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The Structure of PO-Substituted Norcaradienes.
I. The Crystal and Molecular Structure of 7-Dimethoxyphosphoryl-7-phenylnorcaradiene

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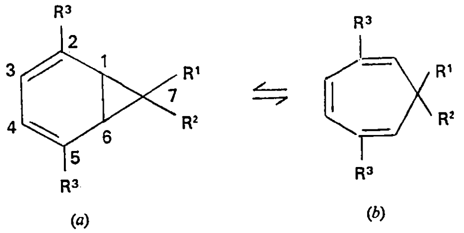
7-Dimethoxyphosphoryl-7-phenylnorcaradiene crystallizes in the space group $P\bar{1}$, with $a = 13{\cdot}259$ (2), $b = 8{\cdot}698$ (3), $c = 6{\cdot}507$ (2) Å, $\alpha = 110{\cdot}97$ (2), $\beta = 97{\cdot}62$ (2), $\gamma = 91{\cdot}26$ (3)°. The structure has been solved by direct methods; refinement by block-diagonal least-squares cycles gave $R = 4{\cdot}07$% for 2184 observed reflexions collected on a Siemens single-crystal diffractometer with Cu $K\alpha$ radiation. Whereas in solution a rapid equilibrium between the norcaradiene and its valence-isomeric cycloheptatriene can be observed, the molecules in the crystalline state show clearly the norcaradiene structure with an *endo* phenyl ring. The three C–C bonds of the cyclopropane ring are equal within the standard deviation.

Introduction



(Ia,b)$R^1 = R^2 = R^3 = H$

(IIa,b)R^1 = phenyl, $R^2 = PO(OCH_3)_2$, $R^3 = H$

(IIIa,b)R^1 = phenyl, $R^2 = PO(OCH_3)_2$, $R^3 = Cl$

(IVa,b)R^1 = phenyl, $R^2 = PO(OCH_3)_2$, $R^3 = Br$

(Va,b)$R^1 = R^2 = CN$, $R^3 = CH_3$

In the valence-isomeric equilibrium norcaradiene $\rightleftharpoons$ cycloheptatriene (I$a \rightleftharpoons$ Ib), the monocyclic system dominates to the extent that no norcaradiene could be observed by the usual analytical methods. However, appropriate substitution of the system leads to a remarkable stabilization of the norcaradiene skeleton [for a review see Maier (1967)]. In recent years, several compounds have been prepared, where the norcaradiene form is stabilized by introducing one or two π-electron acceptors in the 7-position. Hoffmann (1970) and Günther (1970) have discussed this π-type conjugation of the three-membered ring with neighbouring π-systems on the basis of the Walsh (1949) model for the cyclopropane ring. Their results are as follows: If the group R possesses a low-lying unoccupied molecular orbital, interaction with the cyclopropane electrons leads to weakening of 1,6-*anti*-bonding and 6,7 (1,7)-bonding. Norcaradienes stabilized in this way should therefore have C(1)–C(6) bond shorter than the C(6)–C(7) and C(1)–C(7) bonds. This has been confirmed in the structure of 2,5-dimethyl-7,7-dicyanonorcaradiene (Va) (Fritchie, 1966), with C(1)–C(6) = 1·501 Å and C(1)–C(7), C(6)–C(7) 1·554, 1·558 Å. Among the norcaradienes/cycloheptatrienes (II)–(IV), (II) exhibits a rapid equilibrium between the two valence isomers in solution. On the other hand, the compounds substituted by chlorine or bromine (III, IV) prefer the norcaradiene form. This can be derived from the increasing independence on temperature of their n.m.r. spectra (Günther, Tunggal, Regitz, Scherer & Keller, 1971). We undertook structural studies of these three compounds in order

(*a*) to obtain an insight into the acceptor strength of the group by considering the bonding parameters in the cyclopropane ring according to the theory cited above, and

(*b*) to explore how the increasing stability of the norcaradiene form caused by halogen substitution appears in the molecular geometry.

The structure analysis of (II) (Fig. 1) is described here, those of (III) and (IV) will be reported in forthcoming papers.

Experimental

The compound was prepared by the method given by Scherer, Hartmann, Regitz, Tunggal & Günther (1972). After recrystallization from ether, colourless prisms were obtained. A crystal with dimensions 0·212 × 0·356 × 0·091 mm was selected: precession photographs showed it to be triclinic. Precise lattice constants were obtained from a least-squares fit of 21 diffraction angles measured on a Siemens off-line diffractometer (AED). Crystal data are given in Table 1.

For the collection of intensities the crystal was mounted with **c** parallel to the φ axis of the diffractom-

Table 1. *Crystal data of 7-dimethoxyphosporyl-7-phenylnorcaradiene*

Formula: $C_{15}H_{17}O_3P$
F.W. 276·3
Space group: $P\bar{1}$ (No. 2)
Unit cell: $a = 13{\cdot}259$ (2) Å
$b =$ 8·698 (3)
$c =$ 6·507 (2)
$\alpha = 110{\cdot}97$ (2)°
$\beta =$ 97·62 (2)
$\gamma =$ 91·26 (3)
$V_c = 692{\cdot}5$ (4) Å^3
$D_m = 1{\cdot}35$ g cm^{-3}
$D_c = 1{\cdot}326$
$Z = 2$
$F(000) = 292$
$\mu(\text{Cu } K\alpha) = 17{\cdot}68$ cm^{-1}

eter equipped with a Cu tube (Ni filter), a scintillation counter and a pulse-height discriminator. With the $\theta/2\theta$-scan technique and the five-values method, 2552 independent reflexions were measured in the range $2° \le \theta \le 68{\cdot}50°$. A standard reflexion ($5\bar{7}2$) was monitored after every 50 reflexions to detect decomposition of the crystal or instability of the diffractometer. At the end, its intensity was 3·6% less than at the beginning. Assuming a linear and isotropic decomposition, all intensities were rescaled according to the observed time-dependent loss. 54 strong reflexions were remeasured with a 0·085 mm thick Cu foil as attenuator. The attenuation factor was determined experimentally.

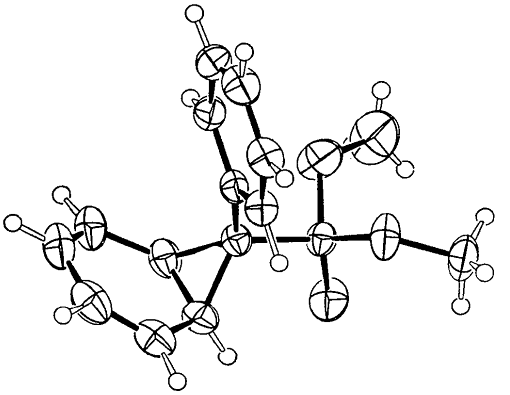


Fig. 1. Perspective view of the molecule. The thermal ellipsoids correspond to 50% probability.

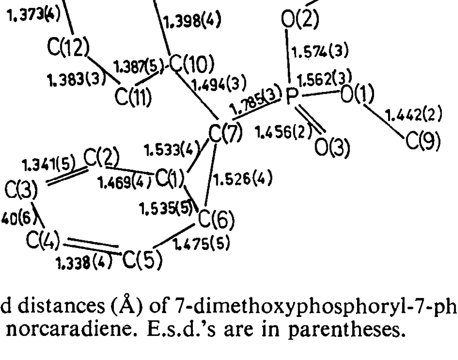


Fig. 2. Bond distances (Å) of 7-dimethoxyphosphoryl-7-phenylnorcaradiene. E.s.d.'s are in parentheses.

Corrections for Lorentz and polarization effects were made in the usual way. No absorption correction was applied. All reflexions with $F_o < 5\sigma(F_o)$ were treated as unobserved. The remaining 2189 reflexions were used for solution of the structure. From a Wilson plot, a scale factor and an overall temperature factor were obtained. The space group was determined from a statistical test based on the magnitudes of the normalized structure factors (Karle, Dragonette & Brenner, 1965). This test indicated a centric distribution, although the expected C_s symmetry of the molecule suggested a critical look at this result; nevertheless, refinement later confirmed the centrosymmetric space group. All calculations were carried out on a CDC 3300 computer at the Universität des Saarlandes, Saarbrücken.

Determination of the structure

The structure was solved by direct methods with the program *MULTAN* (Main, Woolfson & Germain, 1971). With 340 reflexions with normalized structure factors $|E| > 1{\cdot}5$, phases were computed from a starting set of six reflexions, three of which determined the origin. From the resulting eight sets of phases, the most consistent (apart from the trivial solution for which all phases are zero) was used to calculate an E map. It revealed all 19 non-hydrogen atoms. A structure factor calculation with these coordinates led to an R of 0·246. The atomic form factors were those of Onken & Fischer (1968), who have represented the scattering curves from *International Tables for X-ray Crystallography* by

$$f(\sin\theta/\lambda) = \exp\left[\sum_{n=1}^{7} a_n(\sin\theta/\lambda)^{n-1}\right].$$

Refinement was based on $|F|$'s and carried out with the block-diagonal least-squares program *BLKLS* (Bartlett, 1972). The shifts of positional parameters were multiplied by 0·75, those of thermal parameters by 0·4. After 4 cycles with isotropic temperature factors, R had decreased to 0·131. Another 4 cycles with anisotropic thermal parameters lowered R to 0·084. During these cycles the two strongest reflexions ($\bar{1}01$ and 020) were removed because they showed considerable extinction, and also three other reflexions ($\bar{1}\bar{1}3$, $1\bar{1}3$ and $3\bar{1}4$) which had unreasonably high residuals.

