8
4	2	-18	0.0	0.1
4	2	-17	10.1	13.0
4	2	-16	8.5	8.4
4	2	-15	29.9	- 30.5
4	2	-14	0.0	6.3
4	2	-13	13.8	11.7
4	2	-12	39.9	46.0
4	2	-11	6.2	4.8
4	2	-10	0.0	8.2
4	2	- 9	22.4	22.0
4	2	- 8	0.0	20.0
4	2	- 7	54.1	- 46.5
4	2	- 6	13.3	23.6
4	2	- 5	80.4	- 79.5
4	2	- 4	18.5	26.2
4	2	- 3	56.3	55.0
4	2	- 2	31.0	33.4
4	2	- 1	0.0	7.8
4	2	0	22.4	22.0
4	2	1	10.7	13.5
4	2	2	104.7	95.5
4	2	3	18.5	15.0
4	2	4	10.1	23.2
4	2	5	10.5	15.0
4	2	6	10.2	9.9
4	2	7	0.0	3.6
4	2	8	10.7	9.4
4	2	9	0.0	3.0
4	2	10	28.8	- 20.7
4	2	11	35.2	18.0
4	2	12	13.8	1.5
4	2	13	27.8	11.4
4	2	14	33.3	- 15.9
4	2	15	0.0	1.0
4	2	16	27.1	- 24.7
4	2	17	0.0	3.6
4	2	18	18.7	- 14.6
4	2	19	0.0	1.5
4	2	20	0.0	0.3
4	2	21	0.0	0.4
4	2	22	0.0	1.0
4	2	23	0.0	0.2
4	2	24	0.0	0.2
4	2	25	0.0	0.2
4	2

Table 1 (*cont.*)

