could also explain the observed differences in the intensity data.

The bond distances calculated from the three sets of positional parameters are presented in Table 2. The average difference in bond distances between P and MM is 0·004 Å. The largest differences are between N(2)–C(2) (0·010 Å) and C(3)–C(4) (0·007 Å), although neither of these is significantly different. There are significant differences in the values of BH compared with those of either MM or P. However, two of the three significantly different distances involve an NO_2 group, where anisotropic thermal motion is the greatest. Since BH used only one asymmetric thermal parameter, this difference is not surprising.

Table 2. *Comparison of the bond distances (in Å) found in the three studies of potassium picrate*

	P	MM	BH
C(1)–O(1)	1·245 (3)	1·243 (7)	1·282 (13)
C(1)–C(2)	1·455 (2)	1·452 (5)	1·467 (10)
C(2)–C(3)	1·370 (2)	1·372 (6)	1·373 (9)
C(3)–C(4)	1·389 (2)	1·382 (5)	1·407 (9)
C(4)–N(1)	1·440 (3)	1·436 (8)	1·423 (15)
N(1)–O(4)	1·224 (2)	1·228 (5)	1·228 (8)
C(2)–N(2)	1·459 (2)	1·457 (6)	1·472 (10)
N(2)–O(2)	1·222 (3)	1·232 (5)	1·251 (10)
N(2)–O(3)	1·230 (3)	1·229 (5)	1·194 (11)

One last point that was not discussed by MM relates to the possible existence of a C–H···O hydrogen bond involving the lone hydrogen atom and the oxygen atom O(3). The H···O(3) distance of 2·47 (2) Å is slightly less than a van der Waals contact. In addition, the C–H···O angle of 175 (2)° and the C–H distance of 0·99 (2) Å suggest that an interaction does exist. The corresponding N(2)–O(3) distance found by P is longer than the N(2)–O(2) distance, in agreement with the presence of a hydrogen bond involving O(3) but not O(2).

Conclusions

The results of three independent determinations of the crystal structure of potassium picrate using different methods for measuring the intensity data are in excellent agreement. The only significant differences in the positional parameters involve the visual data which were not completely refined. There are three significantly different thermal parameters when the values of P and MM are compared. However, the source of the differences is obscure since a number of different factors may be involved.

This present comparison indicates that the stationary-crystal stationary-counter technique can give as valid a measurement of integrated intensities as densitometer data from films. Two independent studies of histamine acid phosphate monohydrate (Veidis, Palenik, Schaffrin & Trotter, 1969) and μ-oxo-bis(nitrosyltriphenylphosphine)-diiridium(I) (Dellaca, Mathew, Palenik & Robinson, 1971) indicated that stationary-crystal stationary-counter and moving-crystal data yield identical results. A similar conclusion was reached recently by DeCamp & Stewart (1971). Therefore, one can conclude that stationary-crystal stationary-counter measurements are indeed a valid measurement of the integrated intensity and compare favorably with other methods of intensity measurements.

References

Abrahams, S. C., Hamilton, W. C. & Mathieson, A. McL. (1970). *Acta Cryst.* **A26**, 1.

Bettman, M. (1952). Ph. D. Thesis. California Instit. of Technology, Pasadena, California.

Bettman, M. & Hughes, E. W. (1954). *Structure Reports for* 1954 (1961) Vol. 18, pp. 715-716. N. V. A. Oosthoek's Uitgevers MIJ, Utrecht.

DeCamp, W. H. & Stewart, J. M. (1971). *Acta Cryst.* **B27**, 1227.

Dellaca, R. J., Mathew, M., Palenik, G. J. & Robinson, W. R. (1971). In preparation.

Hanson, H., Mathew, M. & Palenik, G. J. (1971). Unpublished results.

International Tables for X-ray Crystallography (1962). Vol. III, p. 211. Birmingham: Kynoch Press.

