distances between the sulphurs and these atoms are all greater than 4 Å. The mercuritetraiodide ion is approximately tetrahedral.

Table 3. *Bond lengths and angles in the mercuritetraiodide ion and their standard deviations*

Bonds		σ			σ
Hg–I(1)	2·80 Å	0·01 Å	Hg–I(3)	2·69 Å	0·01 Å
Hg–I(2)	2·73	0·02	Hg–I(4)	2·68	0·02

Angles		σ			σ
I(1)–Hg–I(2)	105·2°	0·2°	I(2)–Hg–I(3)	119·8°	0·2°
I(1)–Hg–I(3)	109·3	0·2	I(2)–Hg–I(4)	110·3	0·3
I(1)–Hg–I(4)	113·1	0·2	I(3)–Hg–I(4)	108·9	0·4

Lopez-Castro & Truter (1964) have determined the conformation of the sulphonium ion to be pyramidal with carbon–sulphur distances 1·82 Å and carbon–sulphur–carbon angles 103°. A test was made to ensure that there is sufficient space in the proposed structure for such an ion in each of the proposed positions.

For the sulphonium ion about S(1), an orientation was found for which the minimum carbon–iodine distance was 3·5 Å; for the sulphonium ion about *T*(1), an orientation was found for which the minimum carbon–iodine distance was 3·7 Å, and for an orientation about *T*(2) the minimum carbon–iodine distance was 3·8 Å.

This investigation showed that there is adequate space between the mercuritetraiodide ions for a sulphonium ion centered on S(1) and either of *T*(1) or *T*(2) and there is no evidence from spatial considerations against the distribution of the second ion between the two latter positions. With these orientations, the minimum distance between the carbons bonded to S(1) and those around either *T*(1) or *T*(2) is 3·5 Å.

The structure including the possible carbon positions is illustrated in Fig. 1.

I wish to thank Dr D. C. Phillips for suggesting the problem and his advice, Dr J. W. H. Oldham for preparing the compound and Sir Lawrence Bragg and Professor R. King for their interest and encouragement. I am indebted to the Managers of the Royal Institution for financial support and to Drs J. J. Daly, G. A. Mair, V. R. Sarma and Mr R. M. Simmons for the use of computer programs.

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The Crystal and Molecular Structure of 2,5-Dimethyl-7,7-dicyanonorcaradiene*

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The substituted norcaradiene, $C_{11}H_{10}N_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in a cell having $a = 11{\cdot}044$, $b = 7{\cdot}126$, $c = 12{\cdot}113$ Å. Copper $K\alpha$ diffraction data measured by scintillation counter gave an R of 3·9 % when fit by least squares to a model including σ bonds. The molecule has nearly exact C_s symmetry; the cyclopropane ring is inclined at about 73° to the approximately planar C_6 ring. Bonds adjacent to the C_3 ring are shortened by 0·02–0·03 Å from corresponding unstrained values; cyclopropane C–C bonds are 1·558, 1·553, and 1·500 Å. The experimental electron density is matched much better by a 'bent' bond cyclopropane model than the straight-bond model; the angle of bending is roughly 20°.

Introduction

Cyclopropane rings present opportunities to study carbon in unusual hybridization states for which little accurate geometrical information is available. The present study was undertaken with the additional purpose of confirming the bicyclic nature of the material $C_{11}H_{10}N_2$, one of the simplest containing the norcaradiene skeleton (Ciganek, 1965).

Experimental data

Clear, block-like crystals of $C_{11}H_{10}N_2$, 2,5-dimethyl-7,7-dicyanonorcaradiene, and of $C_9H_6N_2$, 7,7-dicyanonorcaradiene, were supplied by Dr Ciganek. On Cu

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Kα Weissenberg and Mo *Kα* precession photographs both showed reciprocal lattice extinctions characteristic of space group $P2_12_12_1$ (D_2^4). The unit-cell constants of $C_9H_6N_2$ were determined from Cu *Kα* rotation and Weissenberg photographs to be $a=11.07\pm0.05$, $b=5.76\pm0.02$, $c=12.16\pm0.05$ Å. The dimethyl compound had a somewhat more equidimensional habit and was chosen for a complete study. A zero layer [100] Weissenberg photograph made in a special lattice-constant camera (Fritchie, 1966*a*) with Cu *Kα* radiation gave $b=7.126\pm0.001$, $c=12.113\pm0.001$ Å. The *a*-axis dimension of 11.044 ± 0.002 Å was measured on a Picker goniometer with Cu *Kα* radiation. Wavelengths used in the calculations were 1.54050 and 1.54434 Å for Cu $K\alpha_1$ and Cu $K\alpha_2$. Calculated densities are 1.21_3 g.cm^{-3} and 1.186 g.cm^{-3} for $C_9H_6N_2$ and $C_{11}H_{10}N_2$, respectively, assuming four molecules per cell in each case.

A polyhedral specimen about 0.4 mm in diameter was chosen for intensity collection. The crystal was found to sublime rather rapidly; after collection of the *h0l*, *0kl*, and *hk0* data the crystal was coated with a layer of Krylon acrylic ester resin about 0.05 mm thick. This plastic was essentially amorphous and completely halted the sublimation without excessively increasing the background. All intensity data were collected with a Picker scintillation counter, using a pulse-height discriminator symmetrically set to collect about 90% of the Cu *Kα* pulse distribution. The generator was line-voltage stabilized; more serious intensity variation caused by crystal sublimation was eliminated by measurement of one or two standard reflections about every four hours during data collecting periods. All measurements were made with the moving-crystal moving-counter method (Furnas, 1956), scanning a range of 2° in 2θ for all reflections having $2\theta\leq130°$, and an appropriately larger range for higher order reflections. All scans were made at the rate of $\frac{1}{2}°$ (2θ) per minute; all reflections with $2\theta\leq159°$ were measured.

A few very low order reflections required special measuring conditions to eliminate β radiation. For each reflection four 20-second background counts were made: two at the beginning and two at the end of each scan. Nickel foil 0.0008 inch thick was used as a filter. Goniometer settings were calculated with a program by Dr C. T. Prewitt of this laboratory.

Measurement of equivalent reflections generally gave agreement in integrated intensity within 3%. Systematic variation within this limit attributable to crystal shape was noticed but considered negligible. The μr value of approximately 0.11 leads, with an estimate of 10% variation in *r*, to relative absorption errors of ±2% in intensity. Despite a change in volume of nearly 30% by sublimation, collection of sets of ten or so data at various times showed that a consistent scale could be maintained within about ±0.7% by measuring a single standard. A second standard was measured from time to time as a safeguard. The final set of data is considered by internal consistency, including the measurement of equivalent reflections, to be accurate to within ±3% in intensity.

Standard deviations (σ) were assigned to all reflections on the basis of statistical errors in the integrated peak and in the backgrounds, and of a 1% uncertainty in the (relative, time-dependent) scale factor. The 'minimum observable' level for each reflection was considered to be twice the standard deviation.

Trial structure

Expectation of a nearly flat cyclohexadiene ring in the structure led to examination of the sharpened Patterson function near the origin for closed sets of vectors of length 1.5, 2.6, and 3.0 Å. An arrangement was quickly found which seemed also consistent with the presence of the methyl groups and indeed the complete expected molecule. This orientation agreed with the early observation that the similarity in unit cells of $C_9H_6N_2$ and $C_{11}H_{10}N_2$ indicated the methyl–methyl axis might be at not too large an angle to **b**. Despite this early partial success the Harker sections and a three-dimensional Patterson function displayed on stacked polyethylene sheets were studied in vain for the placement of the molecules. Finally, realization that a large peak at $(0, \frac{1}{2}, 0)$ in the Patterson function could occur only by close overlap in the *h0l* projection of oppositely oriented CN dipoles led with previous information to an *h0l* trial structure. This structure refined in about 10 cycles of least-squares and difference syntheses to $R=16\%$. Comparison of models with the $(\frac{1}{2}, V, W)$ and $(U, V, \frac{1}{2})$ Patterson sections then gave a complete structure which refined in 12 least-squares cycles from 34% to 12.5%. During this initial refinement, each reflection was weighted by $1/\sigma$ rather than $1/\sigma^2$. To stabilize the refinement process in these early cycles, calculated shifts were multiplied by partial shift factors of 0.5 to 0.7 for positional parameters and 0 to 0.1 for thermal parameters. Parameters were sometimes readjusted subjectively to maintain reasonable bond lengths and thermal parameters.

Refinement

From the moment when an essentially correct model was found reduction of *R* to 12.5% had been pleasingly rapid; at this point serious refinement began with the idea of driving the model to an *R* of *ca.* 2%, the estimated validity of the data. Standard refinement procedures which are outlined only briefly below, applied to a data list from which all strong reflections and some apparent errors had been removed, produced convergence at $R=3.9\%$. Examination of a difference map calculated at this stage suggested that further improvement could be made by considering bonding effects. This extended treatment is described in more detail.

