# The Crystal and Molecular Structure of 1,2,3,4-Tetrachloro-5,6-di-n-propylcalicene*

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1,2,3,4-Tetrachloro-5,6-di-n-propylcalicene, $C_{14}H_{14}Cl_4$, a stable derivative of a new non-benzenoid aromatic compound, calicene, forms orthorhombic colourless needle crystals of space group *Pnam*, with four molecules in the unit cell of dimensions: $a = 23\cdot056$, $b = 9\cdot150$, $c = 7\cdot017$ Å. The structure was solved by direct methods and was refined by the least-squares method. The final $R$ value is $0\cdot073$ for the observed *hkl* reflexions. The molecule has essentially *mm*2 symmetry, including the propyl groups. In the calicene nucleus a considerable bond localization, but with some contribution of the dipolar resonance form, is observed and this is consistent with the evidence based on the nuclear magnetic resonance and dipole moment. Some short intermolecular contacts are found.

## Introduction

In the series of hydrocarbons with a cyclic cross-conjugated π-bond system, cyclopropenylidenecyclopentadiene (calicene) (I), has not yet been synthesized (Prinzbach, 1964). This type of hydrocarbon would be especially interesting because a significant contribution of the resonance form (I*a*) is to be expected as a result of the well-known tendency of unsaturated three- and five-membered rings to carry positive and negative charges respectively (Roberts, Streitwieser & Regan, 1952). The localization energies have been calculated
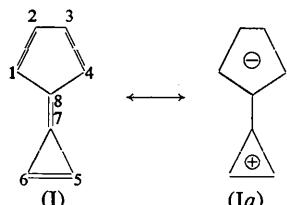


by various methods (Chalvet, Daudel & Kaufman, 1964). Recent semi-empirical SCF MO calculations have led to the conclusion that the resonance energy of calicene is negligibly small and that it is of essentially a polyolefin form (I) (Dewar & Gleicher, 1965; Nakajima, Kohda, Tajiri & Karasawa, 1967).

On the other hand, syntheses of a number of derivatives of calicene have been reported (Ueno, Murata & Kitahara, 1965; Kende & Izzo, 1965*a*; Kende & Izzo,

1965*b*; Prinzbach, Seip & Fischer, 1965; Jones & Pyron, 1965; Prinzbach & Fischer, 1965; Bergmann & Agranat, 1965; Kitahara, Murata, Ueno, Sato & Watanabe, 1966; Bergmann & Agranat, 1966; Prinzbach & Fischer, 1966; Prinzbach, Fischer & Cruse, 1966; Kende, Izzo & McGregor, 1966; Kende, Izzo & Fulmor, 1966). The derivatives having one or more electron-withdrawing substituents on the five-membered ring are generally stable and were found to show a considerable degree of cyclopropenium-cyclopentadienide aromatic character in nuclear magnetic resonance studies (Kende, Izzo, & McGregor, 1966; Kende, Izzo, & Fulmor, 1966). 1,2,3,4-Tetrachloro-5,6-diphenylcalicene (II*a*) and 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene (II*b*) synthesized by two of the present authors (I. M.&Y. K.) have been studied from the organic and physico-chemical points of view (Ueno, Murata & Kitahara, 1965; Kitahara, Murata, Ueno, Sato & Watanabe 1966; Murata, Ueno, Kitahara & Watanabe, 1966).



R = Ph          (II*a*)
R = n-C₃H₇      (II*b*)
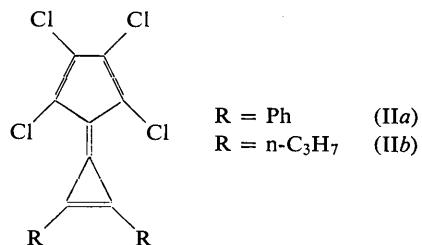
These derivatives are very stable. The propyl derivative (II*b*) was selected for the present study, because this one seemed to be the most similar to calicene itself (I) with respect to the π-electron system. The determination of the precise molecular dimension would also