Maartmann-Moe, K. (1969). *Acta Cryst.* **B25**, 1452.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Veidis, M., Palenik, G. J., Schaffrin, R. & Trotter, J. (1969). *J. Chem. Soc.* (*A*) p. 2659.

Acta Cryst. (1972). **B28**, 1635

The crystal structure of 4-phenylazoazobenzene.

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4-Phenylazoazobenzene ($C_{18}H_{14}N_4$) crystallizes in the space group $P2_1/c$, with $a=13{\cdot}870$ (5), $b=4{\cdot}617$ (2), $c=11{\cdot}920$ (5) Å, $\beta=113{\cdot}20$ (3)°, and $Z=2$. The calculated crystal density is 1·34 g.cm^{-3}. The asymmetric unit, a half-molecule, was determined using the symbolic addition procedure from 1213 reflection intensities measured on a diffractometer with Cu $K\alpha$ radiation. The structure was refined to a final R value of 0·078. The 22 atoms of a whole molecule are planar to within ±0·05 Å. The molecules stack in a herringbone pattern, with the planes of adjacent parallel molecules separated by only 3·325 (5) Å.

The crystal structure of 4-phenylazoazobenzene (PAAB) was determined primarily to obtain the orientation of the molecules in the crystal. This information can be used to relate theoretically estimated molecular properties and anisotropic crystal properties (Lonsdale & Krishnan, 1936), such as the polarization of crystal absorption spectra (Anex & Fratini, 1964).

Crystals of PAAB, grown from methyl ethyl ketone, were supplied by Dr B. Anex of the Yale University Chemistry Department. The space group is $P2_1/c$, and with a half-molecule asymmetric unit the calculated density is 1·34 g.cm^{-3}. The cell dimensions are a = 13·870 (5), b = 4·617 (2), c = 11·920 (5) Å, and β = 113·20 (3)°. A very thin, lath-shaped, transparent orange crystal (0·7 × 0·3 × 0·01 mm)

Table 1. *Fractional coordinates and thermal parameters*

The thermal expression was of the form:

$$T = \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	0·16142 (18)	0·46989 (54)	0·20169 (21)	3·44 (10)	3·15 (11)	3·11 (10)	−0·50 (9)	1·34 (8)	−0·31 (9)
N(2)	0·15787 (18)	0·57614 (52)	0·10540 (20)	3·55 (11)	2·87 (10)	2·75 (10)	−0·72 (9)	1·08 (8)	−0·18 (8)
C(1)	0·24575 (19)	0·25658 (59)	0·25035 (25)	2·26 (10)	2·24 (11)	3·53 (12)	0·12 (9)	0·30 (9)	−0·24 (10)
C(2)	0·25107 (23)	0·12708 (67)	0·35705 (26)	3·62 (13)	3·14 (13)	3·43 (13)	0·32 (11)	1·36 (10)	−0·17 (11)
C(3)	0·32806 (25)	−0·07616 (70)	0·41344 (27)	4·59 (15)	3·39 (14)	3·10 (12)	0·46 (12)	1·14 (11)	0·05 (11)
C(4)	0·39983 (22)	−0·14749 (67)	0·36447 (28)	2·98 (12)	3·03 (13)	3·89 (14)	0·64 (11)	0·19 (10)	0·02 (11)
C(5)	0·39380 (23)	−0·02189 (72)	0·25654 (29)	3·32 (13)	3·69 (14)	4·71 (15)	0·26 (12)	1·83 (11)	−0·10 (12)
C(6)	0·31665 (24)	0·18355 (68)	0·19918 (28)	4·05 (14)	3·14 (13)	3·41 (13)	−0·31 (11)	1·19 (11)	0·52 (11)
C(7)	0·07509 (19)	0·79025 (55)	0·05736 (23)	2·26 (10)	1·95 (10)	2·95 (11)	−0·11 (8)	0·44 (8)	−0·14 (9)
C(8)	0·06803 (20)	0·91068 (61)	−0·05245 (24)	2·75 (11)	2·81 (11)	2·89 (11)	−0·21 (9)	1·36 (9)	−0·34 (9)
C(9)	0·00672 (21)	0·87951 (61)	0·10994 (23)	3·15 (11)	2·75 (12)	2·37 (10)	−0·45 (10)	0·97 (9)	0·10 (9)
H(2)	0·2023 (28)	0·1788 (84)	0·3932 (32)						
H(3)	0·3372 (29)	−0·1554 (86)	0·4935 (33)						
H(4)	0·4573 (27)	−0·2886 (85)	0·4045 (32)						
H(5)	0·4462 (27)	−0·0826 (88)	0·2216 (34)						
H(6)	0·3084 (28)	0·2614 (86)	0·1223 (33)						
H(8)	0·1156 (26)	0·8519 (79)	−0·0907 (30)						
H(9)	0·0153 (25)	0·8056 (79)	0·1908 (30)						