A difference synthesis computed at this stage revealed all 17 H atoms. Six cycles in which the positional and isotropic thermal parameters of the hydrogens were also allowed to vary, reduced R to 0·0415 and $R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$ to 0·039. The error of fit, $[\sum w(\Delta F)^2 / m-n]^{1/2}$ (with $m = 2184$, $n = 240$), was still 9·48. This relatively high value indicated that either refinement was not yet finished or the weighting

Table 2. *Observed and calculated structure factors.*

Column headings are *h*, $10F_o$, $10F_c$, $100w\Delta F$.

H	FO	FC	WD
H, 0, 0			
2	317	-335	8
3	15	11	2
4	77	71	2
5	535	536	-1
6	37	-31	-3
7	150	-150	-0
8	116	120	-2
9	81	78	1
10	245	-247	1
11	148	155	-3
12	94	-99	2
13	31	-25	-1
14	79	89	-1
15	42	-41	-0
H, 1, 0			
0	51	-53	1
1	461	-509	22
2	337	355	-8
3	434	-454	9
4	476	-475	-0
5	258	255	2
6	87	-85	-1
7	132	-129	-1
8	102	110	-3
9	281	-280	-1
10	27	-20	-3
11	78	76	1
12	83	-82	-0
13	125	130	-2
14	13	-11	-1
14	13	-11	-1
15	41	-41	0
H, 2, 0			
1	315	-332	8
2	272	-274	1
3	203	-205	1
4	38	43	-2
5	116	108	3
6	170	-167	-2
7	10	-8	-1
8	56	-50	-3
9	144	-148	2
10	279	293	-1
11	83	-87	2
12	20	-15	-2
13	70	69	0
14	12	-14	1
15	14	16	-1
H, 3, 0			
0	154	-160	3
1	82	-77	-2
2	164	163	0
3	243	245	-1
4	258	256	1
5	85	-84	-0
6	15	-16	1
7	149	151	-1
8	64	-70	3
9	127	131	-2
10	28	22	3
11	9	-7	-1
12	79	78	0
13	10	-10	-0
14	77	-80	1
H, 4, 0			
0	444	441	1
1	85	92	-3
2	57	-56	-0
3	201	207	-3
4	64	55	4
5	50	-52	1
6	43	42	0
7	67	-66	-1
8	61	65	-2
9	85	83	1
10	87	-87	0
11	27	28	-0
13	57	-57	0
H, 5, 0			
0	23	25	-1
1	69	-65	-2
2	91	85	3
3	75	76	-1
4	309	-315	2
5	38	40	-1
6	29	-28	-0
7	56	-59	1
8	121	128	-3
9	94	-96	1
10	68	-68	-0
11	10	-10	-0
13	18	-16	-1
H, 6, 0			
0	46	50	-2
1	170	-170	0
2	158	155	1
3	137	-136	-1
4	97	-97	0
5	128	129	-0
6	32	-32	0
7	12	13	-1
8	41	-43	1
9	64	-65	1
10	92	95	-1
11	13	13	0
H, 7, 0			
0	11	12	-0
1	55	53	1
2	51	47	2
3	168	-163	-2
4	113	111	1
5	58	57	1
6	56	-53	-1
7	55	56	-0
9	26	-29	1
10	28	28	-0
H, 8, 0			
0	95	-94	-0
1	29	26	1
2	49	-42	-3
3	30	29	0
4	34	33	0
5	44	-46	1
7	46	45	1
8	27	-28	0
H, 9, 0			
0	30	31	-0
1	48	-44	-2
2	48	-52	2
3	48	45	1
4	15	14	1
5	24	-22	-1
H,-1, 0			
1	378	413	-16
2	89	-87	-1
3	688	708	-9
4	285	-285	-0
5	183	-181	-1
6	359	355	1
7	74	-37	-17
8	66	60	3
9	148	144	2
11	93	-101	4
12	33	32	1
13	91	-89	-1
14	61	65	-2
H,-2, 0			
1	344	376	-15
2	182	-189	3
3	63	-64	1
4	30	-20	-4
5	335	-335	0
6	36	35	1
7	65	65	0
8	18	11	3
9	72	-71	-0
10	84	88	-2
11	60	-62	1
12	96	99	-1
13	11	-11	-0
14	114	-122	4
15	58	55	2
H,-3, 0			
1	248	-255	3
2	415	421	-3
3	137	-146	4
4	111	-110	-0
5	73	76	-1
6	197	-194	-2
7	112	115	-2
8	49	-44	-2
9	95	-92	-1
10	53	50	2
11	73	79	-3
12	76	-77	1
13	93	95	-1
14	34	-32	-1
H,-4, 0			
1	174	-175	0
2	135	-124	-5
3	155	153	1
4	19	-21	1
5	241	236	2
6	85	-82	-1
7	153	-152	-0
8	193	191	1
9	61	-62	0
10	36	-40	2
11	82	82	-0
12	68	-68	0
13	40	40	-0
14	28	28	-0
H,-5, 0			
1	49	-51	1
2	123	-119	-2
3	206	205	0
4	119	-117	-1
5	39	-41	1
6	163	165	-1
7	231	-233	1
8	75	78	-1
9	75	77	-1
10	43	-45	1
11	15	-18	1
12	76	-79	1
14	100	104	-2
H,-6, 0			
1	85	82	1
2	114	-120	2
3	37	45	-4
4	11	-13	1
5	84	-80	-2
6	80	79	1
8	81	-87	0
9	47	47	0
10	101	-105	2
11	52	52	-0
12	75	79	-2
13	83	-87	2
H,-7, 0			
1	77	74	1
2	93	-108	7
3	20	21	-0
4	109	111	-1
5	27	-25	-1
6	11	10	1
7	59	57	1
8	50	-50	-0
9	13	12	1
10	33	35	-1
11	13	-13	-0
H,-8, 0			
1	58	57	0
2	69	73	-2
3	81	-84	1
4	18	-19	1
6	42	45	-1
7	29	31	-1
8	24	21	1
9	50	-46	-2
10	37	37	-0
H,-9, 0			
1	24	-23	-1
2	33	33	0
3	30	-33	1
4	85	-77	-3
5	31	28	1
6	19	-20	1
7	36	-33	-1
H, 0, 1			
0	21	22	-1
1	257	-255	-1
2	482	485	-1
3	343	339	2
4	40	41	-0
5	109	-106	-2
6	259	-254	-3
7	375	370	2
8	108	104	2
9	282	-275	-3
10	78	77	1
11	48	51	-2
12	18	-17	-1
13	77	74	1
14	78	-75	-1
15	15	14	1
-2	87	-75	-6
-3	126	-126	-0
-4	293	290	1
-5	95	-93	-1
-6	196	196	-0
-8	15	8	3
-9	138	134	2
-10	93	-90	-1
-11	116	-122	3
-12	79	83	-2
-13	21	-19	-1
-14	34	35	-1
-15	39	42	-2
-16	52	-56	2
H, 1, 1			
0	131	-145	6
1	125	131	-3
2	480	-496	7
3	314	-319	2
4	98	95	2
5	94	90	1
6	181	-185	2
7	40	-38	-1
8	117	-113	-2
9	55	-54	-1
10	171	173	-1
11	159	-156	-2
12	51	49	1
13	19	-17	-1
14	34	-37	1
15	79	89	-3
-1	377	400	-11
-2	114	118	-2
-3	159	-163	2
-4	82	-84	-3
-5	97	-97	-5
-6	246	232	6
-7	146	144	1
-8	18	-30	5
-9	102	-92	-4
-10	168	166	1
-11	17	-20	1
-12	43	-46	1
-13	56	-59	1
-14	43	-46	2
-15	62	68	-3
H, 2, 1			
0	22	27	-3
1	462	-491	13
2	243	-241	0
3	188	-192	2
4	141	138	1
5	9	-10	1
6	60	-59	-1
8	115	-113	-1
9	170	167	1
10	28	-30	1
11	47	-46	-0
12	71	67	2
-1	256	-282	12
-2	58	65	-3
-3	84	-90	3
-4	196	-191	-2
-5	44	49	-2
-6	220	-207	-6
-7	14	-10	-2
-8	15	8	3
-9	84	88	-2
-10	14	12	1
-11	47	53	-3
-12	81	-93	2
-13	42	43	-0
-14	9	-8	-0
-15	45	-56	3
H, 3, 1			
0	18	25	-3
1	37	-42	2
2	217	222	-2
3	76	81	-3
4	140	129	5
5	118	122	-2
6	124	123	0
7	73	-73	-0
8	33	34	-1
9	127	126	1
10	27	-28	0
11	67	62	2
12	30	-28	-1
13	19	-18	-0
-1	151	-152	0
-2	119	-109	-5
-3	287	281	3
-4	93	-87	-3
-5	47	-35	-5
-6	83	-79	-2
-7	152	-144	-4
-8	74	75	-0
-9	34	-37	1
-10	53	-49	-2
-11	104	104	-0
-12	16	20	-2
-14	26	28	-1
-15	44	-47	1
H, 4, 1			
0	49	-50	0
1	16	-6	-5
2	216	221	-2
3	329	326	2
4	66	-66	-0
5	58	-54	-2
6	104	-101	-2
7	35	35	0
8	142	148	-3
9	122	-125	1
10	9	-7	-1
12	28	-28	0
13	17	-17	-0
-1	217	217	0
-2	134	-132	-1
-3	181	190	-4
-4	123	115	4
-5	67	-69	1
-6	147	153	-3
-7	186	-193	3
-8	112	116	-2
-9	18	10	4
-10	140	-140	0
-11	10	-10	0
-12	57	62	-2
-13	11	14	-1
-14	23	27	-2
H, 5, 1			
0	12	-12	0
1	19	-21	1
2	132	137	-2
3	207	-207	-0
4	119	-114	-2
5	9	7	1
6	146	-150	1
7	49	50	-1
8	22	-26	2
9	87	-86	-0
10	35	33	1
11	23	-22	-1
12	33	-33	0
-1	52	53	-1
-2	73	-74	0
-3	8	3	2
-4	30	24	3
-5	102	-108	3
-6	222	227	-2
-7	99	103	-2
-8	200	-198	-1
-9	35	34	0
-10	31	-33	1
-11	60	62	-1
-12	11	-13	1
-13	110	-120	5
H, 6, 1			
0	68	-71	1
1	50	49	0
2	40	36	2
3	250	-251	1
4	25	22	1
5	27	-22	-2
6	30	28	1
7	96	93	2
8	71	-70	-0
9	23	25	-1
10	23	24	-0
-1	41	40	1
-2	84	-86	1
-3	105	-101	-2
-4	95	94	1
-6	78	-77	-0
-7	48	49	-1
-8	40	-43	1
-9	128	131	-2
-10	20	20	0
-11	111	-116	2
-12	24	22	1
H, 7, 1			
1	64	48	7
2	149	-144	-2
3	44	44	0
4	134	132	1
5	9	-10	0
6	38	41	-1
7	40	42	-1
8	10	-10	-0
-1	74	76	-1
-2	35	32	1
-3	93	-94	0
-4	25	26	-0
-5	11	10	0
-6	55	-57	1
-7	9	8	0
-8	59	57	1
-9	53	-50	-1
-10	46	48	-1
H, 8, 1			
0	49	44	2
2	43	-40	-1
3	46	45	0
5	33	37	-2
6	33	34	-0
-1	43	-42	-0
-2	36	37	-1
-3	33	32	1
-4	32	-32	-0
-5	27	25	1
-7	45	-45	0
-8	34	33	0
H, 9, 1			
0	11	-9	-1
1	67	-70	1
2	52	56	-2
-2	17	-17	-0
-3	57	60	-1
-4	51	-52	0
H,-1, 1			
0	454	487	-15
1	57	64	-3
2	604	602	1
3	524	-522	-1
4	468	-462	-3
5	677	658	9
6	100	103	-1
7	159	-159	-0
8	18	-14	-2
9	50	-51	0
10	38	33	2
11	123	123	0
12	119	-115	-2