Throughout the refinement with *R* below 12.5%, reflections were discarded when it was believed they were in error. Nearly 100 were omitted in the final calculations, including all strong reflections reduced by extinction and some thirty or so apparent clerical errors. It should be remembered that all difference maps shown were computed with this truncated data list. The final structural model including bonding produced an R of 3.5% (compared with 3.9% for the conventional model) for the list of 1084 retained structure factors. The complete list, containing many remeasured reflections and including strong reflections corrected for extinction (Zachariasen, 1963) gave $R=3.9\%$.

All least-squares calculations were performed with modifications of the Sparks–Gantzel–Trueblood block-diagonal least-squares program. A thermal-ellipsoid extraction sub-routine written by R. Deverill (private communication) was used. The remaining programs were those of the author.

The initial 12.5% difference map showed seven hydrogens as well-defined peaks 0.3 to 0.7 e.Å^{-3} in height and gave indications of thermal anisotropy in at least the cyano groups. Inclusion of these observations in the structural model lowered R to 9.2% after three least-squares cycles. Refinement proceeded through two cycles of alternately calculating difference maps and subjecting chosen parameters to a few least-squares iterations, resulting in a model containing only the four non-methyl hydrogen atoms, but with anisotropic vibration for all heavy atoms. This model produced an R of 6.6%. Some methyl hydrogen atoms had been included in previous cycles, but were removed because of difficulty in placing all six. Sections in the expected methyl planes of a difference map computed at this stage are shown in Fig. 1. These maps indicate librating rather than fixed or freely rotating methyl groups. Tetrahedral methyl groups were added to the model with B's of 3.0 as for the other hydrogen atoms. Refinement of the heavy atom parameters through two cycles lowered R to 4.9%. Six further cycles in which all hydrogen positional and (isotropic) thermal parameters were also allowed to vary produced convergence at an R-value of 3.9%.

A difference map calculated at this stage showed 15 peaks larger than about 0.08 e.Å^{-3}; fourteen of these were in or near positions expected for interatomic bonds. Three sections of this difference map: (*a*) in the mean plane of the C_6 ring; (*b*) through the dicyanomethylene group; and (*c*) in the C_3 plane, are shown in Fig. 2. No reflections suffering from noticeable extinction were used in preparing this map; most positional and thermal parameters seem to have been estimated accurately by the least-squares procedure.

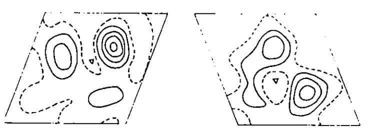

Fig. 1. Sections of an early difference map in the planes of (left) the C(9) and (right) the C(8) methyl hydrogen atoms. Contours are drawn at intervals of 0·05 e.Å^{-3} with the zero contour dashed.

At this stage considerable theoretical work was done, following McWeeny's procedures (McWeeny, 1951, 1952, 1953, 1954) and reported elsewhere (Fritchie, 1966*b*), which showed that the observed peaks were of the magnitude expected for interatomic σ bonds. The π bonds, which have lower densities, were not observed

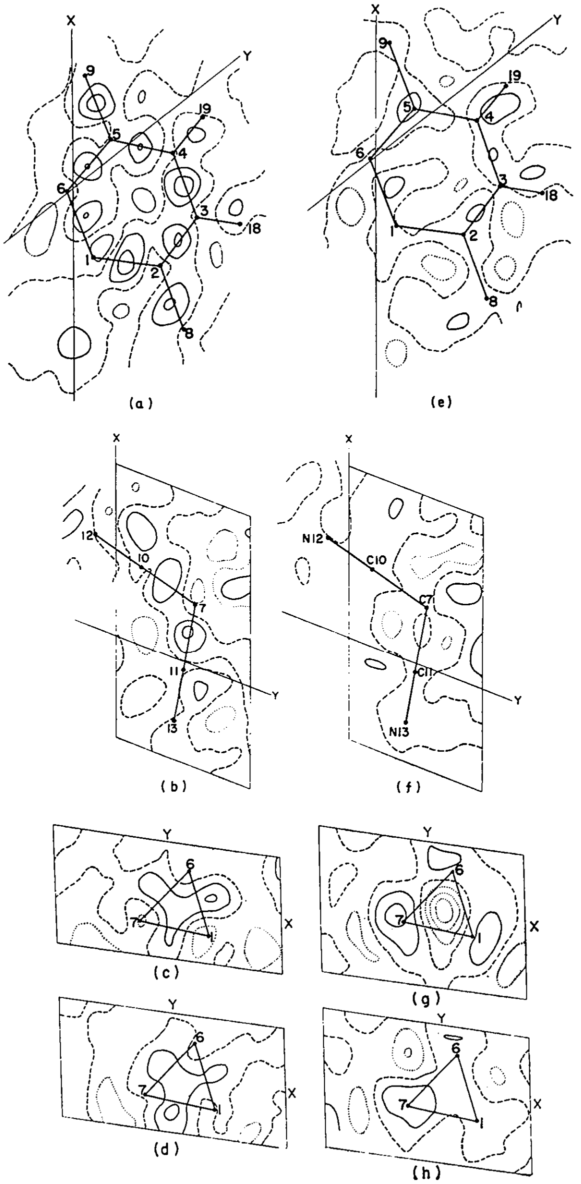

Fig. 2. Sections of difference maps computed using various assumptions about bonding in the molecule. In all sections contours are drawn at 0·05 e.Å^{-3} intervals with the zero contour dashed and negative contours dotted. Sections (*a*)–(*c*) show the result of refinement using the usual spherically symmetric form factors. Sections (*d*)–(*f*) are parts of a map in which bond form factors were used for all bonds except the three in the cyclopropane ring. Section (*g*) shows the cyclopropane ring under the assumption of normal bonds of cylindrical symmetry; section (*h*) shows the same ring when a 'bent' bond model is used in calculating the F_c's. Straight lines labelled X and Y are traces of planes of constant x and y, respectively.

and are not further considered in this discussion. The Sparks–Gantzel–Trueblood program was extensively modified so that the form factor for each atom (excluding hydrogen) is given by $f_e = f_{\text{core}} + \Sigma \frac{1}{2} q_{\text{bond}} f_{\text{bond}} \exp\{-2\pi i\mathbf{S} . (\mathbf{R}_{\text{bond}}/2)\}$. Here, f_e is McWeeny's *effective* atomic form factor, f_{core} is the perhaps asymmetric *core* form factor representing scattering by all non-valence electrons and a partial valence shell, and f_{bond} is the normalized two-center scattering integral, $\int \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \exp(-2\pi i\mathbf{S} . \mathbf{r})d\mathbf{r} / \int \varphi_i(\mathbf{r})\varphi_j(\mathbf{r})d\mathbf{r}$, where the center of the bond is chosen as origin for **r**. Assuming each σ bond has the form $\Psi_{ij} = x_i\varphi_i + x_j\varphi_j$, q_{bond} is given by $2S_{ij}x_ix_j$. $\mathbf{R}_{\text{bond}}$ is the vector between the atom under consideration and that at the other end of the bond (or some equivalently defined point in the case of a 'bent' bond. S_{ij} is the overlap integral $\int \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r})d\mathbf{r}$ and should not be confused with the scattering vector **S**. Finally, the summation is taken over all bonds adjoining the atom in question. The bond form factor, f_{bond}, is axially rather than spherically symmetric (for straight bonds) and in the program is approximated by $f^{\parallel} \cos^2\xi + f^{\perp} \sin^2\xi$, where ξ is the angle between **S** and the bond. This approximation, which is discussed more fully by Fritchie (1965*b*) introduces errors as large as 0.04 in f_{bond}. The errors are reduced by thermal averaging of the electron density, however, and are not serious in the present case. It may also be remarked here that f_{bond} differs in general for each of a set of symmetry-equivalent atoms, and that calculationally it should be treated in a manner similar to the ellipsoidal temperature factor.

The net effect of the procedure described here is to divide the electron density in each bond equally between the two atoms forming the bond, and to treat all the electron density thus associated with each given atom as a part of that atom in all calculations. In particular, the derivative of a structure factor with respect to a given atom includes the effect of its associated bonding electrons, so that the number of parameters to be artificially reset after each cycle is minimized. Under the approximations used here, only **R** for each bond is readjusted between cycles.