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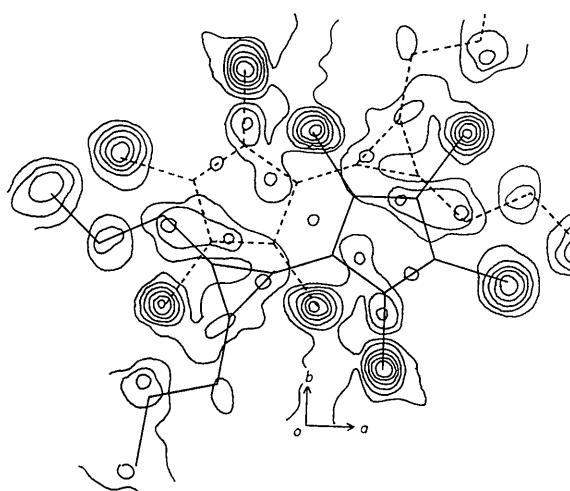
Fig. 1. The first electron density projection along the $c$ axis. The map was computed with only 82 reflexions whose signs were obtained by direct methods. The contours are at equal intervals on an arbitrary scale. The final skeleton of the molecule is superimposed. The molecule drawn with broken lines is displaced half-period down the $c$ axis.

throw light on the nature of the highly strained cyclopropenylidene ring.

A preliminary report on the structure has already been published (Shimanouchi, Ashida, Sasada, Kakudo, Murata & Kitahara, 1967).

## Experimental

1,2,3,4-Tetrachloro-5,6-di-n-propylcalicene crystallizes in the form of colourless needles elongated along the $c$ axis.

Crystallographic and physical data obtained are: 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene, $C_{14}H_{14}Cl_4$; m.p. $180°C$ (decomp.); orthorhombic, $a = 23.056 \pm 0.015$, $b = 9.150 \pm 0.007$, $c = 7.017 \pm 0.002$ Å. Absent spectra, $0kl$ when $k + l$ is odd and $h0l$ when $h$ is odd. Space group, $Pna2_1$ or $Pnam$. Four molecules per unit cell. Volume of the unit cell, $1480.3$ Å$^3$. Density (by flotation), $1.438$ g.cm$^{-3}$. Density (calculated), $1.454$ g.cm$^{-3}$. Linear absorption coefficient for Mo $K\alpha$ radiation, $\mu = 7.67$ cm$^{-1}$. Total number of electrons per unit cell, $F(000) = 664$.

The intensities of all reflexions with $2\theta \le 54°$ were measured with a proportional counter, using Mo $K\alpha$ radiation filtered through a Zr metal foil. The crystal,

## Table 1. *Final atomic coordinates and temperature factors*

The anisotropic temperature factors are expressed in the form

$$\exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\}.$$

|  | $x/a$ | $y/b$ | $z/c$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cl(1) | −0.0069 | 0.7116 | 0.25 | 0.00247 | 0.01204 | 0.03418 | 0.00140 | 0.0 | 0.0 |
| Cl(2) | 0.1395 | 0.7161 | 0.25 | 0.00243 | 0.01821 | 0.03804 | −0.00494 | 0.0 | 0.0 |
| Cl(3) | 0.1882 | 0.3668 | 0.25 | 0.00130 | 0.02564 | 0.03667 | 0.00122 | 0.0 | 0.0 |
| Cl(4) | 0.0712 | 0.1396 | 0.25 | 0.00230 | 0.01308 | 0.03622 | 0.00206 | 0.0 | 0.0 |
| C(1) | 0.0375 | 0.5613 | 0.25 | 0.00211 | 0.01070 | 0.02433 | 0.00031 | 0.0 | 0.0 |
| C(2) | 0.0965 | 0.5649 | 0.25 | 0.00175 | 0.01481 | 0.02308 | −0.00365 | 0.0 | 0.0 |
| C(3) | 0.1171 | 0.4151 | 0.25 | 0.00150 | 0.01736 | 0.02516 | −0.00052 | 0.0 | 0.0 |
| C(4) | 0.0704 | 0.3257 | 0.25 | 0.00155 | 0.01525 | 0.02245 | 0.00001 | 0.0 | 0.0 |
| C(5) | −0.0772 | 0.2490 | 0.25 | 0.00164 | 0.01233 | 0.02739 | −0.00098 | 0.0 | 0.0 |
| C(6) | −0.0976 | 0.3838 | 0.25 | 0.00151 | 0.01270 | 0.02284 | −0.00084 | 0.0 | 0.0 |
| C(7) | −0.0378 | 0.3640 | 0.25 | 0.00154 | 0.01071 | 0.02132 | −0.00036 | 0.0 | 0.0 |
| C(8) | 0.0183 | 0.4135 | 0.25 | 0.00159 | 0.01277 | 0.01935 | 0.00087 | 0.0 | 0.0 |
| C(9) | −0.0877 | 0.0909 | 0.25 | 0.00203 | 0.01006 | 0.03775 | 0.00177 | 0.0 | 0.0 |
| C(10) | −0.1508 | 0.0498 | 0.25 | 0.00207 | 0.01373 | 0.04217 | −0.00172 | 0.0 | 0.0 |
| C(11) | −0.1616 | −0.1133 | 0.25 | 0.00305 | 0.01329 | 0.04606 | −0.00273 | 0.0 | 0.0 |
| C(12) | −0.1452 | 0.4901 | 0.25 | 0.00153 | 0.01294 | 0.02987 | 0.00024 | 0.0 | 0.0 |
| C(13) | −0.2052 | 0.4193 | 0.25 | 0.00139 | 0.01336 | 0.04084 | 0.00100 | 0.0 | 0.0 |
| C(14) | −0.2530 | 0.5319 | 0.25 | 0.00178 | 0.01739 | 0.04113 | 0.00297 | 0.0 | 0.0 |