13	69	69	0
14	13	9	2
15	80	-84	2
-1	425	-445	9
-2	511	-511	-0
-3	361	365	-2
-4	48	45	1
-5	106	-112	3
-6	188	189	-1
-7	213	-222	4
-8	82	-69	-7
-9	173	167	3
-10	224	-227	1
-11	101	104	-1
-12	36	-37	0
-13	13	-15	1
-14	68	75	-3
-15	30	-35	2
H,-2, 1			
0	118	126	-4
1	125	-120	-2
2	243	-256	6
3	156	166	-5
4	210	-212	1
5	41	-37	-2
6	189	177	5
7	263	-261	-1
8	144	136	4
9	52	-51	-0
10	128	-121	-3
11	26	15	3
13	69	-68	-1
14	57	58	-1
15	12	-8	-2
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-5	43	-27	-7
-6	49	31	8
-7	151	-145	-3
-8	210	207	1
-9	240	-242	1
-10	63	-65	1
-11	158	159	-0
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-13	15	-12	-1
-14	25	24	1
-15	53	-56	2
H,-3, 1			
0	40	37	1
1	173	183	-4
2	91	-95	2
3	61	60	0
4	136	138	-1
5	211	-205	-3
6	127	124	1
7	76	85	-4
8	53	-57	2
9	132	133	-1
10	60	-58	-1
11	111	-108	-1
12	69	64	2
13	18	-18	0
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-1	91	-95	2
-2	131	140	-4
-3	18	-17	-1
-4	159	-156	-2
-5	267	258	4
-6	232	-230	-1
-7	28	-23	-2
-8	152	149	1
-9	92	-91	-0
-10	122	121	1
-11	71	-68	-1
-12	14	-14	-0
-13	95	102	-3
-15	53	-54	0
H,-4, 1			
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1	191	-186	-2
2	236	239	-1
3	60	55	2
4	96	99	-1
5	81	-72	-4
6	295	-296	1
7	391	393	-1
9	13	13	0
10	95	94	0
11	50	-46	-2
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13	53	49	2
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-5	22	-29	3
-7	167	161	3
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-12	23	23	-0
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H,-5, 1			
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1	121	-125	2
2	89	96	-3
3	137	-132	-2
4	164	-166	1
5	273	268	2
6	175	-186	5
7	175	-178	2
8	109	111	-1
9	126	-131	3
10	169	168	0
11	10	-9	-0
12	84	-83	-0
13	94	94	0
14	45	-50	2
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-2	217	-218	0
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-5	71	-73	1
-6	182	185	-1
-7	77	-82	2
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-12	8	8	-0
-13	48	-50	1
H,-6, 1			
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1	152	-157	2
2	27	-22	-2
3	102	102	-0
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5	96	97	-0
6	33	39	-3
7	266	-274	3
8	78	77	0
9	95	-96	0
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11	101	102	-0
12	124	-126	1
13	26	-24	-1
-1	35	-37	1
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-4	205	-207	1
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-6	63	64	-0
-7	34	-32	-1
-8	40	43	-1
-9	123	-125	1
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-11	83	84	-1
H,-7, 1			
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3	150	154	-2
4	58	-60	1
6	176	180	-2
7	39	28	5
8	62	-65	1
9	35	35	0
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12	28	29	-0
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-2	124	122	1
-3	52	-49	-2
-4	7	-71	0
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-7	136	-132	-2
-8	95	93	1
-9	48	49	-0
-10	13	-10	-1
-11	16	-15	-0
H,-8, 1			
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1	136	130	-2
2	120	-125	2
3	50	-52	1
4	43	41	1
6	54	56	-1
7	46	43	1
8	13	-11	-1
9	59	63	-2
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-1	58	-59	1
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-7	43	45	-1
-8	39	40	-0
-9	34	-35	0
H,-9, 1			
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2	27	26	1
3	61	-58	-1
5	71	-75	2
6	63	-60	-1
7	41	42	-1
8	45	42	1
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-2	50	-46	-2
-3	31	-33	1
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H-10, 1			
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3	16	13	2
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-2	8	-4	-2
H, 0, 2			
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1	197	194	-3
2	46	-49	1
3	70	-71	1
4	106	106	-0
5	52	53	-0
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7	20	-10	-5
8	209	-202	-3
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12	50	41	4
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-3	82	-86	2
-4	93	98	-2
-5	94	83	5
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-8	15	-5	-5
-9	13	17	-2
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-13	13	14	-0
-14	28	-26	-1
-15	70	70	-0
H, 1, 2			
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2	51	-52	1
3	48	-45	-2
4	77	77	-0
5	40	-47	3
7	30	-28	-1
8	91	-92	1
9	109	108	1
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11	32	-32	-0
12	18	18	-0
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-5	145	-143	-1
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-15	16	-18	1
H, 2, 2			
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4	15	-19	2
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7	36	-32	-2
8	16	14	1
9	69	68	0
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12	55	-54	-0
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-2	88	95	-3
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-4	147	-144	-1
-6	35	29	3
-7	10	-10	0
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-9	15	-12	-1
-10	78	-75	-1
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-12	49	-46	-2
-13	66	-67	1
-14	36	33	2
-15	37	-37	-0
H, 3, 2			
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3	101	105	-2
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5	91	89	2
6	111	-107	-2
8	181	186	-2
9	17	-14	-1
10	13	-16	1
11	37	-41	2
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-3	140	143	-0
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-5	126	-130	2
-6	149	158	-4
-7	102	-103	0
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-10	64	-65	-1
-11	9	10	-0
-12	104	103	-0
-13	55	-55	-1
-14	38	36	1
H, 4, 2			
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1	29	-30	1
2	174	177	-1
3	54	-56	1
4	29	28	1
5	13	13	-0
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7	105	105	-0
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10	67	70	-1
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-2	39	-41	1
-3	117	-116	-1
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-6	102	107	-3
-7	16	-7	-4
-8	212	-215	1
-9	142	138	2
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-11	84	-85	0
-12	54	57	-1
-13	31	-32	0
H, 5, 2			
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1	178	174	2
2	22	18	2
3	181	-178	-1
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5	147	-137	-4
7	59	57	1
8	95	-99	2
9	20	17	1
10	30	-28	-1
-1	118	-117	-0
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-5	86	-83	-1
-6	200	-202	1
-7	213	220	-1
-8	29	28	0
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-11	76	-81	2
-12	46	47	-0
-13	37	39	-1
H, 6, 2			
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1	97	90	3