(The hydrogen atoms were assigned thermal parameters equal to those of the adjoining heavier atom.)

Table 2. *Observed and calculated structure factors*

The columns contain h, 10 $|F_o|$, and $10F_c$.

H	0	0
1	319	348
2	258	-280
3	305	308
4	182	-181
5	136	134
6	6	-6
7	92	87
8	0	-8
9	138	-143
10	58	-60
11	48	-60
12	252	255
13	201	200
14	45	-48
15	65	71
H	0	2
-15	120	119
-14	245	242
-13	38	-34
-12	0	-3
-11	51	47
-10	43	-41
-9	58	64
-8	89	-88
-7	87	90
-6	139	-151
-5	608	-614
-4	136	-138
-3	136	146
-2	1038	1070
-1	378	377
0	322	-321
1	456	459
2	93	-87
3	62	57
4	28	28
5	15	19
6	91	91
7	379	-378
8	230	-229
9	10	10
10	42	46
11	79	86
12	30	-32
13	17	11
H	0	4
-16	34	33
-15	11	10
-14	29	-26
-13	10	4
-12	13	-9
-11	14	13
-10	101	-79
-9	0	-2
-8	23	-28
-7	498	-491
-6	131	-130
-5	311	111
-4	246	-228
-3	28	-21
-2	32	28
-1	376	-364
0	248	-230
1	90	83
2	111	-110
3	51	-57
4	87	82
5	226	-212
6	202	-189
7	52	48
8	54	-47
9	61	-67
10	0	6
11	30	-32
12	44	-49
H	0	6
-16	13	-17
-15	78	-86
-14	0	3
-13	15	-10
-12	103	-109
-11	28	-28
-10	21	20
-9	35	-29
-8	8	-2
-7	0	6
-6	63	-56
-5	52	-51
-4	46	40
-3	128	-121
-2	172	-153
-1	128	121
0	340	-332
1	276	-269
2	65	63
3	27	-22
4	24	25
5	0	-2
6	21	24
7	56	58
8	0	-10
9	34	34
10	26	25
H	0	8
-16	6	-1
-15	15	-15
-14	141	-143
-13	57	-55
-12	33	38
-11	89	76
-10	103	97
-9	44	-46
-8	139	144
-7	109	108
-6	61	-62
-5	273	268
-4	190	191
-3	15	9
-2	186	-179
-1	251	-241
0	45	42
1	2	13
2	42	50
3	5	-1
4	20	14
5	156	152
6	46	-43
7	82	83
8	217	217
H	0	10
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-14	26	27
-13	8	4
-12	44	36
-11	5	-11
-10	43	43
-9	91	99
-8	72	-63
-7	301	293
-6	350	342
-5	46	-45
-4	32	-29
-3	52	-55
-2	10	-10
-1	27	30
0	0	10
1	25	24
2	43	-44
3	0	6
4	42	-48
5	47	46
6	210	216
H	0	12
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-11	78	-63
-10	18	-9
-9	102	90
-8	160	144
-7	12	-14
-6	25	-20
-5	24	-18
-4	20	-21
-3	18	16
-2	29	-26
-1	17	23
0	43	-47
1	120	-129
2	38	-44
H	0	14
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-6	16	-17
-5	0	5
H	1	0
1	130	-118
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3	799	775
4	65	62
5	69	-67
6	120	121
7	55	54
8	46	43
9	127	-123
10	92	-91
11	21	23
12	42	-38
13	38	-38
14	0	-8
H	1	1
-15	15	-7
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-13	68	68
-12	52	-52
-11	157	159
-10	141	146
-9	12	-9
-8	80	-85
-7	298	-296
-6	36	-33
-5	120	126
-4	347	366
-3	252	251
-2	237	-239
-1	385	399
0	208	-205
1	184	177
2	1010	1040
3	126	122
4	14	12
5	231	-221
6	227	-222
7	72	67
8	4	17
9	76	77
10	19	-20
11	37	-39
12	0	-9
13	31	-30
14	87	92
H	1	2
-15	12	14
-14	21	22
-13	22	-23
-12	122	118
-11	226	224