|  | $x/a$ | $y/b$ | $z/c$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H(1) | −0.0692 | 0.0494 | 0.3642 | 5.06 |
| H(2) | −0.0692 | 0.0494 | 0.1358 | 5.06 |
| H(3) | −0.1705 | 0.0904 | 0.3657 | 5.42 |
| H(4) | −0.1705 | 0.0904 | 0.1343 | 5.42 |
| H(5) | −0.1434 | −0.1544 | 0.3652 | 6.47 |
| H(6) | −0.1434 | −0.1544 | 0.1348 | 6.47 |
| H(7) | −0.2014 | −0.1359 | 0.25 | 5.63 |
| H(8) | −0.1410 | 0.5520 | 0.3647 | 5.09 |
| H(9) | −0.1410 | 0.5520 | 0.1353 | 5.09 |
| H(10) | −0.2068 | 0.3591 | 0.3658 | 5.00 |
| H(11) | −0.2068 | 0.3591 | 0.1342 | 5.00 |
| H(12) | −0.2489 | 0.5926 | 0.3635 | 5.51 |
| H(13) | −0.2489 | 0.5926 | 0.1365 | 5.51 |
| H(14) | −0.2919 | 0.4835 | 0.25 | 5.63 |

with dimensions of $0.06 \times 0.15 \times 0.20$ mm, was mounted on a single-crystal orienter of a General Electric XRD–5 Spectrogoniometer. The intensity of each reflexion was counted for 20 sec with a stationary-counter and stationary-crystal technique (Furnas, 1957). The background count was plotted as a function of $2\theta$ and each reflexion was corrected from this curve. Of these 1747 independent reflexions, 632 were recorded as having zero intensity, while the others ranged in relative intensities from 1 to 33000. The corrections for Lorentz and polarization factors were made in the usual way but that for absorption was omitted.

## Structure determination

Systematic absences showed that the space group is either $Pna2_1$ or $Pnam$. Pyroelectricity tests for the crystals did not give any positive result. Moreover, the statistical investigation of the intensity data for the $h0l$ zone showed that the crystal should be centrosymmetric (Howells, Phillips & Rogers, 1950). The values of the statistical averages for $\langle|E|\rangle$ and $\langle|E^2-1|\rangle$ for $hkl$ reflexions were 0.632 and 1.089 repectively as compared with 0.798 and 0.968, the theoretical values for centrosymmetric space groups (Karle & Karle, 1964). The space group was therefore chosen to be $Pnam$ for

the subsequent analysis. There are four molecules in the unit cell of this space group and the molecule must include a crystallographic mirror plane.

The sharpened Patterson function, $P(uvw)$, was calculated. Patterson peaks were found only on the two sections, $w=0$ and $w=\frac{1}{2}$, which implied that the molecule was planar as a whole and that the molecular plane coincided with the crystallographic mirror plane. This was confirmed by the fact that the unitary structure factors, $|U(00l)|$, were found to be unity.

The trial for interpreting the Patterson function failed to locate the four chlorine atoms owing to the heavy overlapping of peaks as a result of high crystallographic symmetry. A similar observation has been reported in the case of 1,2,3,4-tetrachlorobenzo[g]sesquifulvalene (Nishi, Sasada, Ashida & Kakudo, 1966).