Because of anticipated bent bonds in the cyclopropane ring, initial calculations of structure factors with inclusion of bonds omitted these three bonds. Carbon–hydrogen bonds were assumed to be described by the form factor for the hydrogen atom given by McWeeny (1951), *i.e.* by the conventional treatment of hydrogen atoms. The bond charge or population factor, q was taken as 0.863 for all bonds. This value is appropriate for a C_{sp^2}–C_{sp^2} bond 1.47 Å in length and does not differ greatly for other bonds. The form factor appropriate for such a bond was used for all σ bonds, C–N as well as C–C. Initially f_{core} for each atom was isotropic and was simply f_{1s} plus enough of f_{valence} (McWeeny, 1951) to give the appropriate charge of 6 or 7. Later f_{core} for atoms 2 and 5 was changed to the more appropriate $f^{\parallel} \cos^2\nu + f^{\perp} \sin^2\nu$ (McWeeny, 1951, 1954), where ν represents the angle between **S** and the $2p_z$ orbital not used in σ bonding; little if any significant change was noted. Form factors f_{1s} and f_{valence} (isotropic), together with $f^{\parallel}_{\text{val}}$ and $f^{\perp}_{\text{val}}$ for sp^2 carbon, are given in Table 1 for convenience; these were derived from data in McWeeny's papers. The bond form factor used is also included. The $f^{\parallel}$ table differs from McWeeny's, presumably because of arithmetic errors in his hand-calculated values. Initial calculations with bond form factors used the scale and temperature factors

Table 1(*a*). *Partial atomic form factors*

$\sin\theta/\lambda$ (a.u.$^{-1}$)*	f_{1s}(C)	f_{val}(C)	f_{1s}(N)	f_{val}(N)	$f^{\parallel}_{sp^2}$(C)	$f^{\perp}_{sp^2}$(C)
0·000	2·000	4·000	2·000	5·000	4·705	4·705
0·025	1·997	3·806	1·998	4·824	4·555	4·580
0·050	1·988	3·283	1·991	4·383	4·150	4·238
0·075	1·973	2·608	1·980	3·723	3·623	3·789
0·100	1·952	1·850	1·965	2·925	3·051	3·280
0·125	1·926	1·211	1·946	2·218	2·570	2·835
0·150	1·895	0·734	1·922	1·567	2·211	2·483
0·175	1·859	0·396	1·895	0·997	1·957	2·214
0·200	1·818	0·180	1·865	0·642	1·789	2·017
0·250	1·727	−0·016	1·795	0·248	1·610	1·772
0·300	1·624	−0·058	1·715	−0·018	1·516	1·621
0·400	1·400	−0·033	1·533	−0·069	1·349	1·391
0·500	1·175	−0·005	1·339	−0·023	1·159	1·175
0·600	0·966	0·007	1·148	0·008	0·964	0·971

Table 1(*b*). *Bond form factors used*

$\sin\theta/\lambda$ (Å^{-1})	$f_b^{\parallel}$	$f_b^{\perp}$	$\sin\theta/\lambda$ (Å^{-1})	$f_b^{\parallel}$	$f_b^{\perp}$
0·00	1·000	1·000	0·35	0·250	0·145
0·05	0·979	0·960	0·40	0·137	0·086
0·10	0·918	0·848	0·45	0·054	0·051
0·15	0·818	0·691	0·50	0·000	0·030
0·20	0·688	0·520	0·55	−0·029	0·018
0·25	0·539	0·362	0·60	−0·040	0·010
0·30	0·388	0·236	0·70	−0·032	0·001

* 1 a.u. = 0·5292 Å.

Table 2. *Observed and calculated structure factors*

Each group of four columns contains in order l, $100\,|F_o|$, $100\,|F_c|$, and α, and is headed by values of h and k common to the group. Negative numbers in the $|F_o|$ column are minimum observable values of unobserved reflections. Asterisks mark reflections omitted from the final least-squares calculations.