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-9	25	23
-8	199	194
-7	26	25
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-5	52	-46
-4	0	-6
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-2	51	-65
-1	50	-52
0	36	40
1	809	832
2	161	156
3	169	-164
4	406	403
5	176	166
6	20	-15
7	32	23
8	34	27
9	14	6
10	65	-65
11	30	-26
12	16	-13
13	56	57
H	1	3
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-14	3	-13
-13	85	84
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-11	37	-36
-10	16	-9
-9	142	-139
-8	74	-70
-7	77	86
-6	139	-125
-5	46	52
-4	65	-73
-3	476	-484
-2	215	-213
-1	102	104
0	360	356
1	82	70
2	52	-48
3	35	-27
4	177	-167
5	59	57
6	36	-34
7	40	-31
8	33	38
9	129	-133
10	102	-107
11	0	-8
12	13	6
13	11	-6
H	1	4
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-14	41	40
-13	128	124
-12	0	-1
-11	1	-6
-10	107	109
-9	19	15
-8	14	7
-7	6	22
-6	66	69
-5	74	-77
-4	176	-178
-3	70	58
-2	45	-39
-1	237	237
0	154	150
1	98	-98
2	50	48
3	12	4
4	12	-6
5	14	9
6	21	19
7	25	28
8	92	-92
9	49	-44
10	7	-1
11	8	8
12	58	56
H	1	5
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-15	10	2
-14	18	-23
-13	0	-12
-12	12	-6
-11	9	-8
-10	10	-14
-9	15	9
-8	80	-68
-7	22	-18
-6	0	-6
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-3	106	105
-2	282	-273
-1	183	-184
0	48	44
1	120	-109
2	49	-40
3	11	7
4	21	-22
5	21	26
6	20	15
7	46	-40
8	37	-40
9	19	18
10	27	-28
11	78	-70
H	1	6
-16	0	3
-15	32	33
-14	19	10
-13	29	-30
-12	57	-54
-11	26	-23
-10	16	16
-9	85	-85
-8	22	-18
-7	18	21
-6	198	-189
-5	33	-42
-4	7	4
-3	79	75
-2	166	160
-1	24	-18
0	113	-114
1	114	-119
2	40	38
3	90	-100
4	142	-147
5	49	48
6	78	-76
7	122	-118
8	0	-3
9	0	6
10	45	43
H	1	7
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-14	0	9
-13	15	-21
-12	43	40
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-10	0	6
-9	33	36
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-7	108	114
-6	101	105
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-4	129	-127
-3	166	-163
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0	32	-18
1	35	39
2	98	-101
3	22	23
4	11	-15
5	40	40
6	163	161
7	17	18
8	8	2
9	0	-1
H	1	8
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-14	48	-51
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-11	119	-129
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-8	125	-125
-7	118	-124
-6	21	16
-5	76	78
-4	92	94
-3	12	-2
-2	12	13
-1	3	-13
0	13	14
1	80	-79
2	160	-159
3	45	48
4	40	-47
5	169	-168
6	30	-25
7	25	25
8	43	35
H	1	9
-15	11	-2
-14	19	17
-13	13	-6
-12	60	-66
-11	19	17
-10	0	-6
-9	189	178
-8	224	223
-7	45	-50
-6	43	47
-5	15	19
-4	26	-27
-3	122	122
-2	80	80
-1	31	31
0	93	-95
1	79	-85
2	4	-13
3	34	33
4	143	168
5	24	23