H	K	L	F OBS	F CALC
7	3	-11	13.1	10.6
7	3	-10	6.9	12.6
7	3	-9	54.9	- 57.6
7	3	-8	0.0	17.3
7	3	-7	19.5	20.9
7	3	-6	0.0	- 11.6
7	3	-5	27.1	- 29.3
7	3	-4	4.6	- 10.8
7	3	-3	44.4	45.6
7	3	-2	6.6	4.6
7	3	-1	0.0	2.7
7	3	0	22.6	3.9
7	3	1	11.3	9.6
7	3	2	10.5	1.2
7	3	3	14.2	- 12.2
7	3	4	0.0	5.5
7	3	5	9.7	- 10.1
7	3	6	17.9	2.7
7	3	7	11.3	20.6
7	3	8	18.5	33.7
7	3	9	7.4	9.8
7	3	10	42.3	35.7
7	3	11	7.6	3.4
7	3	12	10.9	- 8.8
7	3	13	0.0	0.7
7	3	19	16.8	- 6.5
7	3	20	25.1	2.9
8	3	-24	26.3	- 14.9
8	3	-23	21.0	12.6
8	3	-22	26.7	- 15.9
8	3	-19	29.4	27.2
8	3	-18	0.0	2.1
8	3	-17	11.5	- 15.1
8	3	-16	14.8	- 21.3
8	3	-15	13.3	14.5
8	3	-14	17.7	- 25.1
8	3	-13	35.6	- 35.7
8	3	-12	0.0	16.3
8	3	-11	35.0	34.6
8	3	-10	19.8	28.4
8	3	-9	10.1	- 14.9
8	3	-8	0.0	14.2
8	3	-7	34.7	37.9
8	3	-6	23.7	- 37.0
8	3	-5	24.1	- 24.5
8	3	-4	0.0	12.5
8	3	-3	0.0	2.0
8	3	-2	28.0	28.3
8	3	-1	29.4	- 25.4
8	3	0	18.7	- 4.9
8	3	1	0.0	2.2
8	3	2	17.0	- 19.4
8	3	3	15.9	23.3
8	3	4	0.0	2.2
8	3	5	24.8	24.2
8	3	6	40.0	39.4
8	3	7	0.0	- 6.1
8	3	8	0.0	- 3.5
8	3	9	0.0	1.1
8	3	10	25.0	- 24.5
8	3	11	0.0	- 5.0
8	3	14	20.9	13.7
9	3	-22	23.0	13.3
9	3	-20	23.7	15.6
9	3	-17	8.2	- 15.0
9	3	-16	19.1	- 17.9
9	3	-15	18.7	21.6
9	3	-14	0.0	2.6
9	3	-13	19.1	- 23.7
9	3	-12	14.4	16.9
9	3	-11	24.0	24.4
9	3	-10	0.0	- 4.4
9	3	-9	22.0	- 16.8
9	3	-8	0.0	- 10.2
9	3	-7	11.7	10.9
9	3	-6	37.2	38.7
9	3	-5	28.6	- 32.7
9	3	-4	0.0	18.4
9	3	-3	0.0	- 1.8
9	3	-2	0.0	4.1
9	3	-1	0.0	1.3
9	3	0	11.5	- 3.7
9	3	1	22.2	20.0
9	3	2	0.0	- 7.9
9	3	3	25.1	- 22.4
9	3	4	0.0	12.5
9	3	5	0.0	- 8.5
9	3	6	0.0	- 1.8
9	3	7	0.0	- 5.5
9	3	17	33.1	31.1
10	3	-19	20.0	20.6
10	3	-18	13.3	7.8
10	3	-16	17.5	11.8
10	3	-14	0.0	9.4
10	3	-13	21.0	- 20.7
10	3	-12	0.0	1.3
10	3	-11	9.9	11.4
10	3	-10	0.0	- 5.7
10	3	-9	13.0	- 8.2
10	3	-8	0.0	4.7
10	3	-7	0.0	5.5
10	3	-6	0.0	10.0
10	3	-5	10.4	- 14.3
10	3	-4	0.0	12.1
10	3	-3	0.0	9.2
10	3	-2	0.0	- 16.1
10	3	-1	14.2	- 8.9
10	3	0	16.3	- 10.9
10	3	1	12.4	8.2
10	3	2	12.4	- 4.1
10	3	3	8.0	- 15.8
10	3	9	12.2	9.9
10	3	10	20.9	15.8
11	3	-14	15.8	- 12.8
11	3	-13	15.6	- 9.7
11	3	-12	15.6	- 13.7
11	3	-11	20.2	18.9
11	3	-7	17.1	10.9
11	3	-5	19.1	- 18.9
11	3	-3	18.3	12.5
11	3	-1	17.5	- 9.4
11	3	1	11.9	- 9.1
11	3	4	25.7	- 17.8
11	3	5	12.2	10.9
12	3	-11	12.2	11.7
12	3	-9	19.9	- 12.7
12	3	-8	18.1	- 17.9
12	3	-2	16.1	12.0
12	3	-1	16.1	- 9.5
12	3	1	12.4	8.4
12	3	6	19.5	8.2
0	4	0	66.9	91.6
0	4	1	49.0	59.5
0	4	2	63.2	- 57.6
0	4	3	27.8	25.6
0	4	4	105.1	121.7
0	4	5	34.3	- 34.4
0	4	6	16.8	- 24.8
0	4	7	63.7	- 68.4
0	4	8	59.1	70.8
0	4	9	22.0	8.6
0	4	10	55.9	- 57.5
0	4	11	63.2	- 57.6
0	4	12	27.8	25.6
0	4	13	22.2	18.7
0	4	13	0.0	- 15.1
0	4	14	13.1	7.0
0	4	15	36.1	- 35.4
0	4	16	23.7	21.1
0	4	17	0.0	- 0.8
0	4	18	25.5	- 27.9
0	4	19	13.8	21.4
0	4	20	0.0	- 3.6
0	4	21	12.2	12.2
1	4	-21	16.6	- 11.7
1	4	-20	0.0	3.1
1	4	-19	0.0	1.8
1	4	-18	23.0	- 18.6
1	4	-17	13.3	18.2
1	4	-16	22.4	18.6
1	4	-15	0.0	- 9.8
1	4	-14	0.0	- 4.8
1	4	-13	20.0	- 9.8
1	4	-12	44.8	49.4
1	4	-11	16.4	7.4
1	4	-10	20.5	15.6
1	4	-9	50.2	59.6
1	4	-8	57.5	74.8
1	4	-7	13.4	13.1
1	4	-6	21.0	- 32.7
1	4	-5	31.7	- 38.5
1	4	-4	14.4	14.2
1	4	-3	71.8	- 92.3
1	4	-2	63.9	72.9
1	4	-1	44.6	68.7
1	4	0	54.9	53.8
1	4	1	19.3	- 24.2
1	4	2	10.9	12.0
1	4	4	60.9	76.8
1	4	5	18.9	- 21.5
1	4	6	71.8	- 86.7
1	4	7	38.9	37.3
1	4	8	15.2	21.0
1	4	9	12.4	14.5
1	4	10	33.1	- 47.7
1	4	11	9.7	13.4
1	4	12	47.9	53.0
1	4	13	23.5	- 34.8
1	4	14	31.1	- 28.2
1	4	15	8.3	- 4.2
1	4	16	0.0	11.3
1	4	17	20.7	24.4
1	4	18	25.3	- 24.6
1	4	19	0.0	8.5
1	4	20	0.0	6.7
2	4	-21	0.0	5.0
2	4	-20	0.0	6.8
2	4	-19	0.0	0.9
2	4	-18	22.2	10.1