l	$100\lvert F_o\rvert$	$100\lvert F_c\rvert$	α
0 0			
2	290*	302	0
4	7279*	7735	0
6	1858*	1862	0
8	459	404	18000
10	870	875	18000
12	332	323	0
14	683	688	0
0 1			
1	3498*	3969	27000
2	6235*	5980	27000
3	139*	140	9000
4	46*	134	9000
5	137*	130	27000
6	1039*	1191	27000
7	1164	1140	27000
8	181	135	27000
9	720	711	9000
10	756	754	9000
11	169	188	9000
12	1070	1077	9000
13	349	350	27000
14	248	275	27000
15	-73	56	9000
0 2			
0	3444*	3519	0
1	4512*	4501	18000
2	3233*	3323	0
3	2895*	2828	0
4	267*	415	0
5	1163*	1239	18000
6	310	294	0
7	326	330	18000
8	969	931	18000
9	567	564	18000
10	238	213	0
11	830	835	18000
12	71*	152	0
13	83	59	18000
14	230	258	0
0 3			
1	2402*	2259	9000
2	3037	2912	27000
3	1134*	1005	9000
4	1565*	1596	27000
5	449*	493	27000
6	1702	1615	27000
7	712	702	9000
8	281	278	27000
9	1294	1286	27000
10	497	508	9000
11	241	220	9000
12	312	335	9000
13	433	431	27000
13	442	431	27000
14	352	363	9000
0 4			
0	465*	403	0
1	1451*	1350	18000
2	1887	1829	0
3	506*	550	0
4	1478*	1439	18000
5	1218	1142	18000
6	598	547	18000
7	163	149	18000
8	851	870	18000
9	655	638	18000
10	966	952	18000
11	376	352	18000
12	124	152	0
13	82	82	0
0 5			
1	169	126	9000
2	82	24	27000
3	691	631	9000
4	1231	1159	27000
5	217	223	27000
6	329	376	27000
7	-66	71	27000
8	-70	25	9000
9	156	131	27000
10	115*	126	9000
11	257	247	9000
12	193	196	27000
0 6			
0	719	697	18000
1	1476	1443	0
2	1436	1423	0
3	-68	29	18000
4	313	322	0
5	691	687	0
6	656	686	18000
7	231	234	0
8	166	173	18000
9	186	193	0
10	282	276	0
11	328	345	18000
0 7			
2	80*	23	27000
3	1275	1254	27000
4	1392	1409	27000
5	347	342	27000
6	194	185	27000
8	310	313	27000
8	319	313	27000
9	619	629	27000
9	625	629	27000
0 8			
0	377	368	0
1	360	356	0
2	66*	54	0
3	-55	43	0
4	-50	15	18000
5	225	240	18000
5	229	240	18000
6	181	202	18000
7	146	154	0
0 9			
1	44*	35	9000
1 0			
1	1040*	1038	9000
2	7621*	8426	0
3	2506*	2493	27000
4	2484*	2550	18000
5	788	787	27000
6	1984	2004	0
7	1061	1102	27000
8	341	292	0
9	563	580	27000
10	458	471	18000
11	291	306	27000
12	1351	1360	18000
13	540	545	27000
14	-63	165	0
15	-75	14	9000
1 1			
0	6741*	6643	9000
1	2062*	2233	25873
2	2219*	2342	29176
3	2380*	2545	23325
4	584	547	21062
5	605*	557	8506
6	263	240	13590
7	1587	1554	24734
8	949	927	28326
9	610	600	27526
10	520	532	28609
11	318	325	1199
12	266	261	14528
13	84	118	13053
14	502	499	2967
15	303	298	30158
1 2			
0	3034*	3170	9000
1	1335*	1444	14119
2	5830*	5929	27226
3	2273*	2431	20864
4	394	378	19582
5	1070*	936	6037
6	1093	1147	27841
7	507*	529	22800
8	882	896	20748
9	603	608	2100
10	830	824	21627
11	159	172	22950
12	277	258	17879
13	398	417	33865
14	194	192	16565
15	122	125	27026
1 3			
0	444*	324	9000
1	879	861	23633
2	1433*	1222	33094
3	2505*	2181	10354
4	1393	1338	28041
5	1014	1063	21964
6	1170	1098	27438
7	674	674	7844
8	1715*	1711	30490
9	527	517	17129
10	746	735	26861
11	502	501	26812
12	397	384	27873
13	-71	15	797
14	388	385	35886
1 4			
0	313*	131	9000
1	2425	2407	24619
2	1146*	1113	35344
3	1888*	1946	12916
4	1329	1240	32015
5	481	475	23069
6	729	696	7186
7	1015	981	15011
8	589	594	35389
9	117	140	8702
10	302	285	18126
11	691	680	15736
12	505	510	12902
13	152	130	8414
1 5			
0	1182	1035	27000
1	658	663	32233
2	629*	661	34832
3	262	267	9153
4	718	686	21427
5	564*	559	4975
6	814	824	28811
7	251	238	1529
8	257	266	30127
9	264	248	35042
10	-77	30	25006
11	97	90	15321
12	144	129	4596
1 6			
0	-82	74	9000
1	1124	1077	18306
2	821	809	13636
3	205	238	17926
4	1184	1218	35411
5	409	425	13468
6	395	401	5520
7	137	113	10050
8	108	118	16452
9	277	270	35799
10	-96	39	30382
11	249	249	5274
1 7			
0	91	149	27000
1	826	814	6248
2	970	988	9486
3	363	359	5427
4	-76	37	23734
5	297	296	30411
6	330*	338	23392
7	435	457	7345
8	166	162	25237
9	207	202	9264
1 8			
0	273	278	27000
1	372	382	10232
2	174	179	2828
3	436	437	32512
5	153	139	12457
6	83	75	14735
7	-64	18	485
1 9			
0	82	78	27000
1	282	284	13920
2	-56	80	19470
2 0			
0	2931*	2950	18000
1	1280*	1410	9000
2	2892*	3238	18000
3	1059*	1139	9000
4	1255*	1359	0
5	-58	54	27000
6	2394	2460	18000
7	191	184	27000
8	150	155	0
9	185	131	9000
10	291	319	0
11	393	400	9000
12	106	89	18000
13	-66	19	27000
14	103	99	18000
15	134	115	9000
2 1			
0	508*	457	0
1	3858*	3896	7026
2	5927*	5847	948
3	1522*	1495	26399
4	2373*	2452	31476
5	1588*	1674	7111
6	1020	1117	4317
7	634	643	35023
8	102	102	28027
9	288	274	28340
10	717	723	2663
11	774	775	33110
12	457	460	14971
13	394*	395	1482
14	153	155	3610
15	232	230	35735
2 2			
0	181	129	18000
1	1870*	1853	23150
2	2677*	2744	7125
3	1975*	1928	29697
4	2025*	2123	21171
5	934	1019	21552
6	838*	871	9439
7	314	294	6266
8	777	754	13060
9	183	172	22097
10	896	903	16714
11	476	479	9661
12	214	215	27816
13	-73	12	31017
14	529	521	10013
2 3			
0	224	295	0
1	169	144	10880
2	814	953	35833
3	966	991	4465
4	2281*	2213	1243
5	1066	1085	12964
6	577	491	15781
7	376	357	28927
8	803	790	2476
9	710	690	10283
10	722	713	2765
11	403	404	13658
12	385	393	18516
13	136	158	29603
14	184	174	4648
2 4			
0	2350	2282	18000
1	1135	1059	5239
2	946	893	6957
3	796	713	28942
4	1152	1035	22493
5	803	817	5356
6	537	527	21473
7	464	461	32981
8	928	940	11328
9	106	109	7673
10	328	323	30330
11	332	323	30964
12	260	251	10195
13	335	349	13548
2 5			
0	1048	1054	18000
1	1152	1131	6010
2	709	656	30437
3	662	686	17707
4	183	157	28468
5	713	713	14902
6	783	777	21302
7	609	626	15021
8	226	204	21706
9	-82	58	34104
10	87	57	18928
11	492	497	20271
12	408	415	16707
2 6			
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1	996	1029	4730
2	574	603	15680
3	830	833	15313
4	398	366	18024
5	533	507	4595
6	118	137	34236
7	737	739	11052
8	326	330	14676
9	-72	68	12329
10	294	308	22643
11	238	236	5489
2 7			
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2	-84	54	28273
3	645	657	6209
4	255	244	5647
5	152	158	14359
6	-76	48	24602
7	246	246	30549
8	129	162	3934
9	316	321	9333
2 8			
0	280	284	0
1	183	188	24884
2	294	301	23583
3	301	308	2621
4	404	405	33817
5	290	280	32004
6	399	402	22056
2 9			
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3 0			
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2	1439	1471	0
3	2484*	2459	27000
4	304*	465	0
5	2398	2314	9000
6	1089	1126	0
7	191	213	9000
8	984	942	18000
9	214	194	9000
10	266	280	18000
11	766	752	9000
12	640	629	18000
13	-64	13	27000
14	-94	92	0
15	-62	62	9000
3 1			
0	7728*	7436	9000
1	4713*	4645	6374
2	5703*	5639	9799
3	1574	1651	31695
4	2386*	2400	3976
5	197	187	14840
6	1020	1042	5858
7	97	51	34184
8	168	202	17361
9	562	547	20150
10	706	717	28942
11	427	436	25201
12	629	658	9844
13	397	411	26379
14	245	246	18756
3 2			
0	2025*	2071	9000
1	336	295	34871
2	3250*	3191	35247
3	1228	1150	25486
4	3216*	3196	6095
5	1498	1421	28690
6	730*	648	27612
7	152	148	25841
8	1336	1308	2193
9	339	315	32683
10	1278	1302	14099
11	221	245	10851
12	616	654	22283
13	277	284	4676
14	325	310	11447
3 3			
0	684*	724	9000
1	843*	882	29926
2	1789	1690	14511
3	1342	1268	33189
4	859*	779	29283
5	230	243	26673
6	240	273	23677
7	424	427	29140
8	1449	1416	21915
9	1267	1270	28451
10	439	440	34246
11	238	272	5879
12	217	202	17715
13	509	508	29196
14	208	209	13127
3 4			
0	380	361	27000
1	1468	1445	20863
2	443	414	9125
3	582	580	12651
4	1642	1587	2245
5	943	888	24219
6	1229	1216	29614
7	312	307	2258
8	226	190	23921
9	155	189	5642
10	239	237	19853
11	365	351	29053
12	548	576	28262
13	178	187	7475
3 5			
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1	1050	1032	8193
2	353	350	13705
3	411	396	636
4	495	470	3832
5	211	198	20737
6	822	775	29832
7	755	752	17179
8	634	665	22849
9	-81	113	6661
10	203	204	32480
11	498	487	23415
12	209	210	25627
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1	141*	117	29848
2	744	721	859
3	772	789	357
4	665	673	30938
5	662	638	25368
6	520	528	34242
7	605	601	781
8	190	201	18
9	138	152	12987
10	-87	69	35315
11	238	224	32659
3 7			
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2	307	304	6277
3	293	313	16155
4	187	185	4004
5	367	387	8688
6	158	162	26366
7	258	279	19224
8	318	266	32574
9	135	126	34197
3 8			
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2	181	180	8021
3	407	400	32513
4	309	306	35140
5	511	472	906
6	440	461	680
4 0			
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2	3668*	3807	18000
3	799	807	27000
4	309*	45	18000
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6	546	509	18000
7	801	774	9000
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14	215	215	0
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3	1734	1669	2922
4	1107*	1131	17726
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6	964*	984	35630
7	605	610	1702
8	661	645	8589
9	201*	243	5219
10	1333	1360	28162
11	553*	527	10545
12	592	597	29359
13	154	158	27739
14	214	195	29137
4 2			
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3	1974	2009	1520
4	2571*	2428	33997
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6	1390	1355	11129
7	777	785	32516
8	1844	1822	31942
9	1096	1081	31520
10	1414	1406	3654
11	139	138	26326
12	299	300	22682
13	468	481	33867
14	144	156	9089
4 3			
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2	1044*	926	5182
3	1498	1485	28843
4	948*	978	8751
5	739	723	25525
6	540	535	803
7	632	614	11476
8	344	324	14512
9	595	595	24994
10	707	687	24945
11	225	232	19423
12	339	346	27564
13	187	194	9000
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3	644	668	25750
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8	900	885	82
9	599	567	6723
10	338	347	7161
11	282	290	25497
12	436	423	674
13	330	329	4655
4 5			
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2	461	429	10268
3	173	198	13734
4	1004*	986	11506
5	1289	1296	31440
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7	315	258	23058
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9	-77	22	16558
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11	105	95	15340
12	284	303	31212
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2	302	287	22432
3	339	349	13612
4	131*	147	13351
5	143	133	15096
6	512	507	30891
7	491	500	23180
8	194	208	1197
9	198	180	14030
10	122	123	29597
4 7			
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1	131	149	28267
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3	145	125	17180
4	391	419	7760
5	211	205	12439
6	490	522	11702
7	188	158	12731
8	239	237	27456
4 8			
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2	370	369	15279
3	491	487	17208
4	349	342	14010
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5 0			
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9	527	503	9000
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12	371	359	18000
13	613	619	9000
14	143	108	0
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3	455	429	14222
4	600	522	12905
5	654	613	3982
6	2178	2093	23626
7	442*	371	14204
8	286	281	6999
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10	415	414	13820
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12	466	476	28479
13	221	226	17475
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3	1984	1972	12523
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5	845	849	1955
6	811	742	7409
7	1748	1723	15625
8	1091	1097	16464
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10	516	504	2341
11	557	525	17733
12	180	203	34758
13	157	111	9730
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5	994	959	27333
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7	495	504	10293
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10	368	374	9208
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12	239	229	20514
13	208	213	9614
5 4			
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2	122	103	35593
3	338	347	24493
4	404	365	11738
5	541	534	30907
6	1160	1127	18282
7	605	574	23518
8	912	901	2864
9	253	265	33350
10	518	511	17767
11	323	336	24743
12	141	132	6198
5 5			
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2	271	279	20853
3	506	501	15907
4	611	641	26752
5	601	623	15571
6	511	529	12394
7	255	292	28937
8	187	208	27621
9	86	86	18017
10	177	176	22161
11	172	162	5901
5 6			
0	197	233	27000
1	111	104	10146
2	646	626	9680
3	218	244	19727
4	91	123	21425
5	278	264	17144
6	212	233	17898
7	183	175	34362
8	260	248	30572
9	558	549	20234
10	271	261	20752
5 7			
0	150	170	27000
1	115	149	11774
2	159	160	23250
3	269	281	24735
4	491	505	28401
5	187	201	13336
6	262	265	5131
7	319	315	23017
8	-58	48	31487
5 8			
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1	149	168	10579
2	366	381	33138
3	381	391	18226
4	346	366	14978
6 0			
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2	460	480	18000
3	2048	2090	9000
4	1350	1377	18000
5	700	706	27000
6	481	489	0
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8	449	488	18000
9	842	859	27000
10	-75	4	0
11	177	212	27000
12	-69	7	0
6 1			
0	626	624	0
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2	1202	1235	17857
3	824	821	26555
4	772	775	11126
5	143	146	2035
6	816	824	12983
7	251	237	9670
8	1007*	971	22655
9	583	576	19484
10	320	337	15457
11	123*	114	10243
12	359	362	21551
13	552	538	17821
6 2			
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1	901	942	10011
2	1669	1655	19236
3	523	563	9162
4	1018	939	15903
5	828	801	4054
6	883	806	4661
7	207	195	2004
8	816	847	28712
9	470	440	6679
10	508	528	13254
11	387	388	35718
12	391	401	32010
13	291	289	7834
6 3			
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2	1338	1273	16701
3	818	818	2396
4	1271	1204	15391
5	1195	1171	1307
6	880	870	15
7	875	832	27892
8	318	341	18267
9	622	622	5594
10	230	235	32609
11	141	122	24549
12	215	226	31947
6 4			
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1	786	793	4749
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3	767	798	13492
4	560	532	2663
5	569	531	4553
6	527	550	24355
7	725	719	26412
8	557	554	28839
9	371	359	7336
10	305	317	34523
12	207	230	19650
6 5			
0	1042	998	0
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2	564	569	7532
3	417	411	28524
4	586	565	2781
5	356	360	3483
6	528	538	3309
7	360	365	12531
8	426	429	4884
9	-71	62	34817
10	160	136	30722
11	-54	23	24026
6 6			
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1	259	247	26456
2	311	314	20674
3	167	156	31003
4	766	751	7933
5	409	441	24750
6	156	118	33697
7	409	388	32336