6	11	-5
7	62	66
H	1	10
-14	17	-12
-13	36	-45
-12	32	-40
-11	26	23
-10	71	-68
-9	99	-98
-8	8	-3
-7	67	71
-6	88	68
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-4	120	118
-3	126	126
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-1	11	2
0	0	9
1	28	30
2	19	-12
3	80	-80
4	13	-18
5	6	10
H	1	11
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-13	42	-56
-12	17	16
-11	52	43
-10	98	90
-9	8	-13
-8	12	11
-7	28	34
-6	42	-42
-5	137	135
-4	128	123
-3	8	3
-2	38	-39
-1	102	-108
0	22	-25
1	22	18
2	16	25
3	10	14
H	1	12
-12	16	-12
-11	16	-11
-10	8	-6
-9	4	7
-8	28	32
-7	19	-12
-6	87	80
-5	134	129
-4	12	-20
-3	14	14
-2	46	73
-1	3	17
0	0	-2
1	12	6
H	1	13
-11	12	3
-10	57	-51
-9	80	-71
-8	20	-19
-7	47	46
-6	42	42
-5	0	-4
-4	14	-12
-3	50	-57
-2	20	-21
-1	10	10
H	2	0
0	71	65
1	11	10
2	48	41
3	204	-172
4	289	-256
5	180	156
6	226	210
7	110	104
8	21	-21
9	112	-103
10	10	-12
11	3	-0
12	5	-6
13	0	2
H	2	1
-14	7	-5
-13	37	40
-12	20	-15
-11	58	56
-10	143	159
-9	18	-8
-8	94	96
-7	87	94
-6	41	-42
-5	97	-97
-4	177	-182
-3	77	78
-2	8	-7
-1	0	16
0	43	46
1	94	-91
2	439	411
3	138	116
4	67	61
5	435	401
6	92	81
7	23	-19
8	34	-22
9	0	8
10	20	22
11	15	-18
12	29	29
13	19	-17
H	2	2
-14	8	-7
-13	17	-15
-12	26	27
-11	34	-35
-10	83	-88
-9	187	189
-8	139	145
-7	23	-25
-6	28	-33
-5	218	-219
-4	72	-69
-3	91	90
-2	45	-45
-1	1	-1
0	30	-29
1	42	-37
2	249	-255
3	140	133
4	430	425
5	19	17
6	10	6
7	8	-10
8	64	-72
9	28	27
10	25	-24
11	37	-37
12	5	4
H	2	3
-14	5	10
-13	6	13
-12	91	94
-11	19	-17
-10	143	143
-9	250	261
-8	14	-14
-7	15	-15
-6	79	73
-5	74	71
-4	9	-8
-3	110	115
-2	145	151
-1	119	-121
0	8	-6
1	46	-46
2	36	37
3	431	425
4	108	95
5	42	-40
6	78	79
7	13	28
8	0	10
9	10	8
10	83	80
11	11	1
12	44	-45
H	2	4
-15	0	-2
-14	12	-9
-13	0	6
-12	32	-35
-11	96	96
-10	176	178
-9	56	-56
-8	0	6
-7	15	-9
-6	82	-79
-5	69	73
-4	196	-180
-3	110	-107
-2	15	-22
-1	182	-176
0	49	-44
1	0	3
2	265	255
3	109	111
4	67	-64
5	78	78
6	22	16
7	17	16
8	22	-21
9	74	-70
10	0	8
11	47	-58
H	2	5
-15	48	-41
-14	47	-43
-13	21	-19
-12	56	57
-11	72	72
-10	27	-30
-9	15	16
-8	25	-23
-7	25	-30
-6	13	19
-5	64	76
-4	192	191
-3	83	-81
-2	218	-223
-1	89	-100
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3	70	-57
4	52	-52
5	16	-24
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0	10	-8
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4	44	-59
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0	15	-14
1	14	13
2	69	-69
3	38	-51
H	5	4
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-5	25	24
-4	8	-12
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-2	28	31
-1	69	74
0	3	2
1	18	-24
2	88	-58
H	5	5
-4	80	83
-3	107	113
-2	54	57
-1	27	32
0	23	-22