2	156	-151	-2
3	12	4	4
5	43	-44	0
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7	32	-33	0
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-2	80	75	2
-3	95	-94	-0
-4	79	-79	0
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-8	60	61	-1
-9	76	-77	0
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-11	9	9	0
H, 7, 2			
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1	35	-32	-1
2	23	-21	-1
3	77	77	-0
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5	39	41	-1
6	78	86	-4
-3	10	6	2
-4	59	-58	-1
-5	15	17	-1
-6	20	19	1
-7	80	-82	1
-8	32	34	-1
-9	37	40	-1
H, 8, 2			
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1	73	-74	1
2	38	38	-0
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-3	14	10	-2
-5	13	-12	-0
-6	36	36	-0
H,-1, 2			
0	12	-13	1
1	267	-264	-2
2	9	12	-1
3	420	-406	-7
4	387	375	5
5	35	42	-3
6	304	-300	-2
7	71	72	-1
8	16	14	1
9	36	34	1
10	72	-74	1
11	51	-52	0
12	105	103	1
13	152	159	-3
14	71	-73	1
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-2	28	-2	-12
-3	237	240	-1
-4	168	153	7
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-7	123	116	3
-8	34	-32	-1
-9	168	165	1
-10	11	-9	-1
-11	138	-133	-2
-12	68	68	0
-13	10	-10	-0
-14	24	22	1
-15	15	-13	-1
H,-2, 2			
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1	194	-191	-1
2	285	279	2
3	321	-310	-5
4	221	-215	-2
5	108	102	3
6	168	-163	-2
7	232	217	7
8	103	-99	-2
9	234	-223	-5
10	73	-76	1
12	60	-58	-1
13	19	16	1
14	12	-8	-2
-1	8	-11	1
-2	99	-100	1
-3	49	46	1
-4	248	239	4
-5	283	-284	0
-6	56	-50	-3
-7	17	-10	-3
-8	41	-43	1
-9	162	161	1
-10	286	-287	0
-11	21	22	-0
-12	19	-17	-1
-13	88	-90	1
-14	20	21	-0
-15	9	11	-1
H,-3, 2			
0	44	-38	-3
1	31	28	1
2	215	206	4
3	263	256	3
4	250	-239	-5
5	88	84	1
6	73	81	-4
7	30	-33	1
8	209	213	-2
9	91	-87	-2
10	18	-5	-6
11	51	-55	2
12	47	-45	-1
13	39	-38	-1
14	33	31	1
-1	210	212	-1
-2	101	-97	-2
-3	22	25	-1
-4	408	-414	3
-5	120	-122	1
-6	300	294	3
-7	161	-166	2
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-10	61	-60	-1
-11	80	78	1
-12	27	-25	-1
-14	88	91	-1
-15	34	-35	0
H,-4, 2			
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1	39	43	-2
2	48	43	2
3	167	160	3
5	98	-101	1
6	181	176	2
7	17	-17	-0
8	29	31	-1
9	172	170	1
10	52	59	-3
11	48	47	1
12	16	9	3
13	49	-52	2
14	54	56	-1
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-3	66	75	-4
-4	161	-167	3
-5	141	143	-1
-6	37	35	1
-7	21	23	-1
-8	124	121	1
-9	109	-110	0
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-11	90	89	0
-12	40	41	-0
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-14	17	17	0
H,-5, 2			
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1	74	-65	-4
2	81	-84	2
3	98	-100	1
4	213	208	2
5	94	-95	1
6	227	-232	2
7	53	54	-1
8	98	-101	1
9	144	143	0
11	82	-78	-2
12	86	91	-2
13	31	33	-1
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-2	120	121	-0
-3	102	-102	-0
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-5	60	55	2
-6	13	-10	-2
-7	83	87	-2
-8	61	-67	2
-10	57	55	1
-11	26	26	0
-12	23	-24	0
-13	44	44	0
H,-6, 2			
1	10	-7	-2
2	24	29	-2
3	207	-216	4
4	74	75	-1
5	112	112	-0
6	153	-156	1
7	18	19	-0
8	81	-82	0
9	167	-168	0
10	121	119	1
11	67	-64	-1
12	43	-42	-0
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-2	218	-223	2
-3	72	70	1
-4	237	244	-3
-5	92	-95	2
-6	82	-76	-3
-7	66	-70	2
-8	24	-24	-0
-9	65	66	-0
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-11	66	-64	-1
-12	22	20	1
H,-7, 2			
0	43	37	3
1	187	-189	1
2	190	196	-3
3	13	11	1
4	105	-105	-0
5	173	177	-2
6	18	18	-0
7	26	-28	1
8	66	64	1
9	104	-105	1
10	57	56	1
11	48	47	1
-1	181	180	0
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-3	103	101	1
-4	214	-217	1
-5	38	-38	-0
-6	165	166	-0
-7	94	-94	-0
-8	82	-80	-1
-9	56	53	1
-10	14	12	1
H,-8, 2			
0	154	150	2
1	50	-52	1
2	14	-13	-0
3	109	112	-1
4	117	-116	-0
5	36	36	-0
6	41	37	-2
7	13	11	1
8	83	88	-2
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-7	32	-31	-0
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H,-9, 2			
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5	78	-76	-1
6	64	69	-2
7	8	-12	2
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-7	14	8	3
H-10, 2			
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3	72	-69	-1
4	71	70	1
5	18	-19	1
-1	20	17	1
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-3	16	-15	-1
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H, 0, 3			
0	242	-236	-2
1	83	80	2
2	39	-40	1
3	97	92	2
4	11	11	0
5	32	-33	0
6	212	207	2
7	27	-24	-1
8	70	-71	0
9	163	162	0
11	45	39	3
12	73	71	1
13	27	-22	-2
H, 0, 3			
-1	361	-373	5
-2	339	328	5
-3	15	16	-0
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-5	79	80	-1
-6	127	-130	2
-7	31	26	2
-8	61	58	1
-9	22	19	1
-10	81	85	-1
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-13	61	62	-1
-14	44	42	1
-15	48	-47	-0
H, 1, 3			
0	245	248	-1
1	173	-181	4
3	118	115	1
4	88	85	1
5	41	41	0
7	134	-131	-2
8	48	46	1
9	76	76	-0
10	74	-74	-0
11	67	67	0
12	90	-92	1
-1	145	-147	1
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-3	28	-11	-7
-4	111	-106	-2
-5	129	122	3
-6	22	-18	-2
-7	195	-198	-0
-8	83	-81	-1
-9	37	32	2
-10	98	-96	-1
-11	96	-98	-1
-13	77	-76	-0
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-15	15	-17	1
H, 2, 3			
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3	31	-29	-1
4	30	-27	-1
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6	117	-121	2
7	65	-67	1
8	58	-61	-1
9	50	-51	0
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11	55	-59	2
12	87	-95	4
-1	214	221	-3
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-3	57	52	2
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-13	68	-67	-0
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H, 3, 3			
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2	36	-35	-0
3	116	-116	-0
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6	61	-62	0
7	125	126	-0
9	30	-33	1
10	32	33	-0
11	40	-40	0
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-2	34	26	4
-3	176	-183	3
-4	209	212	-1
-5	45	-41	-2
-7	174	173	-0
-8	103	-103	-0
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-11	80	-82	1
-12	30	30	-0
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-14	41	-43	1
H, 4, 3			
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2	16	15	0
3	23	-25	1
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6	120	120	-0
7	57	62	-3
8	71	-75	2
9	63	70	-3
10	38	-42	2
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-4	111	-111	-0
-6	111	-113	1
-7	212	209	1
-9	86	-87	-0
-10	54	55	-0
-12	23	-27	2
-13	66	71	-2
H, 5, 3			
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1	41	-38	-1
2	181	-170	-5
3	110	102	3
4	30	30	-0
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6	42	47	-2
7	60	-69	4
8	9	5	2
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-3	41	-40	-1