Table 2 (*cont.*)

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4	138	139	4538
5	385	363	3294
6	167	138	32316
7	186	177	2723
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2	96	95	13258
3	186	196	12226
		7	0
1	686	675	9000
2	672	626	18000
3	819	787	9000
4	283	292	18000
5	973	951	9000
6	641	670	0
7	307•	353	9000
8	185	214	18000
9	307	263	27000
10	685	707	0
11	123	106	27000
12	437	448	0
13	526	528	27000
		7	1
0	2323	2277	27000
1	278•	222	11781
2	1006	1043	29512
3	583	597	1254
4	540	559	26580
5	928	918	30662
6	303	311	2168
7	1089	1092	2963
8	617	608	6612
9	305	308	48
10	103	84	11972
11	558	559	3541
12	168	155	10551
13	157	158	15954
		7	2
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2	1210	1129	25200
3	653	645	14392
4	1538	1461	22389
5	671	650	1762
6	782	825	13206
7	374	389	19277
8	560	562	30144
9	316	319	32535
10	405	400	35171
11	341	347	22272
12	282	272	1056
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2	810	762	159
3	658	660	19975
4	1571	1547	14970
5	1022	986	7273
6	641	632	10712
7	536	526	1051
8	561	569	6987
9	230	227	141
10	474	475	10916
11	575	566	7611
12	177	184	17758
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1	970	965	35479
2	1177	1193	20781
3	775	799	2843
4	282	301	2254
5	1068	1055	7858
6	714	772	13772
7	320	330	33641
8	172	145	31269
9	274	278	19531
10	174	153	24435
11	122	106	33746
		7	5
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2	211	210	915
3	206	218	22363
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5	662	662	31514
6	603	589	8234
7	394	398	34127
8	295	309	8975
9	75	76	6392
10	465	470	9927
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1	110	127	32036
2	506	487	25923
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5	320	321	13192
6	368	372	15927
7	264	267	35519
8	209	195	13377
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2	261	267	25187
3	445	460	23714
4	230	230	13675
5	287	284	2918
6	152	137	20645
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5	749	761	27000
6	1392	1399	0
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11	574	576	9000
12	427	432	0
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2	1150	1078	23440
3	457	430	11430
4	222	199	16063
5	684	697	20031
6	456	475	23046
7	616	624	25887
7	611	624	25887
8	342	354	28075
9	365•	354	21839
10	272	272	7528
11	175	183	28501
12	297	287	8320
		8	2
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2	958	938	5548
3	521	477	16647
4	1291	1305	27860
5	118	88	16552
6	469	496	11154
7	459	466	18321
7	469	466	18321
8	664	685	20619
9	179	155	15895
10	308	312	15105
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12	313	313	22864
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3	720	660	21557
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6	580	588	18953
7	386	399	12312
8	338	329	19244
9	343	341	31438
10	175	172	4002
11	129	96	10835
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5	357	358	6703
6	422	412	13802
8	−76	80	18088
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2	205	206	30384
3	381	393	11135
4	637	630	24769
5	175	142	12898
6	523	549	23554
8	197	191	29144
9	203	178	34290
		8	6
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1	318	322	26302
2	600	614	33983
3	453	467	29504
4	307	323	35210
6	353	348	24140
7	208	206	31966
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2	200	192	13500
3	573	587	23042
4	145	151	28413
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5	786	784	27000
6	125	84	18000
7	101	100	9000
8	330	330	0
9	376	368	27000
10	123	139	18000
11	282	265	27000
		9	1
0	813	781	9000
1	529	525	22487
2	324	323	28006
3	962	946	16063
4	207	205	25021
5	533	526	8140
6	525	513	10378
7	357	351	12037
8	106	119	31818
9	250	248	29960
10	364	370	26627
11	343	297	11115
		9	2
0	1415	1474	27000
1	595	598	33348
2	428	429	5732
3	209	203	13844
4	818	824	27053
5	757	778	3999
6	451	465	34321
7	220	204	20743
8	273	267	30348
9	330	306	736
10	120	142	28482
11	172	190	18010
		9	3
0	153	139	27000
1	434	436	16734
2	850	846	24720
3	375	381	18512
4	663	676	34102
5	450	453	24029
6	−84	84	21075
7	238	232	13807
8	303	314	33655
9	121	110	20024
10	−66	26	24821
		9	4
0	388	364	27000
1	644	630	12371
2	478	470	10868
3	216	221	19156
4	174	148	25222
5	311	313	13282
6	477	475	15396
7	191	174	7359
9	224	220	5592
		9	5
0	268	294	27000
1	189	173	24076
2	509	542	7805
3	240	238	3962
4	144	143	4923
5	238	225	11199
6	−79	71	17266
7	262	265	3170
8	304	299	33197
		9	6
0	585	566	9000
1	288	298	9066
2	461	452	17785
3	374	383	33100
4	490	488	5011
5	298	286	12395
		10	0
0	308	311	18000
1	107	127	27000
2	1559	1552	0
3	264	244	9000
4	546	541	0
5	645	636	9000
6	578	598	18000
7	656	649	9000
8	231	212	18000
9	519	551	9000
10	127	126	0
		10	1
0	347	344	0
1	320	316	518
2	448	444	4490
3	816	798	22120
4	790	799	32072
5	398	393	16141
6	115	73	35818
7	404	402	6074
8	434	442	7586
9	−77	125	3722
10	398	394	778
		10	2
0	196	169	18000
1	778	775	34891
2	345	323	2109
3	668	686	23166
4	346	368	21858
5	508	501	6304
6	−84	79	27825
7	444	443	12253
8	135	158	9481
9	216	207	6651
10	94	106	30525
		10	3
0	590	598	0
1	380	388	9899
2	240	228	29767
3	639	658	13882
4	591	586	30753
5	434	437	17419
6	138	144	25211
7	131	160	19502
8	82	63	25003
9	173	145	34257
		10	4
0	598	609	0
1	325	330	26605
2	278	280	16531
3	187	195	25192
4	334	328	33820
5	388	384	13491
6	561	558	20453
7	228	211	13290
8	295	307	11487
		10	5
0	305	279	18000
1	278	290	13845
2	297	320	27811
3	201	192	21947
4	216	207	6442
5	401	370	16687
6	391	397	18216
		10	6
0	469	486	0
1	139	128	16312
2	206	202	21056
3	294	292	2484
		11	0
1	663	662	27000
2	−82	20	0
3	381	370	27000
4	537	539	0
5	688	671	27000
6	643	639	0
7	−66	77	27000
8	248	229	18000
9	276	289	27000
		11	1
0	273	232	9000
1	497	469	4053
2	578	588	12004
3	467	462	32475
4	311	317	7870
5	681	686	23251
6	209	213	33845
7	214	215	23259
8	437	440	17395
9	308	303	18747
		11	2
0	409	397	27000
1	349	365	11767
2	407	391	7097
3	550	555	26875
4	105	108	13266
5	427	441	29126
6	248	278	23080
7	111	106	19909
8	75	73	31385
		11	3
0	207	215	9000
1	584	588	35325
2	−81	38	20088
3	554	581	1806
4	310	319	33139
5	−73	55	11652
6	320	289	32043
7	159	153	14909
8	419	432	24042
		11	4
0	489	474	27000
1	187	174	15095
2	123	132	30332
3	541	537	27302
4	349	353	35636
5	235	249	24338
6	504	525	28954
		11	5
0	−71	43	9000
1	318	315	4757
2	257	248	22243
3	183	198	959
4	328	326	32175
		12	0
0	889	888	18000
1	90	137	9000
2	124	117	18000
3	152	167	27000
4	651	660	18000
5	403	400	27000
6	−92	35	18000
7	96	113	9000
8	−60	4	0
		12	1
0	432	446	0
1	191	194	11362
2	237	241	3342
3	537	542	5588
4	253	264	20358
6	386	400	683
7	141	144	30926
		12	2
0	205	185	18000
1	456	458	31474
2	339	335	34163
3	385	400	17286
4	289	315	3865
5	421	430	30716
6	364	362	11652
7	184	195	18662
		12	3
0	97	57	0
1	143	158	21019
2	209	198	11799
3	212	246	32220
4	113	132	18291
5	85	93	1719
6	326	332	2974
		12	4
0	414	417	0
1	155	165	12527
2	298	299	21945
3	−64	35	35244
4	266	268	4354
		13	0
1	232	229	27000
2	175	199	18000
3	446	459	9000
4	120	113	0
5	406	421	27000
		13	1
0	240	274	27000
1	95	113	3271
2	424	429	4039
3	−51	98	28816
4	129	144	7627
5	245	254	10686
		13	2
0	−86	20	27000
1	340	341	25334
2	549	550	12063
3	186	198	25527
4	396	414	33424
		13	3
0	−72	3	27000
1	137	168	3429
2	138	133	11276
		14	0
0	65	59	18000
1	−56	32	27000