was used for data collection. 1213 reflections were measured on a four-circle automatic diffractometer, using Cu $K\alpha$ radiation (1·54178 Å). Each peak was scanned using a 2θ scan with a $2{\cdot}0^\circ + 2\theta(\alpha_2) - 2\theta(\alpha_1)$ scan width, and a detector scanning rate of 2·0° min^{-1}. The background was counted for 10 sec at each end of the scan.

The structure was obtained directly from the intensities by using the symbolic addition procedure for phase determination (Karle & Karle, 1966). The coordinates obtained from the E map were refined using a full-matrix least-squares refinement procedure to minimize $\sum w(|F_o| - |F_c|)^2$. The $|F_o|$ values were corrected for absorption errors, which were negligible for most reflections ($\mu = 6{\cdot}7\ \text{cm}^{-1}$), but were as large as 8 % for reflections diffracting along the long axis of the crystal. The weights, w, were equal to the reciprocal of the square of the standard deviation for each $|F_o|$, which was calculated assuming only statistical counting errors. All seven hydrogen atoms were found in a difference map, and subsequently their positions were refined. The final R value for the full set of data was 0·078. The corresponding atomic parameters are listed in Table 1. All observed and calculated structure factors are listed in Table 2.

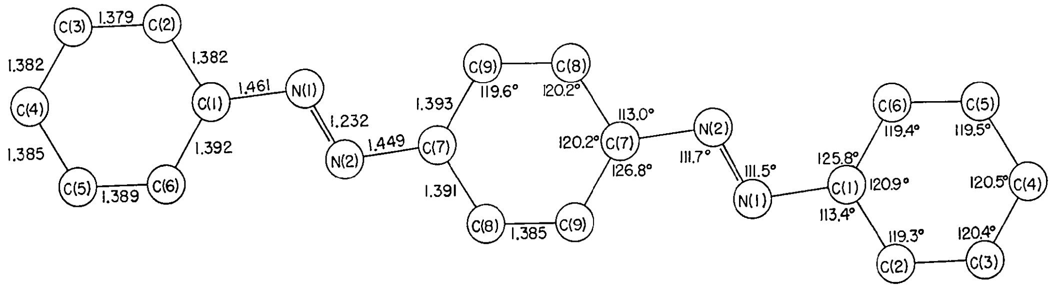

Fig. 1. Bond distances and angles. The e.s.d.'s for bond lengths are from 0·0035 to 0·005 Å (estimated from the convergence of the least-squares refinement). Angle standard deviations are 0·25 to 0·30°.

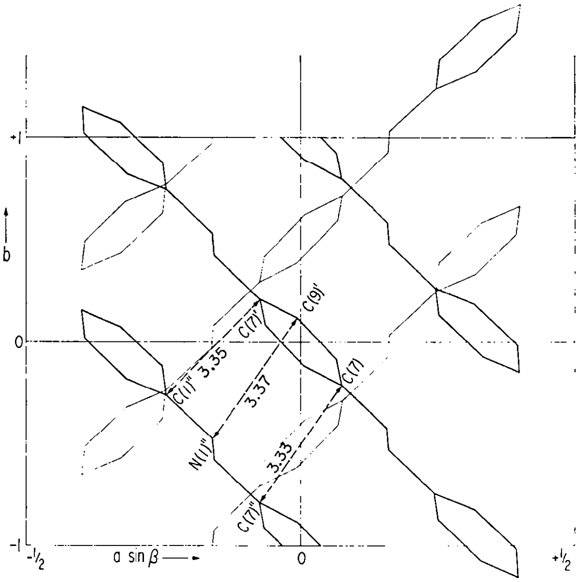

Fig. 2. Packing of 4-phenylazoazobenzene viewed down the c axis. Several close intermolecular approaches are illustrated.