2	4	-17	34.9	- 28.6
2	4	-16	0.0	12.5
2	4	-15	17.3	- 27.6
2	4	-14	0.0	1.6
2	4	-13	23.7	29.1
2	4	-12	19.1	9.1
2	4	-11	29.2	22.9
2	4	-10	42.6	- 54.0
2	4	-9	19.3	- 26.1
2	4	-8	62.3	73.3
2	4	-7	23.4	- 25.6
2	4	-6	22.6	- 46.5
2	4	-5	26.0	- 12.8
2	4	-4	48.5	77.4
2	4	-3	9.4	- 1.1
2	4	-2	45.1	- 68.9
2	4	-1	8.3	9.2
2	4	0	86.2	98.7
2	4	1	27.3	- 26.7
2	4	2	78.1	- 95.1
2	4	3	25.5	- 28.7
2	4	4	21.6	- 2.7
2	4	5	23.4	- 21.5
2	4	6	37.6	- 29.4
2	4	7	14.8	22.5
2	4	8	8.3	- 1.2
2	4	9	6.4	0.4
2	4	10	45.0	- 47.7
2	4	11	37.0	- 32.9
2	4	12	25.3	32.5
2	4	13	9.5	1.2
2	4	14	23.9	- 17.7
2	4	15	9.9	4.6
2	4	16	25.1	- 29.3
2	4	17	0.0	0.9
2	4	18	0.0	8.7
2	4	19	0.0	7.2
2	4	20	0.0	6.2
3	4	-21	0.0	10.2
3	4	-20	12.7	12.2
3	4	-19	0.0	- 17.1
3	4	-18	0.0	13.9
3	4	-17	22.4	- 22.1
3	4	-16	23.0	22.9
3	4	-15	0.0	- 7.6
3	4	-14	26.3	- 36.9
3	4	-13	8.3	9.4
3	4	-12	19.8	21.0
3	4	-11	14.4	12.3
3	4	-10	22.4	- 30.9
3	4	-9	22.8	- 19.9
3	4	-8	51.2	68.0
3	4	-7	28.6	- 31.6
3	4	-6	73.6	- 85.7
3	4	-5	39.9	41.2
3	4	-4	21.4	44.9
3	4	-3	43.6	45.7
3	4	-2	58.2	- 73.3
3	4	-1	26.3	- 38.3
3	4	0	49.8	60.4
3	4	1	26.0	- 28.1
3	4	2	52.2	- 60.9
3	4	3	36.8	46.7
3	4	4	36.4	53.5
3	4	5	46.5	46.5
3	4	6	44.6	- 55.4
3	4	7	18.9	- 10.9
3	4	8	55.5	57.5
3	4	9	43.0	- 44.9
3	4	10	31.3	- 34.9
3	4	11	11.1	- 12.5
3	4	12	19.7	27.5
3	4	13	25.5	19.6
3	4	14	10.1	- 7.8
3	4	15	0.0	6.0
3	4	16	0.0	0.4
3	4	17	16.2	- 26.0
3	4	18	18.2	- 20.8
3	4	19	0.0	8.6
3	4	20	0.0	2.7
4	4	-21	0.0	2.7
4	4	-20	20.0	- 23.1
4	4	-19	20.9	- 27.5
4	4	-18	0.0	2.7
4	4	-17	0.0	8.2
4	4	-16	23.4	27.8
4	4	-15	39.6	35.3
4	4	-14	35.1	- 37.1
4	4	-13	8.3	7.1
4	4	-12	11.7	11.2
4	4	-11	20.5	- 32.3
4	4	-10	36.5	36.5
4	4	-9	25.9	20.4
4	4	-8	23.0	31.0
4	4	-7	46.2	46.2
4	4	-6	8.5	- 26.3
4	4	-5	18.1	28.1
4	4	-4	39.4	47.0
4	4	-3	47.5	- 57.6
4	4	-2	11.7	23.9
4	4	-1	0.0	- 11.0
4	4	0	11.9	- 15.1
4	4	1	11.1	7.0
4	4	2	40.7	- 53.7
4	4	3	45.3	48.1
4	4	4	36.1	42.7
4	4	5	0.0	7.7
4	4	6	39.0	- 32.1
4	4	8	24.9	26.7
4	4	9	38.2	41.2
4	4	10	93.1	- 98.1
4	4	11	33.3	42.5
4	4	12	28.3	21.6
4	4	13	7.2	4.4
4	4	14	20.2	- 12.3
4	4	15	19.0	- 15.9
4	4	16	25.5	17.8
4	4	17	0.0	0.3
4	4	-21	18.8	- 13.4
5	4	-20	0.0	5.8
5	4	-19	15.0	14.0
5	4	-18	12.4	- 9.7
5	4	-17	0.0	0.6
5	4	-16	15.9	15.6
5	4	-15	10.3	- 16.7
5	4	-14	17.7	27.7
5	4	-13	20.0	- 21.8
5	4	-12	14.8	14.6
5	4	-11	22.2	- 5.6
5	4	-10	19.7	- 25.1
5	4	-9	13.1	13.9
5	4	-8	0.0	3.6
5	4	-7	0.0	4.7
5	4	-6	39.3	- 58.8
5	4	-5	18.1	- 35.8
5	4	-4	21.8	33.6
5	4	-3	17.9	- 21.9
5	4	-2	23.0	- 26.2
5	4	-1	0.0	12.7
5	4	0	64.2	71.4
5	4	1	15.6	27.8
5	4	2	21.4	- 26.6
5	4	3	0.0	- 16.3
5	4	4	40.5	36.8
5	4	5	15.2	- 17.4
5	4	6	42.6	- 39.9
5	4	7	6.6	- 10.9
5	4	8	0.0	6.7
5	4	9	22.2	21.2
5	4	10	23.7	- 19.6
5	4	11	11.3	- 8.6
5	4	12	35.0	29.4
5	4	13	10.5	- 21.9
5	4	14	19.6	15.1
5	4	15	0.0	4.2
5	4	16	0.0	4.4
5	4	-20	8.3	11.5
5	4	-19	19.1	21.1
6	4	-18	17.0	16.9
6	4	-17	0.0	8.6
6	4	-16	0.0	5.7
6	4	-15	18.5	- 25.2
6	4	-14	9.2	8.0
6	4	-13	9.0	11.8
6	4	-12	0.0	1.6
6	4	-11	7.0	19.3
6	4	-10	20.0	- 19.5
6	4	-9	6.9	- 7.7
6	4	-8	9.5	12.5
6	4	-7	47.9	- 49.2
6	4	-6	13.3	- 25.7
6	4	-5	0.0	7.5
6	4	-4	43.2	47.8
6	4	-3	0.0	11.2
6	4	-2	40.0	- 45.2
6	4	-1	21.6	- 27.5
6	4	0	53.1	49.0
6	4	1	9.0	- 17.7
6	4	2	0.0	0.3
6	4	3	0.0	- 2.4
6	4	4	21.6	17.8
6	4	5	0.0	0.1
6	4	6	0.0	7.1
7	4	-19	8.3	- 5.7
7	4	-18	17.3	- 11.9
7	4	-17	0.0	12.0
7	4	-16	21.0	- 20.7
7	4	-15	11.1	15.9
7	4	-14	0.0	- 2.4
7	4	-13	22.4	29.9
7	4	-12	19.5	20.1
7	4	-11	0.0	6.0
7	4	-10	0.0	7.4
7	4	-9	8.8	- 20.1
7	4	-7	0.0	- 2.5
7	4	-6	29.3	- 31.6
7	4	-5	34.1	38.6
7	4	-4	35.0	39.1
7	4	-3	0.0	13.4
7	4	-2	0.0	- 6.9