given by the previous cycle, although theoretical models had shown that thermal parameters would decrease by about 10% in changing from the usual kind of model to a model making specific allowance for σ bonds. The first R value was 7.3% rather than 3.9%, chiefly because of these anticipated thermal errors. Convergence of this model was reached in three cycles at 3.5%. Sections of the corresponding difference map are given in Fig. 2(*d*) through (*f*), paralleling (*a*) through (*c*). Peaks in the bonding regions have essentially been removed, although some positive areas remain in both bonding and core areas. The standard deviation in ϱ, estimated both by assuming σ_F is constant (0.3 e) and by assuming $\sigma_F = 0.03\ |F|$, is approximately 0.02–0.03 e.Å^{-3} (Lipson & Cochran, 1957). The estimated root mean square $|\Delta\varrho|$ in the final difference map, in areas away from atoms, is *ca.* 0.025 e.Å^{-3}. Thus, although the original peaks of *ca.* 0.1–0.15 e.Å^{-3} must be considered significant, the variation remaining after subtraction of bonds is scarcely more than random and can be considered negligible in comparison with the largest remaining errors – those near methyl hydrogen atoms (see below). It will be noted that although the C–N bond peaks originally were not between atomic cores, the new difference map shows no holes. It may be assumed that small errors were present in the comparatively large thermal parameters of these atoms, and that these have now been corrected.

The electron density in the cyclopropane ring had been changed but not removed by the preliminary bond refinement; the effect of including these bonds remained to be seen. Inclusion of these bonds, using the same approximations as for the others, gave $R = 4.2\%$. dropping in two least-squares cycles to 3.9%. A difference map computed at this stage showed a large hole in the center of the ring [Fig. 2(*g*)]. It was decided to make an attempt to allow for 'bent' bonds, by directing each half of a cyclopropane bond outward by the calculated amount of 22° (Coulson & Moffitt, 1949). This procedure involves a further approximation. The sum of two half-bond form factors directed away from the bond axis is not the Fourier transform of such a 'bent' bond, but the electron density is essentially properly located by this procedure and further refinements would seem to go beyond the limits of the experimental data. Inclusion of these 'bent' bonds gave the difference map shown in Fig. 2(*h*) and an *R* value of 3.5% in two cycles using, as in the straight-bond case, parameters from the first 11-bond calculation. To see if further refinement would relatively benefit the straight-bond model, each of the two models was allowed to vary for three further cycles. Essentially no change occurred; all shifts were extremely small, averaging about 0.1σ.

At the conclusion of the refinement, all reflections affected to the extent of 0.3% were corrected for extinction by the formula $|F_{\text{corr}}|^2 = |F_{\text{obs}}|^2(1+2.00\times 10^{-5}\beta I_{\text{obs}})$ (Zachariasen, 1963). All reflections which had been omitted during the final refinement cycles were re-examined and corrected if necessary. All observed and calculated structure factors are listed in Table 2, those marked with an asterisk having been omitted

Table 3. *Positional parameters and their standard deviations*

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
C(1)	0·27292 (15)	0·07556 (26)	0·28453 (12)
C(2)	0·36399 (15)	−0·05160 (25)	0·33288 (14)
C(3)	0·40902 (16)	−0·01259 (25)	0·43422 (16)
C(4)	0·37764 (15)	0·15791 (26)	0·49337 (16)
C(5)	0·30138 (15)	0·28862 (25)	0·45278 (15)
C(6)	0·24087 (14)	0·25214 (24)	0·34540 (14)
C(7)	0·14677 (13)	0·08934 (23)	0·34082 (11)
C(8)	0·40156 (23)	−0·21785 (35)	0·26500 (18)
C(9)	0·27202 (20)	0·46913 (28)	0·50984 (19)
C(10)	0·04356 (16)	0·11317 (25)	0·27004 (14)
C(11)	0·12422 (14)	−0·01452 (23)	0·44035 (12)
N(12)	−0·03928 (17)	0·13352 (28)	0·21336 (14)
N(13)	0·10697 (16)	−0·09444 (27)	0·52114 (12)
H(14)	0·2668 (18)	0·0833 (31)	0·2134 (15)
H(15)	0·4366 (22)	−0·1833 (38)	0·1982 (20)
H(16)	0·3483 (52)	−0·3162 (72)	0·2328 (48)
H(17)	0·4723 (24)	−0·2642 (46)	0·2976 (20)
H(18)	0·4591 (18)	−0·0933 (32)	0·4641 (18)
H(19)	0·4145 (20)	0·1903 (30)	0·5665 (19)
H(20)	0·3096 (23)	0·4917 (33)	0·5748 (19)
H(21)	0·1859 (27)	0·4589 (45)	0·5233 (22)
H(22)	0·3020 (30)	0·5652 (55)	0·4724 (28)
H(23)	0·2162 (19)	0·3624 (26)	0·3086 (16)