-4	55	-54	-1
-5	119	115	2
-6	64	-64	-0
-7	107	-101	-3
-8	100	100	-0
-9	53	-53	-0
-10	13	-17	2
-11	24	28	-2
H, 6, 3			
0	47	49	-1
2	14	11	1
3	41	42	-1
4	62	-59	-1
5	37	41	-2
-1	47	-46	-0
-2	67	-65	-1
-3	82	81	1
-4	16	12	2
-5	24	-23	-1
-6	36	32	2
-7	78	-76	-1
-8	19	22	-2
-9	56	56	-0
-10	23	-24	1
H, 7, 3			
2	53	56	-2
3	42	-42	-0
-1	31	-33	-1
-2	39	-38	-0
-4	44	44	0
-5	23	-25	1
-6	8	-2	-1
-7	24	22	1
H,-2, 3			
0	74	-78	2
1	76	-73	-1
2	83	90	-3
3	140	-145	2
4	38	45	-3
5	70	-67	-2
6	165	-157	-4
7	78	76	1
8	119	-110	-4
9	27	-28	1
11	124	-123	-0
12	47	-52	2
13	48	52	-2
-1	299	312	-6
-2	40	44	-2
-3	145	-142	-1
-4	166	170	-1
-5	227	-228	0
-6	71	-62	-4
-7	141	143	-1
-8	56	-57	1
-9	68	69	-1
-10	151	-147	-2
-11	187	-185	-1
-12	93	95	-1
-14	108	-111	1
H,-3, 3			
0	68	-72	2
1	142	131	5
2	253	249	2
3	91	-97	3
4	58	-53	-2
5	100	95	2
6	18	-21	1
7	15	12	1
8	44	45	-0
9	34	-27	-3
11	40	-36	-1
12	53	-51	-1
13	41	42	-1
-1	90	-86	-2
-2	83	-87	2
-3	78	83	-2
-4	21	-15	-3
-5	346	-335	-5
-6	109	110	-0
-7	52	52	-0
-8	121	-120	-0
-9	52	50	1
-10	163	-163	-0
-12	33	32	0
-13	27	-30	1
-14	43	47	-2
-15	44	45	-0
H,-4, 3			
0	12	10	1
1	30	-29	-0
2	28	-25	-1
3	67	63	2
4	111	104	3
5	9	6	1
6	50	51	-1
7	68	-66	-1
8	135	126	4
9	41	39	1
10	17	18	-1
11	29	26	1
12	10	-11	1
13	33	34	-1
-1	152	155	-1
-2	206	-213	3
-3	50	63	-6
-4	84	-89	2
-5	102	93	4
-6	149	146	2
-7	98	-95	-1
-8	36	35	0
-11	68	69	-1
-12	76	77	-1
-13	18	-18	0
-14	78	78	-0
H,-5, 3			
0	35	43	-4
1	86	-88	1
2	45	-45	-0
4	32	28	2
5	71	-65	-3
6	17	15	1
7	37	38	-0
8	58	-59	0
9	47	45	1
10	71	-65	-3
11	64	68	-2
12	38	38	0
13	73	-79	3
-1	30	-27	-1
-2	49	48	1
-3	15	-23	3
-4	56	-53	-1
-5	144	142	1
-6	22	21	1
-7	29	-29	0
-9	27	-29	1
-10	60	60	-0
-11	80	83	-2
-12	36	-39	2
-13	16	-19	1
H,-6, 3			
0	27	-31	2
1	26	-20	-3
2	86	-89	2
3	24	26	-1
4	55	50	2
5	80	-77	-2
6	65	-67	1
7	65	68	-2
8	98	-97	-0
9	72	70	1
10	9	-7	-1
11	86	-89	1
12	33	35	-1
-1	25	21	2
-2	95	96	-0
-3	211	-213	1
-4	94	98	-2
-5	24	24	0
-6	66	-68	1
-7	10	-7	-2
-8	26	-26	0
-9	11	13	-1
-12	35	-34	-0
H,-7, 3			
0	195	-200	0
1	229	232	-2
2	127	130	-1
3	207	-205	-1
4	33	29	2
5	27	25	1
7	20	17	1
8	56	-52	-2
9	20	-22	1
10	117	115	1
11	64	-69	2
-1	25	-24	-1
-2	56	-54	1
-3	126	125	1
-4	110	111	-0
-5	154	-152	-1
-6	19	-15	-2
-7	82	78	2
-8	34	-32	-1
-9	11	14	-1
-10	42	44	-1
-11	57	-57	0
H,-8, 3			
0	50	46	2
1	110	-113	1
2	79	81	-1
3	40	-39	-0
4	65	67	-1
5	52	49	1
6	[illegible]	-94	0
7	[illegible]	32	-1
8	[illegible]	21	-0
9	[illegible]	-76	-1
10	51	-56	-1
-1	151	152	-2
-2	132	-134	-2
-3	52	50	1
-4	59	56	1
-5	24	-22	-1
-6	48	48	-0
-7	27	-27	0
-8	32	-33	0
-9	76	72	-1
-10	25	-27	1
H,-9, 3			
0	55	54	1
1	124	-121	-1
2	41	38	1
3	71	73	-1
4	62	-60	-1
5	68	69	-1
6	27	-29	1
7	15	-18	1
8	30	31	-1
-1	[illegible]	-9	-0
-2	12	11	1
-3	42	43	-0
-4	54	-53	-0
-5	44	-42	-1
-6	34	32	1
-7	81	-78	-1
H-10, 3			
0	15	17	-1
1	20	-17	-2
2	76	-75	-0
3	48	48	0
5	37	-34	-1
-1	15	-15	0
-2	22	21	0
-3	18	-15	-2
-4	88	-84	-2
H, 0, 4			
0	167	170	-1
1	78	-77	-0
2	67	71	-2
3	99	-99	-0
4	96	-99	1
5	223	224	-0
7	68	-66	-1
8	68	65	1
9	16	16	0
11	55	56	-1
-1	143	-140	-1
-2	145	-141	-2
-3	127	125	1
-4	70	65	2
-5	105	-99	-3
-6	68	60	4
-8	77	-73	-2
-9	166	160	3
-10	49	-48	-0
-11	82	83	-0
-12	24	25	-0
-13	57	-59	1
-14	44	45	-1
H, 1, 4			
0	148	-149	0
1	20	21	-0
2	109	106	2
3	68	-74	3
4	32	30	1
5	37	38	-0
6	56	-56	-0
7	71	68	1
8	21	-18	-1
9	76	-78	1
10	41	45	-2
11	15	-17	1
-1	78	78	0
-2	105	-101	-2
-3	89	-89	-0
-4	121	118	1
-5	97	-97	0
-6	40	-41	0
-7	24	23	0
-8	163	-159	-2
-9	13	-18	2
-10	45	45	-0
-11	75	-74	-0
-12	92	92	0
-13	47	-49	1
-14	53	-58	2
H, 2, 4			
0	52	-48	-2
1	161	159	1
2	50	-55	2
4	75	80	-2
5	90	-91	0
6	10	-12	1
7	17	19	-1
8	58	-64	2
10	9	8	0
-1	54	52	1
-2	84	83	1
-3	180	-179	-0
-4	67	66	0
-5	143	148	-2
-6	69	-68	-0
-7	48	38	5
-8	73	-71	-1
-9	76	-74	-1
-10	104	103	0
-11	104	-106	1
-12	27	-31	2
-13	62	67	-2
H, 3, 4			
0	72	68	2
1	27	-27	0
2	85	-82	-1
3	89	94	-2
4	14	3	5
5	139	-138	-0
6	36	40	-2
9	52	57	-2
-1	34	-36	1
-2	175	165	4
-3	51	-46	-2
-4	122	-120	-1
-5	136	135	0
-7	103	104	-0
-8	82	84	-1
-9	94	-92	-1
-11	57	59	-1
-12	30	-32	1
H, 4, 4			
0	113	110	1
1	13	12	0
2	111	-106	-3
3	44	-47	1
4	46	-47	0
5	97	102	-2
6	44	52	-4
7	80	-97	8
-1	109	-106	-1
-2	53	-50	-1
-3	81	79	1
-4	81	-81	0
-5	28	-28	0
-6	22	21	1
-7	28	-27	-1
-8	89	88	1
-9	18	-18	0
-10	19	-21	1
-11	51	57	-3
H, 5, 4			
0	46	-43	-1
1	74	-77	1
2	56	59	-2
3	60	61	-1
4	53	-58	3
5	26	30	-1
-1	20	22	-1
-2	15	-14	-0
-3	47	46	1
-5	80	-77	-2
-6	17	-13	-2
-7	68	-69	0
-8	24	22	1
-9	62	62	0
H, 6, 4			
0	27	-28	0
2	53	55	-1
-1	18	24	-3
-2	13	12	0
-3	17	16	1
-4	39	41	-1
-5	21	-21	-0
-6	19	-16	-2
H,-2, 4			
0	191	-184	-3
1	194	196	-1
2	171	-171	0
3	93	92	0
4	81	83	-1
5	268	-258	-5
6	143	142	0
7	34	-33	-0
8	66	-63	-1
9	66	63	1
10	68	-64	-2
11	18	-19	0
12	79	85	-3
-1	15	-21	3
-2	144	133	5
-3	150	-150	-0
-4	77	-69	-4
-5	254	248	3
-6	167	-160	-4
-7	81	-84	1
-8	90	85	2
-9	56	-55	-1
-10	150	153	-2
-11	159	-161	1
-12	103	-104	1
-13	87	92	-2
-14	20	20	-0
H,-3, 4			
0	93	-98	2
1	11	-4	-3
2	46	-54	4
3	206	-196	-5
4	300	288	6
5	32	-28	-1
6	164	-168	2
7	73	74	-1
8	122	-113	-4
9	89	85	2
10	14	-13	-1
11	49	-49	-0
12	37	37	0
-1	28	28	-0
-2	96	99	-1
-3	189	-184	-2
-4	133	132	0
-5	89	-87	-1
-6	131	-127	-2
-7	258	263	-2
-8	129	-126	-2
-9	90	-83	-3
-10	29	28	1
-11	36	-33	-1
-12	46	49	-1
-14	89	-94	2
H,-4, 4			
0	45	-41	-2
1	108	-108	-0
2	144	142	1
3	20	-20	0
4	45	-41	-2
5	92	95	-1
6	77	-78	1
7	98	95	1
9	105	-100	-2
10	46	44	1
12	9	-6	-1
-1	177	189	-6
-2	60	64	-1
-3	32	-32	0
-4	111	113	-1
-5	161	-154	-3
-6	103	103	0
-7	86	88	-1
-8	130	-128	-1
-9	97	94	1
-10	37	-36	-0
-11	22	-19	-1
-12	60	60	-0
-13	22	-23	0
-14	11	-12	0
H,-5, 4			
0	78	78	-0
1	58	56	1
2	11	-5	-3
3	39	38	0
4	107	-106	-0
5	82	80	1
6	104	113	-4
7	81	-82	1
8	89	89	-0
9	55	-56	0
10	10	15	-2
-1	67	77	-5
-2	116	-118	1
-3	91	91	-0
-4	89	-92	1
-5	41	-44	1
-6	103	101	1
-7	68	-70	1
-9	11	2	4
-10	44	-42	-1
-11	15	14	-0
-12	61	61	-0
-13	58	-62	2
H,-6, 4			
0	44	45	-1
1	35	37	-1
2	47	-53	3
3	40	36	2
4	62	-63	1
5	80	-84	2
6	112	112	-0
7	14	-14	0
9	72	69	1
10	62	-62	0
11	41	42	-0
-1	134	-132	-0
-2	38	-41	1
-3	89	-98	4
-4	77	-80	1
-5	113	122	-4
-6	14	-15	1
-7	105	-110	2
-8	20	12	4
-9	24	29	-3
-11	17	13	2
-12	46	-49	1
H,-7, 4			
1	97	101	-2
2	154	-152	-1
3	39	-42	1
4	133	132	1
5	63	-64	0
6	76	-81	2
7	38	-35	-1
8	22	-20	-1
9	128	133	-2
10	27	-32	2
-1	117	-117	-0
-2	13	12	0
-3	69	-70	1
-4	123	124	-0
-5	56	52	2
-6	63	-63	-0
-7	54	59	-2
-8	28	26	1
-9	48	-46	-1
-10	29	28	0
-11	44	46	-1
H,-8, 4			
0	193	-191	-1
1	34	35	-0
2	111	111	-0
3	19	22	-1
4	40	39	0
5	121	-123	1
6	14	11	1
7	83	86	-1
8	73	-75	1
9	52	-54	1
-1	101	96	2
-2	86	85	1
-3	38	33	2
-4	96	99	-1
-5	10	-13	1
-6	55	-49	-3
-7	62	60	1
-8	14	-16	1