7	4	-1	0.0	- 5.5
7	4	0	39.5	41.0
7	4	1	22.2	- 22.0
7	4	2	22.4	- 24.4
7	4	3	0.0	3.5
7	4	4	44.0	40.4
7	4	5	23.7	31.6
7	4	6	7.2	- 2.8
7	4	7	0.0	2.6
7	4	8	27.6	19.2
7	4	9	17.1	- 26.7
7	4	10	19.8	- 13.2
7	4	11	0.0	- 7.5
7	4	12	17.9	6.6
7	4	12	15.9	0.6
7	4	13	22.4	26.3
7	4	14	25.7	- 21.7
7	4	16	17.3	5.8
7	4	-17	0.0	6.5
8	4	-16	0.0	9.4
8	4	-15	13.8	16.2
8	4	-14	12.4	18.8
8	4	-13	10.9	9.7
8	4	-12	19.5	23.5
8	4	-11	24.6	- 23.1
8	4	-10	0.0	- 13.3
8	4	-9	16.8	- 16.6
8	4	-6	0.0	0.7
8	4	-7	0.0	15.6
8	4	-6	10.3	- 27.9
8	4	-5	0.0	5.2
8	4	-4	30.8	29.6
8	4	-3	21.8	- 23.3
8	4	-2	28.6	- 29.6
8	4	-1	20.5	- 32.9
8	4	0	33.3	34.8
8	4	1	17.7	22.8
8	4	2	17.9	- 11.7
8	4	3	22.8	28.4
8	4	4	10.5	0.4
8	4	5	22.0	- 19.3
8	4	6	9.4	7.1
8	4	7	15.4	- 24.8
8	4	8	0.0	2.7
8	4	9	0.0	0.4
8	4	10	12.9	9.9
8	4	12	10.3	12.7
8	4	14	13.8	- 7.5
8	4	16	12.9	9.3
8	4	18	29.6	- 11.4
9	4	-15	0.0	1.9
9	4	-14	8.2	6.6
9	4	-13	9.9	- 17.3
9	4	-12	8.0	13.3
9	4	-11	0.0	11.2
9	4	-10	7.8	- 17.1
9	4	-9	21.4	29.7
9	4	-8	0.0	11.2
9	4	-7	18.1	- 16.6
9	4	-6	0.0	1.3
9	4	-5	24.1	- 29.8
9	4	-4	19.1	22.9
9	4	-3	0.0	9.2
9	4	-2	18.9	- 18.3
9	4	-1	19.7	19.8
9	4	0	13.1	- 12.6
9	4	1	0.0	4.7
9	4	2	10.9	- 16.8
9	4	3	0.0	4.2
9	4	4	18.5	14.4
9	4	5	12.7	- 10.1
9	4	6	38.4	- 21.8
9	4	8	20.2	15.2
9	4	10	25.5	- 10.9
9	4	14	22.2	- 5.6
10	4	-10	0.0	5.6
10	4	-9	0.0	4.9
10	4	-8	0.0	1.6
10	4	-7	0.0	5.0
10	4	-6	9.9	- 13.0
10	4	-5	0.0	5.3
10	4	-4	0.0	4.6
10	4	-3	0.0	18.1
10	4	-2	12.9	- 14.3
10	4	-1	20.9	17.2
10	4	0	22.2	- 5.6
0	5	1	23.0	12.2
0	5	2	52.2	- 48.8
0	5	3	20.7	- 20.8
0	5	4	38.6	- 35.3
0	5	5	38.6	- 9.1
0	5	6	20.2	11.2
0	5	7	22.6	19.1
0	5	8	33.1	- 29.2
0	5	9	0.0	6.1
0	5	10	41.9	- 42.8
0	5	11	25.3	35.5
0	5	12	19.7	- 13.4
0	5	13	38.4	- 40.9
0	5	14	40.1	32.7
0	5	15	19.8	20.8
0	5	16	0.0	0.2
0	5	17	0.0	8.0
0	5	18	18.5	- 22.5
0	5	19	29.0	26.2
1	5	-13	15.2	- 13.8
1	5	-12	39.7	40.6
1	5	-11	23.7	29.2
1	5	-10	29.2	- 28.4
1	5	-9	21.4	- 32.5
1	5	-8	39.7	- 46.0
1	5	-7	11.9	8.1
1	5	-6	0.0	3.3
1	5	-5	41.3	- 48.0
1	5	-4	25.1	25.3
1	5	-3	17.0	10.5
1	5	-2	21.6	10.6
1	5	-1	19.5	3.5
1	5	0	58.1	- 54.6
1	5	1	24.4	21.0
1	5	2	14.0	- 2.2
1	5	3	17.3	13.8
1	5	4	17.7	7.8
1	5	5	24.1	- 27.6
1	5	6	11.3	- 17.1
1	5	7	29.6	29.8
1	5	8	29.0	- 23.2
1	5	9	7.8	- 8.2
1	5	10	0.0	- 12.4
1	5	11	16.3	15.9
1	5	12	13.6	24.5
1	5	13	34.1	- 37.3
1	5	14	0.0	4.5
1	5	15	19.3	20.8
1	5	16	30.2	- 28.5
1	5	17	0.0	3.6
1	5	18	16.6	- 23.3
1	5	19	15.9	20.0
2	5	-13	18.0	- 18.5
2	5	-12	33.5	44.2
2	5	-11	12.9	20.2
2	5	-10	15.0	- 9.5
2	5	-9	53.6	- 62.3
2	5	-8	18.3	5.6
2	5	-7	14.2	- 3.8
2	5	-6	10.8	- 20.3
2	5	-5	11.3	- 2.5
2	5	-3	18.1	21.2
2	5	-2	28.6	- 35.7
2	5	-1	20.0	27.5
2	5	0	9.2	- 2.7
2	5	1	11.7	- 8.9
2	5	2	8.3	- 5.6
2	5	3	16.8	13.5
2	5	4	19.3	17.5
2	5	5	12.9	- 6.8
2	5	6	23.9	- 28.5
2	5	7	7.6	14.4
2	5	8	32.5	- 33.7
2	5	9	0.0	0.6
2	5	10	37.5	41.3
2	5	11	0.0	- 0.4
2	5	12	20.0	20.8
2	5	13	0.0	- 5.2
2	5	14	0.0	- 11.2
2	5	15	0.0	12.0
2	5	16	25.1	- 23.9
2	5	17	17.3	- 23.0
2	5	18	0.0	4.3
3	5	-13	13.4	- 30.5
3	5	-12	22.8	- 22.1
3	5	-11	23.0	33.8
3	5	-10	11.7	- 9.2
3	5	-9	0.0	4.4
3	5	-8	9.4	14.8
3	5	-7	35.6	48.6
3	5	-6	11.4	- 15.1
3	5	-5	6.2	- 11.8
3	5	-4	23.2	- 22.3
3	5	-3	0.0	0.8
3	5	-2	23.2	21.4
3	5	-1	17.7	20.3
3	5	0	46.2	38.0
3	5	1	28.0	23.1
3	5	2	33.1	26.8
3	5	3	7.6	- 5.4
3	5	4	37.7	- 36.9
3	5	5	9.0	- 10.9
3	5	6	9.0	- 13.6
3	5	7	17.7	22.0
3	5	8	14.8	22.9
3	5	9	0.0	2.8
4	5	-13	15.2	- 13.8
4	5	-12	18.3	- 9.5
4	5	-9	29.2	- 24.0
4	5	-8	16.8	- 29.8
4	5	-5	0.0	12.0
4	5	-4	0.0	3.8
4	5	-3	0.0	8.6
4	5	-2	18.3	17.4
4	5	-11	0.0	11.8
4	5	-10	19.7	22.3
4	5	-9