Table 5. *Final thermal-ellipsoid principal axes*

Caps denote unit vectors

Atom	$\lvert\mathbf{B}_i\rvert$	$\hat{\mathbf{B}}_i\,.\,\hat{\mathbf{a}}$	$\hat{\mathbf{B}}_i\,.\,\hat{\mathbf{b}}$	$\hat{\mathbf{B}}_i\,.\,\hat{\mathbf{c}}$
C(1)	4·18	0·481	0·761	0·435
	2·97	0·685	−0·636	0·356
	2·61	−0·548	−0·127	0·827
C(2)	4·65	0·504	0·564	0·654
	3·45	−0·040	−0·741	0·670
	2·58	−0·862	0·364	0·351
C(3)	4·88	−0·234	0·218	0·948
	3·78	−0·462	−0·882	0·088
	2·79	0·855	−0·418	0·307
C(4)	5·21	−0·472	0·125	0·872
	3·69	0·147	−0·965	0·218
	2·83	0·869	0·231	0·438
C(5)	4·22	−0·339	0·275	0·900
	3·54	0·548	−0·719	0·426
	2·82	0·764	0·638	0·093
C(6)	3·94	−0·124	0·556	0·822
	3·16	0·966	−0·122	0·228
	2·65	−0·227	−0·822	0·522
C(7)	3·32	0·003	0·930	0·367
	2·78	−0·906	−0·152	0·394
	2·53	0·423	−0·334	0·843
C(8)	7·29	0·800	0·582	0·143
	5·12	0·132	−0·404	0·905
	3·10	−0·585	0·706	0·400
C(9)	6·46	−0·427	−0·274	0·862
	4·92	0·903	−0·164	0·396
	3·29	0·033	0·948	0·317
C(10)	4·21	−0·674	−0·414	0·612
	3·58	−0·219	0·903	0·368
	2·74	0·706	−0·114	0·699
C(11)	3·56	0·457	−0·887	0·063
	2·88	0·861	0·459	0·222
	2·83	−0·213	−0·040	0·976
N(12)	6·39	−0·690	−0·028	0·723
	5·39	0·111	0·983	0·144
	3·04	0·715	−0·180	0·675
N(13)	6·14	−0·737	0·675	0·023
	4·08	0·561	0·592	0·579
	3·16	−0·377	−0·439	0·815

Table 4. *Thermal parameters and their standard deviations*

Atom	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0·00646 (11)	0·01806 (29)	0·00504 (9)	0·00265 (34)	0·00156 (18)	0·00254 (28)
C(2)	0·00638 (12)	0·01831 (32)	0·00659 (10)	0·00393 (35)	0·00248 (20)	0·00194 (32)
C(3)	0·00640 (12)	0·01803 (34)	0·00798 (12)	0·00190 (36)	−0·00189 (22)	0·00205 (36)
C(4)	0·00694 (13)	0·01808 (34)	0·00799 (12)	−0·00168 (35)	−0·00357 (23)	0·00045 (34)
C(5)	0·00657 (12)	0·01625 (30)	0·00698 (11)	−0·00263 (32)	−0·00098 (20)	0·00075 (33)
C(6)	0·00646 (12)	0·01506 (26)	0·00606(9)	−0·00095 (31)	−0·00007 (20)	0·00333 (29)
C(7)	0·00562 (10)	0·01586 (25)	0·00457 (8)	0·00023 (29)	−0·00032 (16)	0·00147 (28)
C(8)	0·01194 (20)	0·02387 (46)	0·00826 (14)	0·01173 (56)	0·00270 (31)	−0·00226 (47)
C(9)	0·01068 (18)	0·01760 (40)	0·01007 (16)	0·00082 (44)	−0·00218 (32)	−0·00494 (42)
C(10)	0·00708 (12)	0·01812 (31)	0·00581 (10)	0·00153 (36)	−0·00252 (19)	−0·00053 (31)
C(11)	0·00620 (11)	0·01682 (30)	0·00484 (8)	−0·00174 (31)	0·00012 (18)	−0·00021 (27)
N(12)	0·00958 (14)	0·02618 (43)	0·00826 (13)	0·00205 (43)	−0·00611 (24)	0·00154 (37)
N(13)	0·01041 (14)	0·02385 (35)	0·00593 (9)	−0·00749 (41)	0·00093 (21)	0·00210 (34)
H(14)	2·00 (37)					
H(15)	3·42 (52)					
H(16)	11·58 (151)					
H(17)	3·98 (56)					
H(18)	2·32 (39)					
H(19)	2·62 (42)					
H(20)	3·16 (46)					
H(21)	5·01 (60)					
H(22)	6·70 (76)					
H(23)	1·88 (37)					

from the final cycles. The R value including all observed reflections, but including only those unobserved ones for which $|F_c|$ exceeds $|F_{\text{min}}|$, is 3.9%.

Final structural parameters and their standard deviations are given in Tables 3 and 4. Standard deviations are those obtained by inversion of the 9×9 and 4×4 matrices. The final value of $\Sigma w|\Delta F|^2/(n-s)$ is 11600/926 or over 12. This large value indicates probably that the 1% error in the time-dependent scale factor is somewhat too low and more strongly that the refinement is not finished. The largest errors in the final ΔF map were associated with the methyl groups. These are certainly undergoing large torsional oscillations or hindered rotation and to that extent have been incorrectly treated. Further change in these atoms is unlikely to affect the results described thus far, however.

Table 5 gives the magnitudes and directions of the principal axes of the heavy-atom thermal ellipsoids at the conclusion of the extended refinement procedure. Comparison of these with corresponding figures from the non-bonding refinement showed an average decrease in magnitude of about 5%, although some principal B values remained unchanged or even increased slightly. This average decrease is a proper consequence of using form factors describing a bonded electron distribution which is explicitly more diffuse than that of free atoms. The scale factor for F_{obs} increased 3% during the bonded-atom refinement.

Discussion of the structure

An illustration of the structure viewed along [010] appears in Fig. 3. It should be remembered that the positions shown for hydrogen atoms are most probable positions only. Large motion in these atoms is evident from the thermal parameters and the final difference map. The packing is apparently dominated to a high degree by C–N dipoles. Cyano group C(10)–N(12) and similar groups related by the screw axes parallel to **b** form the slightly tilted rungs of a ladder with C . . . N separations of 3.42 and 3.71 Å. The former distance is close to values usually found in stacks of aromatic rings. The C(11)–N(13) group of the same screw-axis related molecule is so arranged that C(11) is considerably closer to N(12) (3.26 Å) than is C(10). This shorter contact probably represents an aspherical van der Waals shell for the nitrogen atom rather than any unusual intermolecular interaction. All other contacts are normal. It is interesting to note, in view of the probable similarity of the structure of $C_9H_6N_2$, the unmethylated dicyanonorcaradiene, to that described here, that the methyl groups in this structure have no close contacts and thus are not determinative in packing.

Molecular dimensions are shown in Fig. 4 and interbond angles in Fig. 5. The HCH and HCC angles in the methyl groups range from 95° to 129° because of the poorly defined hydrogen positions. The variation in dimensions of three-membered rings with substituents that is found by comparing this material with 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide monohydrate (Ahmed & Gabe, 1964) is interesting to note. In the present material, two bonds are longer (1.554 and 1.558 Å) and one shorter (1.501 Å) than the C–C bonds in cyclopropane (1.510 ± 0.002 Å Bastiansen, Fritsch & Hedberg, 1964), whereas in the com-

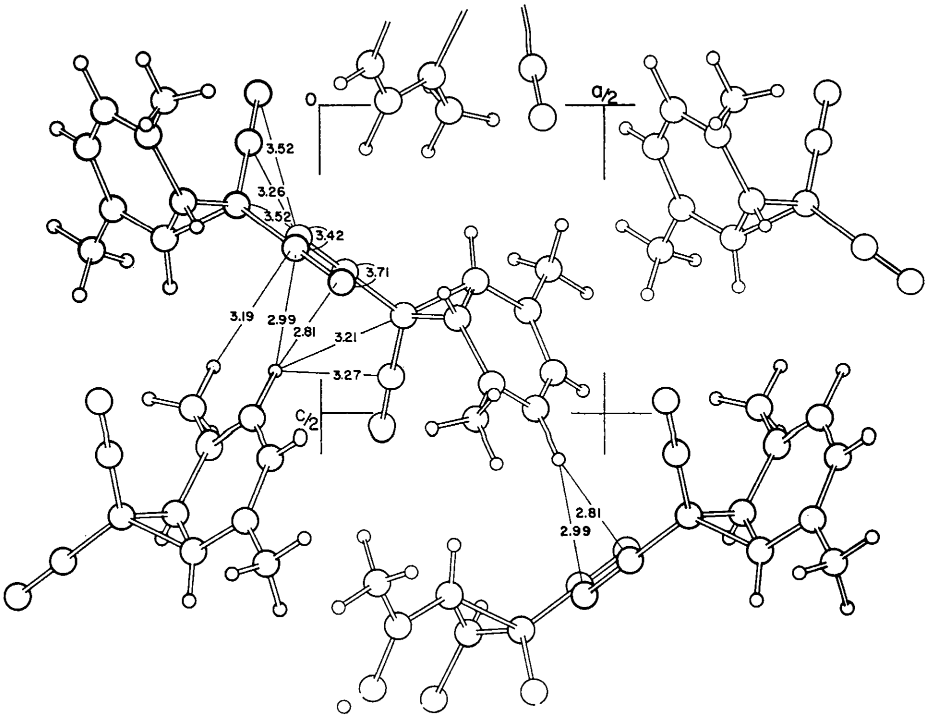

Fig. 3. A [010] view of the structure, showing the packing arrangement and intermolecular contacts. The methyl hydrogen atoms are shown in their most probable positions and in fact undergo hindered rotation or large libration.