Table 2 (*cont.*)

H	FO	FC	WD
	H,-9, 4		
0	46	-45	-0
1	25	-25	-0
2	79	79	0
3	63	-60	-1
4	37	36	0
5	73	74	-0
6	30	-30	1
7	28	27	0
-1	89	85	2
-3	12	11	0
-5	83	-82	-0
-6	22	18	2
-7	8	-3	-2
	H-10, 4		
0	33	32	1
1	66	-64	-1
-2	37	-39	1
-3	11	12	-0
-4	29	-29	-0
	H, 0, 5		
0	35	-37	1
1	97	104	-3
3	58	-57	-1
4	50	50	-0
5	71	-74	1
6	56	-57	0
7	68	70	-1
8	23	27	-1
9	23	-23	2
-1	69	62	3
-2	31	-30	-1
-3	49	-54	2
-4	79	80	-0
-6	50	-47	-1
-7	50	47	1
-8	14	-10	-2
-9	30	-27	-2
-10	66	62	2
-11	77	-77	-0
-12	19	22	-1
-13	22	22	0
	H, 1, 5		
1	92	93	-0
2	137	-143	3
3	19	-22	1
4	14	-14	-0
5	30	-30	-0
6	51	54	-1
8	33	-38	2
-1	34	-37	2
-2	18	9	4
-3	75	-73	-1
-4	20	21	-0
-5	60	61	-0
-6	87	-89	1
-7	29	-29	0
-8	62	63	0
-9	52	-53	0
-10	31	30	0
-11	40	-41	0
-12	31	-31	0
	H, 2, 5		
0	70	68	1
1	42	-44	1
2	41	-40	-1
3	45	47	-1
5	19	21	-1
6	42	47	-2
7	38	-44	3
8	14	-14	0
-1	68	-57	-5
-2	161	97	2
-4	111	-115	1
-5	69	63	2
-6	32	38	-3
-8	20	-21	0
-9	45	-47	1
-11	67	71	-2
	H, 3, 5		
0	58	58	0
1	35	-38	2
2	37	40	-1
3	13	11	1
4	60	-65	2
5	44	54	-5
6	35	44	-4
-1	26	-19	-3
-2	22	-19	-2
-3	64	59	2
-4	41	-39	-1
-5	35	31	2
-6	47	49	-1
-7	29	-28	-0
-8	35	35	0
-10	23	-26	1
	H, 4, 5		
1	54	-63	4
3	23	24	-1
4	15	21	-3
-1	40	39	0
-2	54	-56	1
-3	36	34	1
-5	74	-73	-0
-6	20	18	1
-8	35	35	0
	H, 5, 5		
0	37	-43	3
-1	38	39	-1
-2	17	18	-0
-3	35	-35	0
-4	11	-9	-1
	H,-3, 5		
0	60	67	-3
1	44	-49	2
2	270	-263	-3
3	147	146	0
4	32	-33	0
5	88	-88	-0
6	51	50	0
7	89	-84	-2
9	14	11	1
-1	156	-155	-0
-2	50	43	3
-3	62	63	-0
-4	16	-19	2
-5	117	112	3
-6	151	-152	0
-7	70	-68	-0
-8	205	206	-0
-9	38	-41	2
-12	32	-30	-1
-13	22	30	-3
	H,-4, 5		
0	16	21	-2
1	150	150	-0
2	147	-144	-1
3	61	-55	-3
4	92	91	1
5	36	-33	-1
6	59	62	-1
8	152	-143	-4
9	71	68	2
-1	37	34	1
-2	226	245	-9
-3	146	-149	1
-4	43	43	1
-5	77	82	-3
-6	80	-79	-1
-7	103	111	-4
-9	57	-54	-1
-10	55	59	-2
-11	13	-18	2
-12	49	-45	-2
-13	36	38	-1
	H,-5, 5		
0	25	-26	0
1	115	117	-1
2	54	57	-1
3	102	-108	3
4	114	114	0
5	34	36	-1
6	32	-31	-0
7	72	72	0
8	15	15	0
9	31	-28	-1
10	41	42	-0
-1	159	165	-3
-2	37	-35	-1
-3	112	-120	4
-4	74	80	-3