Table 1 (*cont.*)

H	K	L	F OBS	F CALC
1	6	9	0.0	- 3.5
1	6	10	0.0	5.6
1	6	11	26.5	- 20.1
1	6	12	40.0	37.8
1	6	13	12.9	- 15.2
1	6	14	27.1	- 31.6
1	6	15	15.4	- 13.4
1	6	16	0.0	5.0
1	6	17	30.4	22.5
2	6	0	39.5	60.0
2	6	1	26.9	22.9
2	6	2	15.8	- 26.1
2	6	3	17.1	13.0
2	6	4	22.0	24.0
2	6	5	23.2	20.8
2	6	6	12.4	- 16.8
2	6	7	15.9	15.7
2	6	8	41.3	50.3
2	6	9	11.1	- 18.9
2	6	10	19.9	11.1
2	6	11	20.0	- 21.3
2	6	12	0.0	0.6
2	6	13	0.0	- 6.4
2	6	14	21.0	- 29.3
2	6	15	13.4	18.6
2	6	16	0.0	14.0
3	6	0	44.0	50.6
3	6	1	38.9	- 46.0
3	6	2	16.1	- 21.3
3	6	3	18.3	14.0
3	6	4	20.2	26.6
3	6	5	6.9	10.1
3	6	6	21.6	- 34.3
3	6	7	0.0	1.5
3	6	8	23.4	32.2
3	6	9	16.8	- 14.8
3	6	10	33.8	- 40.1
3	6	11	0.0	- 0.9
3	6	12	23.9	23.3
3	6	13	14.4	8.6
3	6	14	0.0	1.0
3	6	15	21.8	23.6
4	6	0	11.7	13.2
4	6	1	26.3	22.6
4	6	2	19.3	- 26.6
4	6	3	20.0	25.6
4	6	4	23.2	27.9
4	6	5	17.9	- 11.7
4	6	6	11.3	- 21.4
4	6	7	15.9	- 19.3
4	6	8	12.7	18.5
4	6	9	0.0	- 2.7
4	6	10	11.9	- 14.2
4	6	11	0.0	4.6
4	6	12	27.4	28.7
4	6	13	0.0	0.1
5	6	0	22.2	25.7
5	6	1	16.6	22.3
5	6	2	7.0	- 7.7
5	6	3	8.8	- 4.6
5	6	4	15.4	22.5
5	6	5	9.0	- 8.1
5	6	6	42.5	- 47.8
5	6	7	25.9	26.3
5	6	8	16.1	17.8
5	6	9	0.0	5.5
5	6	0	0.0	4.4
5	6	11	0.0	7.4
6	6	0	35.8	39.1
6	6	1	0.0	- 1.9
6	6	2	0.0	- 8.4
6	6	3	0.0	- 6.7
6	6	4	15.0	18.8
6	6	5	0.0	0.3
6	6	6	26.0	- 31.0
6	6	7	25.1	- 15.7
6	6	8	17.5	17.8
6	6	9	0.0	1.7
7	6	0	22.4	28.6
7	6	1	21.0	- 21.9
7	6	2	40.7	- 43.1
7	6	3	0.0	2.5
7	6	4	11.1	- 8.1
7	6	5	11.1	18.0
7	6	6	0.0	4.7
8	6	0	15.6	- 5.6
8	6	1	25.9	31.2
8	6	2	14.0	- 14.5
0	7	1	25.7	26.8
0	7	2	16.6	5.0
0	7	3	21.4	3.8
0	7	4	9.7	14.8
0	7	5	34.9	- 40.9
0	7	6	34.7	36.1
0	7	7	11.1	14.7
0	7	8	0.0	0.3
0	7	9	15.2	- 20.6
0	7	10	0.0	7.7
0	7	11	15.8	- 7.1
0	7	12	0.0	10.2
0	7	13	25.0	- 25.2
0	7	14	0.0	9.4
0	7	15	13.6	14.6
1	7	0	16.1	3.8
1	7	1	17.7	- 16.7
1	7	2	15.4	0.8
1	7	3	12.1	- 0.6
1	7	4	0.0	1.2
1	7	5	23.4	18.7
1	7	6	0.0	1.3
1	7	7	0.0	10.7
1	7	8	0.0	0.5
1	7	9	16.6	- 14.5
1	7	10	19.1	16.9
1	7	11	14.2	- 12.0
1	7	12	0.0	0.6
1	7	13	16.6	13.1
1	7	14	0.0	4.6
2	7	0	0.0	4.8
2	7	1	24.8	- 17.8
2	7	2	12.2	3.6
2	7	3	16.6	17.4
2	7	4	15.8	9.0
2	7	5	21.4	15.8
2	7	6	10.1	- 11.1
2	7	7	9.4	- 6.9
2	7	8	0.0	10.2
2	7	9	27.4	- 27.1
2	7	10	7.6	12.2
2	7	11	18.9	21.0
2	7	12	0.0	1.2
2	7	13	11.3	11.6
3	7	0	12.7	4.4
3	7	1	14.2	9.7
3	7	2	0.0	8.5
3	7	3	29.8	34.8
3	7	4	42.5	- 43.0
3	7	5	7.4	0.6
3	7	6	12.7	9.3
3	7	7	15.8	- 15.7
3	7	8	15.2	21.8
3	7	9	0.0	0.7
3	7	10	10.9	10.3
3	7	11	0.0	17.4
3	7	12	0.0	3.6
3	7	0	17.9	11.9
4	7	1	17.1	22.6
4	7	2	12.7	21.5
4	7	3	29.6	27.6
4	7	4	14.0	12.3
4	7	5	13.1	14.9
4	7	6	0.0	1.6
4	7	7	0.0	1.7
4	7	8	0.0	4.2
4	7	9	16.6	20.8
4	7	10	0.0	7.7
5	7	0	23.2	12.5
5	7	1	0.0	2.3
5	7	2	18.5	18.1
5	7	3	0.0	8.9
5	7	4	9.4	9.5
5	7	5	14.6	7.2
5	7	6	0.0	0.6
5	7	7	11.3	26.1
5	7	8	0.0	0.5
6	7	0	0.0	2.9
6	7	1	0.0	7.6
6	7	2	0.0	1.2
6	7	3	13.6	11.5
6	7	4	17.7	12.2
6	7	5	0.0	0.5
7	7	0	15.8	5.8
7	7	10	0.0	3.4
0	8	0	17.5	25.3
0	8	1	23.2	20.9
0	8	2	11.7	17.3
0	8	3	15.6	11.8
0	8	4	26.0	31.2
0	8	5	14.0	11.7
0	8	6	17.5	13.6
0	8	7	15.9	4.5
0	8	8	15.2	12.5
0	8	9	0.0	1.9
0	8	10	0.0	4.6
0	8	11	0.0	7.6
1	8	0	14.0	20.1
1	8	1	11.9	5.3
1	8	2	15.8	17.2
1	8	3	14.0	8.0
1	8	4	20.7	27.0
1	8	5	0.0	8.4
1	8	6	9.4	17.8
1	8	7	0.0	1.1
1	8	8	9.5	14.5
1	8	9	0.0	4.1
1	8	10	0.0	13.7
2	8	0	28.3	32.8
2	8	1	14.2	10.7
2	8	2	10.8	9.3
2	8	3	0.0	7.4
2	8	4	33.6	21.9
2	8	5	0.0	11.7
2	8	6	15.6	14.1
2	8	7	0.0	7.0
2	8	8	13.6	17.6
2	8	9	0.0	0.1
3	8	0	0.0	0.4
3	8	1	10.9	4.8
3	8	2	43.8	51.7
3	8	3	12.2	11.1
3	8	4	13.6	21.9
3	8	5	7.8	9.5
3	8	6	19.3	13.4
3	8	7	0.0	4.3
4	8	0	15.6	7.7
4	8	1	0.0	2.8
4	8	2	13.6	20.9
4	8	3	14.8	10.8
4	8	4	25.9	34.2
5	8	0	0.0	1.0
5	8	1	0.0	0.6