The shape of the molecule and bond lengths and angles are shown in Fig. 1. To a close approximation (±0·05 Å), the entire molecule is planar. The best plane through the molecule, $6{\cdot}373\,x + 3{\cdot}325\,y + 3{\cdot}564\,z = 0$, passes through the origin; the variables in the equation are fractional coordinates (Schomaker, Waser, Marsh & Bergman, 1959). If planes are fitted to portions of the molecule, it is found that the central benzene ring, planar to ±0·001 Å, is rotated 3° about the long axis of the molecule from the plane of the terminal benzene rings.

The normal to the plane of the molecule is inclined 45° to the b axis, which is also the short stacking axis. Adjacent molecules, related by translation along the b axis, are separated by only 3·325 Å. Fig. 2 illustrates some stacked parallel molecules and short interatomic distances between them. Many aromatic hydrocarbons stack in similar herringbone patterns, but with larger interplanar spacings. Distances of 3·46, 3·53, and 3·55 Å were noted in coronene (Fawcett & Trotter, 1965), pyrene (Camerman & Trotter, 1965), and phenanthrene (Trotter, 1963), respectively. Shorter aromatic stacking distances, such as that found for PAAB, are found in crystals of charge-transfer complexes and dipolar complexes (Wallwork, 1961).

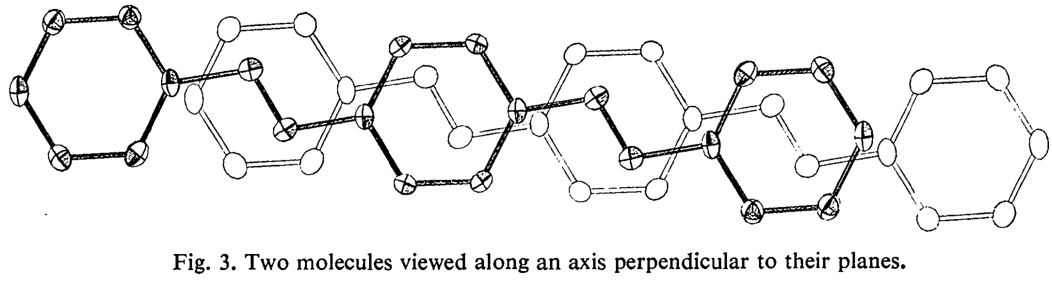

Fig. 3. Two molecules viewed along an axis perpendicular to their planes.

Fig. 3 illustrates two closely stacked PAAB molecules, viewed from a direction perpendicular to the mean molecular planes. Each azo group is sandwiched between two benzene rings, and each central benzene ring is between two azo groups. A similar stacking of aromatic rings and double bonds was reported in the crystal structure of the naphthalene–tetracyanoethylene complex (Williams & Wallwork, 1967), and several other examples involving dipolar molecules are discussed by Prout & Wallwork (1966).

The crystal structure of PAAB shows little resemblance to that reported for *trans*-azobenzene (Brown, 1966). There are two crystallographically independent half-molecules in the asymmetric unit of *trans*-azobenzene; one of these was found to be ordered, and the other probably disordered. The bond distances and angles found for the ordered molecule of *trans*-azobenzene differ insignificantly from the corresponding values reported here for PAAB. However, the *trans*-azobenzene molecule is nonplanar; there is a torsion of 17·1° about the bond connecting the benzene ring and the azo group in the ordered molecule. Moreover, there is a striking difference in the packing. No intermolecular contacts (involving C or N atoms) less than 3·63 Å are reported for *trans*-azobenzene. In PAAB, *every* atom is within 3·6 Å of atoms in at least one other PAAB molecule.