H	FC	FC	WD
-5	68	-63	-2
-6	11	-8	-2
-7	72	72	0
-8	89	-94	2
-10	28	25	1
-11	80	-78	-1
-12	12	14	-1
	H,-6, 5		
0	33	-37	2
1	72	-75	1
2	115	117	-1
3	34	-36	1
4	82	-84	1
5	48	45	1
8	75	76	-0
9	50	-54	2
-1	24	25	-0
-2	165	-161	-2
-3	24	24	-0
-4	81	-86	2
-5	50	-54	1
-6	90	98	-3
-7	16	-20	2
-8	79	-83	2
-9	12	7	2
-11	15	-14	-0
	H,-7, 5		
0	106	107	-1
1	84	-83	-1
2	38	-40	1
3	102	103	-0
4	99	-103	2
5	42	-46	2
8	40	43	-1
-1	149	-146	-2
-2	46	-51	2
-3	49	49	0
-4	25	27	-1
-5	59	64	-2
-6	16	-22	3
-7	66	-68	1
-8	60	64	-2
-9	41	42	-1
-10	48	-49	0

H	FO	FC	WD
	H,-8, 5		
1	102	103	-0
2	68	-67	-0
3	42	42	0
4	15	-17	1
5	14	-11	-1
6	90	92	-1
7	65	-70	2
-1	85	-83	-1
-2	128	128	0
-4	20	18	1
-5	73	71	1
-6	33	-34	0
-8	50	52	-0
	H,-9, 5		
0	102	-98	-2
1	80	80	0
2	19	-18	-1
3	9	-9	-0
4	96	99	-1
5	70	-71	1
-1	18	19	-0
-2	77	74	2
-5	28	-25	-2
-6	56	-57	0
	H, 0, 6		
0	16	13	1
1	81	79	1
4	29	-32	1
5	59	-69	4
6	22	26	-2
7	11	12	-0
-1	20	-17	-2
-2	19	16	1
-5	59	55	2
-6	31	-23	-3
-7	22	19	2
-8	39	39	0
-9	70	-66	-2
-10	17	16	1
-11	22	-21	-0
	H, 1, 6		
0	56	62	-3
1	45	-53	3
2	51	-54	2
4	45	-53	4
5	26	-32	3
6	27	30	-1
-2	12	6	2
-3	27	-32	2
-4	81	-76	-2
5	77	80	-1
-6	21	21	-0
-7	39	-42	1
-8	37	33	2
-9	11	8	1
-10	10	-10	-0
	H, 2, 6		
0	43	45	-1
1	33	-33	0
3	22	-27	2
4	25	-29	2
-1	22	-23	1
-2	41	-41	0
-3	68	69	-0
-4	31	-29	-1
-5	42	-44	1
-6	35	35	-1
-7	36	-33	-1
-8	15	14	0
	H, 3, 6		
0	21	-25	2
1	27	-28	1
-1	53	58	-2
-2	21	-21	0
-3	19	22	-1
-4	26	26	-0
-5	57	-59	1
-6	25	26	-1
	H,-1, 6		
3	10	27	-8
-5	11	-3	-4
	H,-3, 6		
0	19	-18	-0
1	195	-191	-2
2	54	-51	-2
3	63	62	0
4	27	-27	0
5	18	-18	0
6	48	-51	1
7	40	-39	-1
-1	161	155	3
-2	57	-53	-2
-3	16	-27	5
-4	80	-75	-2
-5	34	32	1
-6	102	99	1
-7	96	-93	-1
-9	40	46	-3
-11	23	23	0
	H,-4, 6		
0	93	90	2
1	15	-13	-1
3	36	36	0
4	42	-39	-1
5	9	13	-2
6	32	33	-0
8	33	39	-3
-1	33	-28	-2
-2	25	20	2
-3	118	115	1
-4	96	-92	-2
-5	50	49	0
-7	35	-37	1
-8	94	94	0
-9	15	-17	1
	H,-5, 6		
0	95	98	-1
1	55	54	1
2	48	-48	0
3	42	37	2
4	26	28	-1
6	55	58	-1
7	10	12	-1
8	54	-60	3
-1	93	-93	-0
-2	95	95	-0
-3	53	-50	-1
-4	16	-21	2
-5	74	75	-1
-6	52	-53	0
-7	36	35	0
-8	13	17	-1
-9	60	-64	2
-10	12	15	-2
	H,-6, 6		
0	73	-71	-1
1	98	98	0
2	30	-29	-0
3	71	-74	1
4	27	25	1
6	10	10	0
7	24	31	-3
-1	36	-35	3
-3	57	-58	1
-4	58	63	-2
-5	26	-25	-1
-6	67	-71	2
-7	49	47	1
-8	23	-26	2
-9	25	-25	0
-10	27	31	-2
	H,-7, 6		
0	47	-46	-0
1	54	-56	1
2	45	45	-0
3	27	-25	-1
4	11	-13	1
6	33	-36	1
-1	113	116	-2
-2	65	-63	-1
-3	27	-29	1
-4	15	15	-0
-5	25	-21	-2
-6	25	28	-1
-8	41	-42	0
	H,-8, 6		
0	66	65	0
1	41	-43	-0
2	49	49	0
3	29	27	1
4	61	-60	-0
5	52	54	-1
-1	36	-35	-1
-2	29	-28	-1
-3	61	65	-2
-4	16	-20	2
	H,-8, 6		
-5	19	-19	-0
-6	44	46	2
	H,-9, 6		
0	55	54	0
1	14	13	0
-1	85	-85	0
-2	8	13	-2
-3	34	31	2
	H, 0, 7		
0	53	64	-5
1	13	-18	2
-1	38	-43	2
-3	36	41	-2
-4	23	-22	-1
-5	25	28	-2
-6	15	18	-1
-7	39	-44	2
	H, 1, 7		
-2	37	-37	-0
-3	34	36	-1
-4	11	-9	-1
	H,-4, 7		
0	56	60	-2
1	31	-32	0
4	16	21	-2
-1	15	18	-2
-2	80	-84	2
-3	19	20	-1
-6	61	61	0
-7	40	-41	0
-8	30	-30	-0
	H,-5, 7		
0	33	38	-2
1	35	-34	-0
2	19	-24	2
3	45	47	-1
4	20	-20	0
5	34	34	-0
-1	38	-35	-1
-2	16	-19	1
-3	53	56	-1
-4	14	7	3
-5	20	20	-0
-7	43	-47	2
-8	66	68	-1
	H,-6, 7		
0	26	29	-1
2	58	-60	1
3	11	9	1
-1	25	-30	2
-2	51	50	0
-5	26	28	-1
-6	21	-26	2
-7	20	-17	-1
	H,-7, 7		
0	46	-49	2
1	51	53	-1
2	28	23	-1
-1	16	11	2
-2	44	51	-3
-3	14	-15	1
-4	27	-25	-1
-5	12	-12	-0

Table 3. *Positional and thermal parameters of the non-hydrogen atoms*

Standard deviations are in parentheses. The temperature factor is of the form:

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

All parameters are × 10⁴, except the positional parameters of P, which are × 10⁵.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	36055 (4)	20416 (7)	28871 (11)	298 (3)	306 (3)	396 (4)	56 (2)	57 (3)	151 (2)
O(1)	4414 (1)	3262 (2)	2617 (4)	275 (12)	436 (14)	839 (12)	24 (10)	77 (9)	286 (10)
O(2)	3571 (2)	2607 (3)	5459 (3)	629 (8)	931 (9)	418 (14)	362 (7)	101 (8)	324 (9)
O(3)	3772 (1)	0303 (2)	1827 (4)	474 (10)	334 (8)	794 (14)	87 (7)	100 (9)	196 (8)
C(1)	1516 (2)	1435 (3)	1538 (5)	366 (12)	349 (12)	511 (16)	−49 (9)	−2 (11)	174 (11)
C(2)	0494 (2)	2026 (3)	1787 (5)	336 (13)	521 (15)	667 (20)	−60 (11)	30 (13)	234 (13)
C(3)	0028 (2)	2738 (4)	0438 (6)	330 (13)	600 (16)	709 (22)	−2 (11)	−26 (13)	252 (15)
C(4)	0453 (2)	2807 (4)	−1454 (5)	526 (16)	553 (16)	588 (20)	−10 (12)	−140 (14)	232 (14)
C(5)	1336 (2)	2166 (3)	−1963 (5)	547 (15)	479 (14)	456 (17)	−4 (11)	−51 (13)	153 (12)
C(6)	1976 (2)	1521 (3)	−0466 (4)	443 (13)	346 (12)	388 (15)	2 (9)	14 (11)	98 (10)
C(7)	2426 (2)	2666 (3)	1884 (4)	302 (10)	301 (10)	339 (14)	14 (8)	28 (9)	121 (9)
C(8)	4331 (3)	2188 (6)	6895 (7)	728 (22)	1517 (32)	648 (24)	475 (21)	43 (18)	610 (22)
C(9)	5473 (2)	2931 (4)	2562 (6)	284 (12)	742 (18)	707 (21)	75 (12)	108 (13)	278 (15)
C(10)	2328 (2)	4486 (3)	2665 (4)	252 (10)	310 (11)	384 (14)	15 (8)	−4 (9)	123 (9)
C(11)	2650 (2)	5394 (3)	1470 (4)	355 (11)	367 (12)	463 (16)	23 (9)	46 (11)	185 (11)
C(12)	2636 (2)	7095 (3)	2251 (5)	449 (13)	378 (12)	529 (17)	3 (10)	−10 (12)	214 (11)
C(13)	2283 (2)	7907 (3)	4219 (5)	473 (14)	315 (12)	613 (19)	65 (10)	−22 (13)	132 (11)
C(14)	1957 (2)	7031 (3)	5440 (5)	410 (13)	416 (13)	519 (18)	102 (10)	63 (12)	81 (12)
C(15)	1973 (2)	5324 (3)	4670 (4)	335 (11)	398 (12)	440 (15)	40 (9)	64 (10)	132 (10)

scheme $w=1/\sigma^2(F_o)$ was not the right one. Therefore a weighting scheme of the form

$$w=1/(21\cdot87-0\cdot00134|F_o|+0\cdot0000052F_o^2)$$

was introduced (Cruickshank, 1961) and after another two cycles convergence was reached: $R=0\cdot0407$, $R_w=0\cdot051$. The final parameters differed from those obtained with the previous weighting scheme only in the limits of their standard deviations, thus indicating that the new weighting scheme was not necessary. The corrections for time-dependent decline in intensity during data collection may, therefore, not be quite exact. Observed and calculated structure factors are listed in Table 2.

Results and discussion

The final positional and thermal parameters are listed in Tables 3 and 4. Standard deviations are estimated

Table 4. *Final parameters of hydrogen atoms*

Positional parameters are × 10³.

	x/a	y/b	z/c	B(Å²)
H(1)	166 (2)	45 (3)	202 (5)	1·6 (6)
H(2)	11 (3)	179 (4)	298 (6)	3·0 (8)
H(3)	−62 (3)	316 (4)	72 (6)	4·1 (9)
H(4)	4 (3)	329 (4)	−243 (6)	3·8 (8)
H(5)	163 (3)	212 (4)	−338 (6)	3·9 (8)
H(6)	238 (2)	60 (3)	−114 (5)	2·0 (6)
H(7)	440 (4)	294 (7)	818 (9)	11·2 (1·7)
H(8)	477 (4)	153 (7)	636 (9)	11·7 (1·7)
H(9)	407 (5)	133 (7)	702 (10)	13·4 (2·0)
H(10)	548 (3)	187 (5)	146 (8)	7·2 (1·2)
H(11)	573 (3)	363 (5)	170 (7)	6·6 (1·1)
H(12)	577 (4)	293 (6)	424 (9)	10·0 (1·5)
H(13)	291 (2)	478 (4)	−5 (5)	2·2 (7)
H(14)	287 (2)	771 (4)	121 (5)	2·9 (7)
H(15)	228 (2)	912 (4)	468 (5)	2·6 (7)
H(16)	168 (2)	756 (4)	678 (6)	3·1 (7)
H(17)	174 (2)	463 (3)	553 (5)	1·9 (6)

from the diagonal elements of the inverse matrix. Bond lengths and angles are shown on Figs. 2 and 3.