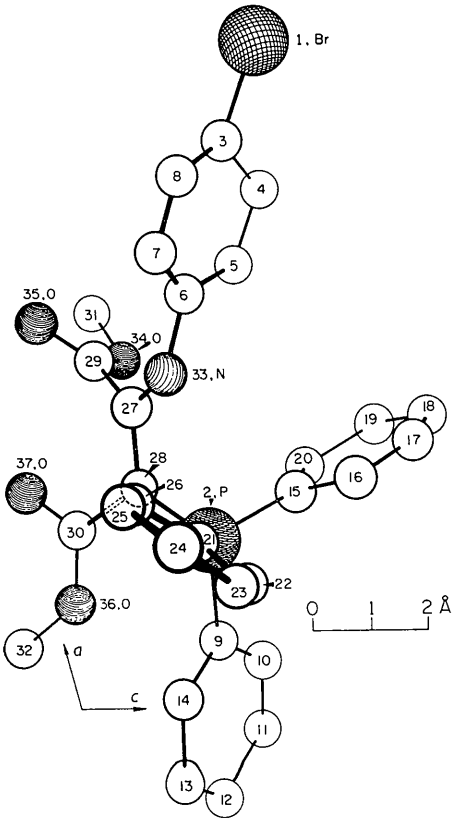

Fig. 1. Perspective drawing of the molecule.