References

Anex, B. & Fratini, A. (1964). *J. Mol. Spectrosc.* **14**, 1.
Brown, C. J. (1966). *Acta Cryst.* **21**, 146.
Camerman, A. & Trotter, J. (1965). *Acta Cryst.* **18**, 636.
Fawcett, J. K. & Trotter, J. (1965). *Proc. Roy. Soc.* A**289**, 366.
Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849.
Lonsdale, K. & Krishnan, K. S. (1936). *Proc. Roy. Soc.* A**156**, 597.
Prout, C. K. & Wallwork, S. C. (1966). *Acta Cryst.* **21**, 449.
Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.
Trotter, J. (1963). *Acta Cryst.* **16**, 605.
Wallwork, S. C. (1961). *J. Chem. Soc.* p. 494.
Williams, R. M. & Wallwork, S. C. (1967). *Acta Cryst.* 22, 899.

Acta Cryst. (1972). **B28**, 1638

The use of a polarized hydrogen atom in X-ray structure refinement.*

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A one-center polarized hydrogen atom formalism has been tested in the routine refinement of a number of crystal structures. The effect on the bond lengths involving hydrogen atoms, and the interaction between anisotropic thermal motion and form factor asymmetry, are discussed.

It is well known that X–H bond lengths (X=C,N,O) as determined by X-ray diffraction are shortened, because an appreciable part of the charge on the hydrogen atom is displaced towards the bond center. As the shortening of the X–H bonds is, to a large extent, the result of an incorrect scattering formalism rather than an inherent property of the X-ray data, it is of interest to examine if an improved nonspherical formalism can correct the effect. In principle, such a formalism should include a two-center term describing the bond density (Stewart, 1969; Coppens, Csonka & Willoughby, 1971), but a one-center model in which a hydrogen atom is polarized towards the X atom may be adequate for a correction of the bond length. Such a model, based on earlier quantum-mechanical calculations (Rosen 1931), has been described by Hirshfeld & Rabinovich(1967). The hydrogen wave function is described as a mixing of 1s and 2p orbitals (μ=mixing coeffecicnt), the positive lobe of the p orbital being directed along the H–X bond:

$$\varphi_{\rm H}=[\varphi(1s)+\mu\varphi(2p)]/(1+\mu^2)^{1/2} \qquad (1)$$

in which $\varphi(1s)=N(1s)\exp(-\lambda r/a_o)$ and $\varphi(2p)=N(2p)z\exp(-\lambda r/a_o)$ (λ=orbital coefficient, N=normalization factor, a_o=Bohr radius, r=distance from the hydrogen nucleus, $z=r$ projected along H–X). The corresponding scattering formalism (Hirshfeld & Rabinovich, 1967) has been applied in a modification of our least-squares program, to determine whether bond lengths compatible with those from other techniques can be obtained with suitable values for μ and λ.

The equations used are as follows. If $f({\rm H})=f'+if''$, with f' and f'' as given by Hirshfeld & Rabinovich, the contributions of the hydrogen atom scattering to the structure factor $F=A+iB$ are:

$$A_{hkl}({\rm H})=\sum_n\sum_s\{[a_nf'\cos 2\pi(hx_{ns}+ky_{ns}+lz_{ns}) - a_nf''\sin 2\pi(hx_{ns}+ky_{ns}+lz_{ns})]T_{ns}\}$$

and

$$B_{hkl}({\rm H})=\sum_n\sum_s\{[a_nf'\sin 2\pi(hx_{ns}+ky_{ns}+lz_{ns}) + a_nf''\cos 2\pi(hx_{na}+ky_{ns}+lz_{ns})]T_{ns}\}, \qquad (2)$$

where the summation is over all n hydrogen atoms in the asymmetric unit and over all s symmetry equivalent potion, and a_n and T_{ns} are occupancy and temperature factors, respectively.

For the calculation of the derivatives, it should be noted that f' and f'' depend on the angle between the reciprocal lattice vector hkl and the axis of the p orbital on the

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