In solution, a rapid equilibrium between norcaradiene and the valence-tautomeric cycloheptatriene can be observed. The solid consists of norcaradiene molecules. This is indicated by the short contacts between C(1) and C(6) (1·535 (5) Å). A similar case has been found for spiro(indene-1,7′-norcaradiene), where the norcaradiene structure is also stable in the crystal (Dreissig, Luger, Rewicki & Tuchscherer, 1973). The configuration of the molecule is that predicted from its n.m.r. spectrum (Scherer *et al.*, 1972): the phenyl ring lies *endo* to the cyclohexadiene skeleton. The most surprising feature of the structure is that all bonds of the cyclopropane ring are equal within their standard deviations: C(1)–C(6) 1·535 (5) Å, C(1)–C(7) 1·533 (4) Å, C(6)–C(7) 1·526 (4) Å. They are also considerably longer than in cyclopropane (1·510 Å, Bastiansen, Fritsch & Hedberg, 1964). According to Hoffmann (1970) and Günther (1970), we would expect an appreciable difference between the bond lengths C(1)–C(6) on the one hand and C(1)–C(7) and C(6)–C(7) on the other. Instead of that, the bonding situation is similar to that in 6,6-diphenyl-3,3-diethyl-3-azoniabicyclo-[3,1,0]hexane bromide monohydrate (Ahmed & Gabe, 1964), in which the bond tengths are all equal to 1·520 (6) Å. For comparison, the cyclopropane bond lengths of some simple norcaradienes, which are stabilized by π-acceptor ligands at C(7), are listed in Table 5. It can be seen that the variation of the bond length is strongly correlated with the π-acceptor strength of the substituents. The phosphoryl group is necessary to influence the norcaradiene–cycloheptatriene equilibrium in favour of the bicyclic structure. Its acceptor strength, however, is not sufficient to cause a notable strengthening of the C(1)–C(6) bond or weakening of the C(1)–C(7) or C(6)–C(7) bonds.

There are two additional features of the structure which have already been pointed out by Fritchie for (V*a*): (i) all bonds adjacent to the cyclopropane ring are shortened: The mean value of the two C_{sp3}–C_{sp2} bonds is 1·472 (4) Å, the C_{sp3}–$C_{sp2,\text{aromatic}}$ bond is 1·494 (3) Å and the C–P distance is 1·785 (3) *vs.* 1·820 Å for a 'normal' C–P bond (Daly & Wheatley, 1967). (ii) The six-membered ring is not quite planar, but folded along the axis C(2)–C(5), C(3) and C(4) lying on the side of the phenyl ring. The normals to the least-squares planes C(2)–C(3)–C(4)–C(5) and C(2)–C(1)–C(6)–C(5) enclose an angle of 6·4 ± 0·4°, which is somewhat greater than that found in (V*a*) (4·2°). The normal to the three-membered ring is inclined at an angle of 68·9 ± 0·4° to that of the plane C(2)–C(1)–C(6)–C(5) (V*a*: 71·9°). Several least-squares planes are given in Table 6.

Table 6. *Some least-squares planes in terms of the triclinic axes and deviations* (Å) *of the atoms defining the plane*

(*a*) Phenyl ring

$$11{\cdot}48567x - 0{\cdot}96617y + 2{\cdot}41838z = 2{\cdot}88218$$

C(10)	0·002	C(12)	0·005	C(14)	0·002
C(11)	−0·005	C(13)	−0·004	C(15)	−0·002

(*b*) Plane C(2)–C(3)–C(4)–C(5)

$$5{\cdot}28484x + 6{\cdot}15166y + 1{\cdot}41556z = 1{\cdot}76043$$

C(2)	−0·0001	C(3)	0·0002	C(4)	−0·0002	C(5)	0·0001

(*c*) Plane C(2)–C(1)–C(6)–C(5)

$$4{\cdot}10285x + 6{\cdot}71114y + 1{\cdot}18429z = 1{\cdot}77153$$

C(1)	−0·005	C(2)	0·002	C(5)	−0·002	C(6)	0·005

In the crystal strong deviations from the ideal C_s–*m* symmetry of the molecule can be noted. Only the bicyclic system itself and the adjacent atoms P and C(10) can be used to describe this 'mirror plane'. It is defined by the atoms C(7) and P and the midpoints of the bonds C(1)–C(6) and C(3)–C(4). From Table 7 it can be seen that the phenyl ring is tilted slightly with respect to this plane by rotation around the bond C(7)–C(10).

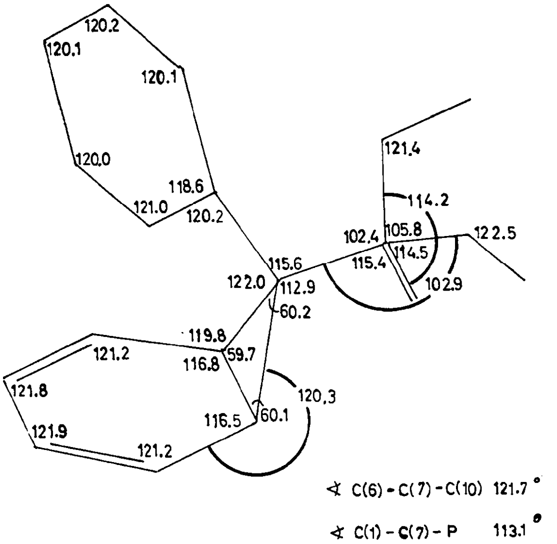

Fig. 3. Bond angles (°). Standard deviations are in the range of 0·1° for the angles involving phosphorus and 0·2–0·35° for all others.

Table 5. *Bond lengths in the cyclopropane skeleton of some norcaradienes in* Å

	C(1)–C(6)	C(1)–C(7)	C(6)–C(7)	
2,5-Dimethyl-7,7-dicyanonorcaradiene	1·501	1·559	1·554	Fritchie (1966)
Spiro(indene-1,7′-norcaradiene)	1·520	1·532	1·536	Dreissig, Luger, Rewicki & Tuchscherer (1973)
7-Phenyl-7-dimethoxyphosphoryl-norcaradiene	1·535	1·533	1·526	This work

The carbons in the phosphonate group show much greater deviations, *e.g.* O(3) lies 0·233 Å from the hypothetical mirror plane.

Table 7. *Distance* (Å) *of the atoms from the 'symmetry plane' of the molecule*

Equation of the plane [defined by P, C(7), midpoints of C(1)–C(6) and C(3)–C(4)]:

$$6{\cdot}69478x+2{\cdot}96418y-5{\cdot}99644z=1{\cdot}28629$$

C(3)	−0·719			C(4)	0·721
C(2)	−1·427			C(5)	1·428
C(1)	−0·768			C(6)	0·766
		C(7)	−0·001		
		P	0·001		
O(2)	−1·396			O(1)	1·067
		O(3)	0·233		
C(8)	−1·873			C(9)	1·710
		C(10)	0·004		
C(15)	−1·188			C(11)	1·205
C(14)	−1·154			C(12)	1·232
		C(13)	0·056		

The phosphonate group itself shows significant differences between 'equivalent' bonds and angles: 1·562 (3) Å for P–O(1) *vs.* 1·574 (3) Å for P–O(2), and 1·426 (5) and 1·442 (4) Å for O(2)–C(8) and O(1)–C(9) respectively. Also, P–O(2)–C(8) is 121·4 (2) ° *vs.* 122·5 (2) ° for P–O(1)–C(9). These findings correspond to the high thermal motion of the atoms of the ester groups. Nevertheless, the mean values of these bond lengths [P–O(–C) = 1·568 ± 0·006 Å; (P–)O–C = 1·434 Å] and the P=O distance fall in the expected range of 1·57 ± 0·02, 1·40–1·45, 1·46 ± 0·02 Å, respectively (Kraut & Jensen, 1963; Chiu & Lipscomb, 1969; Höhne & Lohs, 1969). The deviations from the tetrahedral symmetry around the phosphorus atom due to P–O linkages of different bonding type have already been discussed by several authors [see for example Daly & Wheatley (1967), Kraut & Jensen (1963)]. In the compound discussed here, mutual repulsion between P–O single bond and the shorter P=O bond results in an increase of the bond angle (C–)O–P=O from 109·5 ° to 114·4 °.

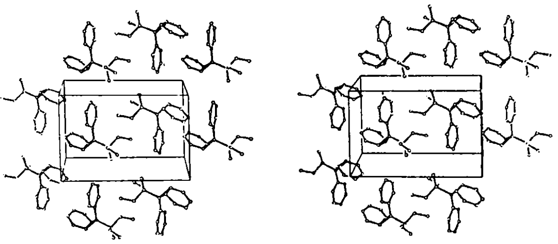

Fig. 4. Stereoscopic view of the unit cell.

The arrangement of the molecules in the unit cell is shown in Fig. 4, which is a stereoscopic view drawn by the program *ORTEP* (Johnson, 1965). All intermolecular contacts are longer than the sum of the van der Waals radii.

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