all gave $R(hkl) \sim 0{\cdot}60$, so that it was not possible to decide which, if any, was the correct structure. Three separate three-dimensional Fourier series were summed, using only those reflexions whose signs seemed reasonably well-established in each case; this involved omitting a large number of reflexions, many with high F_o values, particularly among the three-quarters of the planes to which the bromine does not contribute. The 24 atoms used in the phasing and the thirteen other atoms in the molecule were quite well-resolved in *all three* electron-density distributions; the reason for the good resolution in all three cases is probably that the signs were correct in each case for those planes to which the bromine does contribute. However two of the resulting structures could be ruled out on packing considerations; in one structure ring C(9)–C(14) was too close to the corresponding ring in a neighbouring molecule related by a 2_1 axis, and in a second the methoxycarbonyl groups were too close to those in a molecule related by a centre of symmetry.

For the third structure, which had bromine at $00\frac{1}{4}$ (or at $1\frac{1}{2}\frac{1}{4}$ with a convenient change of origin), structure factors were calculated with all 37 atoms, and R, for the 1940 observed reflexions, was 0·49. One cycle of refinement by means of a differential synthesis reduced R to 0·42 and a second cycle to 0·38. It was evident that some of the atoms were not refining well: C(32) had a very low density, and C(29) and O(34) had refined to the same position. A three-dimensional electron-density distribution was therefore computed; on this map all the atoms were clearly resolved, and revised positions were obtained for C(29), C(32) and O(34). These revisions reduced R to 0·31, and a third cycle of differential synthesis refinement improved the agreement further to 0·26. A three-dimensional $(F_o - F_c)$ synthesis was then computed, and this suggested further small changes in atomic positional parameters and significant changes in thermal parameters, in particular a large increase in B for bromine, and a decrease for phosphorus. These changes reduced R to 0·23.

Further refinement then proceeded by computing a cycle of (block-diagonal) least squares; the function minimized was $\Sigma w(F_o - F_c)^2$, with $\sqrt{w} = |F_o|/60$ when $|F_o| < 60$ and $\sqrt{w} = 60/|F_o|$ when $|F_o| \geq 60$. The para-

meters refined were all the atomic positional coordinates, anisotropic thermal parameters for the bromine atom, isotropic thermal parameters for the other atoms, and an overall scale factor. Structure factors were recalculated with the new parameters, but with a mean isotropic temperature factor for bromine, and R was 0·21.

At this stage it was apparent that the structure had been well established and that any further refinement required introduction of anisotropic thermal parameters for more of the atoms (the bromine thermal motion is strongly anisotropic). Since the isotropic cycle required six hours computing time on our IBM 1620 computer and the core storage (40K) would accommodate only 28 anisotropic atoms, further refinement was not considered profitable. The structure has been refined sufficiently well to establish the molecular formulation conclusively, and to allow some general discussion of molecular dimensions.

The measured structure factors are compared in Table 1 with the values calculated from the final parameters (R=0·21 for 1940 observed reflexions).

Table 2. *Final positional and thermal parameters*

Atom	x	y	z	B
Br(1)	1·0105	0·5028	0·2402	7·6* Å²
P(2)	0·2520	0·4363	0·1156	2·0
C(3)	0·8472	0·4858	0·2005	3·7
C(4)	0·7851	0·3770	0·2159	5·5
C(5)	0·6642	0·3721	0·1863	4·8
C(6)	0·6203	0·4581	0·1446	4·1
C(7)	0·6867	0·5748	0·1300	5·0
C(8)	0·8038	0·5826	0·1610	4·7
C(9)	0·1015	0·3751	0·1054	3·2
C(10)	0·0741	0·2447	0·1314	3·5
C(11)	−0·0362	0·1915	0·1209	4·5
C(12)	−0·1248	0·2746	0·0834	6·5
C(13)	−0·0997	0·4000	0·0568	4·7
C(14)	0·0144	0·4605	0·0698	4·5
C(15)	0·3243	0·3916	0·1851	3·6
C(16)	0·3428	0·4925	0·2280	4·9
C(17)	0·3924	0·4352	0·2804	4·9
C(18)	0·4255	0·2965	0·2921	6·6
C(19)	0·4020	0·1920	0·2478	5·5
C(20)	0·3581	0·2451	0·1963	5·1
C(21)	0·2452	0·6376	0·1064	3·2
C(22)	0·1836	0·7210	0·1369	4·8
C(23)	0·1809	0·8640	0·1295	4·0
C(24)	0·2380	0·9398	0·0934	6·0
C(25)	0·2988	0·8493	0·0649	3·9
C(26)	0·3084	0·6973	0·0705	4·2
C(27)	0·4511	0·3595	0·0880	3·6
C(28)	0·3219	0·3496	0·0739	2·9
C(29)	0·5179	0·2621	0·0707	4·0
C(30)	0·2710	0·2623	0·0254	4·3
C(31)	0·5952	0·0123	0·0765	6·3
C(32)	0·0956	0·1622	−0·0323	5·4
N(33)	0·5004	0·4596	0·1231	4·6
O(34)	0·5229	0·1250	0·0931	4·9
O(35)	0·5817	0·2781	0·0364	5·9
O(36)	0·1533	0·2551	0·0152	5·4
O(37)	0·3261	0·2002	−0·0015	6·0

* Anisotropic thermal parameters for Br are:
B_{11}= 0·01334, B_{22}=0·02694, B_{33}= 0·00268
B_{23}=−0·00168, B_{13}=0·00107, B_{12}=−0·00307

Atomic parameters and molecular dimensions

The final positional and isotropic thermal parameters are given in Table 2, x, y, and z being coordinates referred to the monoclinic crystal axes and expressed as fractions of the unit cell edges. The anisotropic thermal parameters for the bromine atom are included as a footnote in Table 2; the magnitudes of the principal axes of the temperature-factor ellipsoid are 10·2, 8·7 and 4·1 Å², with the smallest vibration in the direction of the Br–C bond, so that the thermal vibration is strongly anisotropic and allowance for this motion alone would improve the structure factor agreement substantially.