pound studied by Ahmed & Gabe all three bonds are within ±0.006 Å of 1.520 Å. Flygare, Narath & Gwinn (1962) report that in 1,1-dichlorocyclopropane all C–C bonds are equal to 1.533±0.004 Å. The 'abnormal' bond lengths in ethylene oxide (C–C is 1.472 Å and C–O is 1.436 Å) and in ethyleneimine (C–C is 1.480 Å and C–N is 1.488 Å) (both references Sutton, 1958) also verify the variation in bond lengths in these small rings according to substituents and ring components. This variation is suggestive of a valuable probe of electronegativity or of conjugative properties of substituents. It should be noted that all bonds adjacent to the cyclopropane ring are shortened in the norcaradiene, paralleling a trend generally seen (Bent, 1961). The two C_{sp^3}–C_{sp^2} bonds average 1.480 Å *vs* the 1.510 Å average found by Brown (1959). C_{sp^3}–C_{sp} values average 1.436 Å *vs* 1.456 Å given by Brown. This shortening of external bonds is in line with the rehybridization (from sp^3) expected for the 'bent' bonds in three-membered rings (see Coulson & Moffitt, 1949, for example).

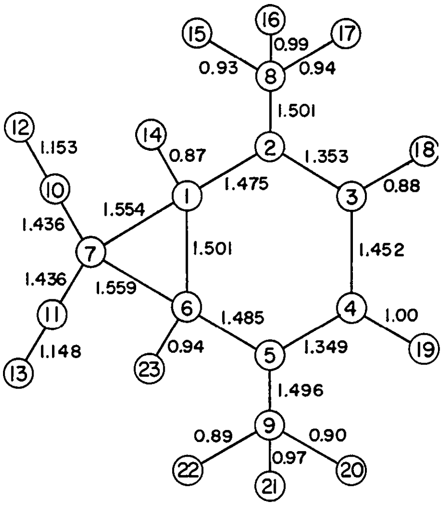

Fig. 4. Interatomic distances. Standard deviations are approximately 0·0027 Å in C–C bonds and 0·05 Å in C–H bonds.

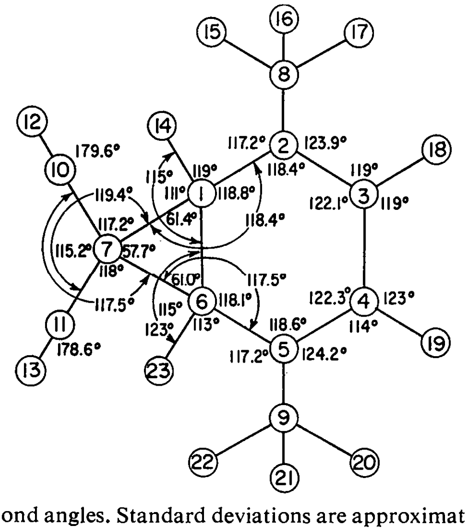

Fig. 5. Bond angles. Standard deviations are approximately 0·1° in CCC angles and 2° in CCH angles.

The three-membered ring is inclined at an angle of 71.9° to the plane of C(1), C(2), C(5), and C(6) in the present structure, compared with an analogous angle of 65.0° in the azabicyclohexane. The cyclohexadiene ring is folded at an angle of 4.2° along the C(2)–C(5) axis, with C(3) and C(4) being moved *toward* C(7). Methyl carbon atoms C(8) and C(9) are displaced in the opposite direction so that they are 0.06–0.11 Å from the plane defined by either half of the cyclohexadiene ring. Several least-squares planes (Blow, 1960) and deviations from them of pertinent atoms are listed in Table 6. The molecule exhibits small but significant distortions from C_s symmetry; these are probably caused by the asymmetric environment.

Table 6. *Various least-squares planes with contributing weights W and deviations Δ*

Plane 1: $0·74732\,x+0·48845\,y-0·45048\,z=1·0145$
2: $0·72803\,x+0·49182\,y-0·47758\,z=0·8177$
3: $0·77314\,x+0·47290\,y-0·42263\,z=1·2290$

	W_1	Δ_1	W_2	Δ_2	W_3	Δ_3
C(1)	6	−0·052 Å	6	−0·004 Å		−0·101 Å
C(2)	6	−0·006	6	0·002	6	0·001
C(3)	6	−0·052		−0·085	6	−0·002
C(4)	6	−0·040		−0·082	6	0·002
C(5)	6	0·007	6	−0·002	6	−0·001
C(6)	6	−0·034	6	0·004		−0·091
C(8)	6	0·095		0·114		0·109
C(9)	6	0·081		0·064		0·064
H(18)		−0·082		−0·138		0·001
H(19)		−0·022		−0·095		0·051

Plane 4: $0·38390\,x-0·38405\,y+0·83972\,z=3·8444$
5: $0·21923\,x-0·85571\,y-0·46872\,z=-2·1197$

	W_4	Δ_4	W_5	Δ_5
C(1)	6	0 Å		0·704 Å
C(6)	6	0		−0·796
C(7)	6	0	6	−0·005
C(10)		−1·223	6	0·002
C(11)		1·201	6	0·009
N(12)		−2·206	7	−0·001
N(13)		2·168	7	−0·004

Some remarks about the accuracy of the measurements of bonds and especially of the cyclopropane bent bonds seem in order. The π-bonds associated with C(2)–C(3), C(4)–C(5), and the cyano groups could not be seen; it is also doubtful that use of different σ-bond form factors for the various C–C bonds and the C–N bonds would be significant in the present case. Effects of thermal motion are quite large compared with the bonding effect, and it seems that it would be necessary to use data collected at much lower temperatures before such details as exact hybridization and π-bonds (of lower electron density than σ-bonds) could be measured accurately. On the other hand, considerable improvement in the difference function (ϱ_o–ϱ_c) and in the R value followed introduction of σ-bonds, bent in the case of the cyclopropane ring. Observation of at least the gross presence of these bonds seems certain. A limit of 20 ± 10° for bending of the cyclopropane bonds seems reasonable. It might reasonably be argued that bending will not be equal in all bonds. The simplest case of equal bending is all that can be considered with the present data. Bending of less than 20° in one or two bonds would require greater bending in the remainder, to accord with the difference map.

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Thermal Expansion of the Alkali Metal Azides

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The lattice parameters of potassium and sodium azide have been determined as a function of temperature by X-ray diffraction. For potassium azide (tetragonal) the lattice constants at room temperature are significantly higher than those obtained by Hendricks & Pauling. The coefficients of thermal expansion are sensibly constant over the temperature range 20 °C to 340 °C. The expansion coefficient along the *c* axis is more than twice as large as the coefficient along the *a* axis. A sample of potassium azide (KN_3) heated at 360 °C gave a diffraction pattern consistent with a cubic structure (lattice parameter 9·6 Å) which is attributed to potassium nitride (K_3N).

The room temperature diffraction pattern of sodium azide is consistent with a monoclinic *C*-face-centred lattice, which can however be referred to a pseudo-rhombohedral unit cell close to that described by Hendricks & Pauling. Above room temperature (about 22 °C) the structure is rhombohedral. In the temperature range – room temperature to 100 °C – the coefficient of thermal expansion in the direction in which anions and cations alternate is 2·3 times the expansion coefficient in the direction in which they do not. This ratio is very close to that found for potassium azide.

POTASSIUM AZIDE

Introduction

Detailed information is now available on a number of the physical properties of the inorganic azides (Gray, 1963). It seems that the alkali metal azides, and to some extent the alkaline earth azides, are typical ionic solids, the atomic structure and the optical and electrical properties of both perfect and irradiated crystals being closely analogous to those of the alkali halides. The other azides are much less stable and show evidence of a large degree of covalent bonding.

The alkali metal azides thus provide a convenient example of an ionic structure in which one of the ions is aspherical. Since the study of the lattice dynamics of simple ionic structures containing spherical ions is in a fairly advanced state, it would be interesting to see what differences the presence of a non-spherical ion would make. Apart from measurements of infrared absorption (Bryant, 1963, 1964) no detailed data on this aspect of the azides appear to have been published.

The present work was undertaken to try to throw light on this point through measurements of thermal expansion, as well as to clarify certain points concerning polymorphic transitions, and the effect of irradiation on the lattice constants. The results could also be of interest in connection with decomposition studies of the azides.