The bond distances and valency angles in the molecule are given in Table 3. The standard deviations of the bond distances, estimated from the variations

Table 3. *Bond lengths* (Å) *and valency angles* (°)

Br(1)–C(3)	1·95	C(23–C(24)	1·45
		C(24)–C(25)	1·41
P(2)–(9)	1·82	C(25)–C(26)	1·41
P(2)–C(15)	1·81	C(26)–C(21)	1·43
P(2)–C(21)	1·87	Mean C_{ar}–C_{ar}	1·41
Mean P–C	1·83		
		C(27)–C(28)	1·48
P(2)=C(28)	1·70	C(27)–C(29)	1·34
		C(28)–C(30)	1·47
C(3)–C(4)	1·36	Mean C–C	1·43
C(4)–C(5)	1·44		
C(5)–C(6)	1·32	C(6)–N(33)	1·39
C(6)–C(7)	1·44		
C(7)–C(8)	1·42	C(27)=N(33)	1·32
C(8)–C(3)	1·35		
C(9)–C(10)	1·45	C(29)–O(34)	1·38
C(10)–C(11)	1·36	C(30)–O(36)	1·35
C(11)–C(12)	1·45	Mean C–O	1·37
C(12)–C(13)	1·41		
C(13)–C(14)	1·42	C(29)=O(35)	1·29
C(14)–C(9)	1·43	C(30)=O(37)	1·20
C(15)–C(16)	1·41	Mean C=O	1·25
C(16)–C(17)	1·42		
C(17)–C(18)	1·35	C(31)–O(34)	1·47
C(18)–C(19)	1·46	C(32)–O(36)	1·50
C(19)–C(20)	1·38	Mean O–Me	1·49
C(20)–C(15)	1·42		
C(21)–C(22)	1·42		
C(22)–C(23)	1·33		

Br–C–C P–C–C C–C–C	Range = 114–128 Mean = 120	
C(9)–P(2)–C(15)		106·1
C(15)–P(2)–C(21)		110·0
C(9)–P(2)–C(21)		106·2
C(28)=P(2)–C(9)		111·9
C(28)=P(2)–C(15)		108·4
C(28)=P(2)–C(21)		113·7
Mean C–P–C		109·4
C–N=C		120
C–C=O		129, 125
C–C–O		116, 112
O=C–O		114, 123
C–O–Me		119, 115

of chemically-equivalent bonds from mean values, are about 0·03 Å for Br–C and P–C distances, and 0·04 Å for other distances.

Discussion

A perspective drawing of the molecule is shown in Fig. 1, from which it is evident that the structure is (III*b*, $X=Br$), and hence the adduct formed from tetraphenylphosphine imide is (III*b*, $X=H$). The general shape of the molecule is also clear from Fig. 1. A detailed description of the disposition of the various phenyl and methoxycarbonyl groups is probably not very useful since the conformation of the molecule will be determined at least to some extent by intermolecular forces; any information required can readily be derived from Table 2.

The bond distances and valency angles in the molecule (Table 3) are all normal. The phosphorus–phenyl bonds average 1·83 Å ($\sigma \sim 0{\cdot}02_5$ Å), not significantly different from the P–C single-bond distance of $1{\cdot}87 \pm 0{\cdot}02$ Å in trimethylphosphine and $1{\cdot}84 \pm 0{\cdot}02$ Å in $[(CH_3)_2P.BH_2]_3$ (*Tables of Interatomic Distances*, 1958). The P=C length is 1·70 Å. This double-bond distance does not appear to have been measured previously; the reduction below the single-bond length is a little greater than the difference between the single-bond and double-bond covalent radii of phosphorus (Pauling, 1960). The angles at the phosphorus atom are all fairly close to the tetrahedral value (mean value 109·4°). The C–N bond measures 1·39 Å, and C=N is 1·32 Å. None of the distances and angles in the aromatic rings and in the methoxycarbonyl groups differs significantly from the usual values.

The intermolecular distances require no special comment, all corresponding to van der Waals interactions.

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Absolute Integrated Intensity Measurement: Application to $CaWO_4$ and Comparison of Several Refinements

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A technique for absolute intensity measurement is described which appears capable of establishing an experimental scale to within 1·25% to 1·50% of the true value. A limited amount of data obtained from absolute measurements on $CaWO_4$ has been compared with a more extensive set of relative data of Zalkin & Templeton. Anisotropic least-squares refinements based on these data as well as neutron data of Kay, Frazer & Almodovar have been compared. The apparent anisotropies of thermal parameters are not entirely consistent between any two experimental techniques. There is evidence for residual systematic error in both X-ray experiments after corrections for absorption, anomalous dispersion, and secondary extinction. As long as some systematic error remains it appears that a limited number of very careful measurements is not as effective for refinement of positional parameters as a very large number of less careful measurements, even for very simple structures.

Absolute intensity measurements have been out of fashion in crystal structure analysis for many years. Originally there was no substitute for such measurements in solving the trial structure stage as exemplified by the classic work of Warren & Bragg (1928) on diopside. With the introduction of photographic techniques based on small crystals bathed in the X-ray beam a direct experimental determination of the