In the next attempt, direct sign-determination methods were applied to the $F(hk0)$'s (Woolfson, 1961). The origin of the unit cell was specified by assigning positive signs to the following two linearly-independent reflexions having large $|U|$ values:

| $h$ | $k$ | $l$ | $|U|$ | Sign |
|-----|-----|-----|-------|------|
| 13  | 7   | 0   | 0.40  | +    |
| 19  | 6   | 0   | 0.44  | +    |

By the use of the Harker–Kasper inequality relation-

Table 2. *Estimated standard deviations*

[$\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ in Å, $\sigma(B)$ in Å$^2$.]

|       | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ | $\sigma(B_{11})$ | $\sigma(B_{22})$ | $\sigma(B_{33})$ | $\sigma(B_{12})$ | $\sigma(B_{13})$ | $\sigma(B_{23})$ |
|-------|------------|------------|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cl(1) | 0.0019 | 0.0018 | 0.0 | 0.00004 | 0.00023 | 0.00056 | 0.00016 | 0.0 | 0.0 |
| Cl(2) | 0.0020 | 0.0022 | 0.0 | 0.00004 | 0.00032 | 0.00064 | 0.00019 | 0.0 | 0.0 |
| Cl(3) | 0.0016 | 0.0025 | 0.0 | 0.00003 | 0.00040 | 0.00063 | 0.00018 | 0.0 | 0.0 |
| Cl(4) | 0.0018 | 0.0018 | 0.0 | 0.00004 | 0.00023 | 0.00060 | 0.00017 | 0.0 | 0.0 |
| C(1)  | 0.0063 | 0.0065 | 0.0 | 0.00014 | 0.00082 | 0.00179 | 0.00058 | 0.0 | 0.0 |
| C(2)  | 0.0061 | 0.0069 | 0.0 | 0.00013 | 0.00097 | 0.00172 | 0.00062 | 0.0 | 0.0 |
| C(3)  | 0.0061 | 0.0073 | 0.0 | 0.00012 | 0.00108 | 0.00182 | 0.00063 | 0.0 | 0.0 |
| C(4)  | 0.0059 | 0.0068 | 0.0 | 0.00011 | 0.00097 | 0.00169 | 0.00060 | 0.0 | 0.0 |
| C(5)  | 0.0058 | 0.0067 | 0.0 | 0.00012 | 0.00085 | 0.00181 | 0.00057 | 0.0 | 0.0 |
| C(6)  | 0.0057 | 0.0064 | 0.0 | 0.00011 | 0.00088 | 0.00166 | 0.00054 | 0.0 | 0.0 |
| C(7)  | 0.0055 | 0.0061 | 0.0 | 0.00011 | 0.00079 | 0.00160 | 0.00052 | 0.0 | 0.0 |
| C(8)  | 0.0057 | 0.0063 | 0.0 | 0.00012 | 0.00087 | 0.00152 | 0.00055 | 0.0 | 0.0 |
| C(9)  | 0.0065 | 0.0064 | 0.0 | 0.00014 | 0.00083 | 0.00239 | 0.00058 | 0.0 | 0.0 |
| C(10) | 0.0070 | 0.0074 | 0.0 | 0.00015 | 0.00102 | 0.00265 | 0.00068 | 0.0 | 0.0 |
| C(11) | 0.0083 | 0.0075 | 0.0 | 0.00020 | 0.00107 | 0.00307 | 0.00079 | 0.0 | 0.0 |
| C(12) | 0.0060 | 0.0067 | 0.0 | 0.00012 | 0.00092 | 0.00198 | 0.00057 | 0.0 | 0.0 |
| C(13) | 0.0060 | 0.0070 | 0.0 | 0.00012 | 0.00094 | 0.00257 | 0.00059 | 0.0 | 0.0 |
| C(14) | 0.0068 | 0.0080 | 0.0 | 0.00014 | 0.00117 | 0.00263 | 0.00070 | 0.0 | 0.0 |

|       | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ | $\sigma(B)$ |
|-------|------------|------------|------------|------------|
| H(1)  | 0.0438 | 0.0476 | 0.0501 | 1.35 |
| H(2)  | 0.0438 | 0.0476 | 0.0501 | 1.35 |
| H(3)  | 0.0459 | 0.0477 | 0.0525 | 1.44 |
| H(4)  | 0.0459 | 0.0477 | 0.0525 | 1.44 |
| H(5)  | 0.0487 | 0.0506 | 0.0541 | 1.58 |
| H(6)  | 0.0487 | 0.0506 | 0.0541 | 1.58 |
| H(7)  | 0.0721 | 0.0773 | 0.0 | 0.01 |
| H(8)  | 0.0440 | 0.0472 | 0.0495 | 1.37 |
| H(9)  | 0.0440 | 0.0472 | 0.0495 | 1.37 |
| H(10) | 0.0440 | 0.0468 | 0.0521 | 1.37 |
| H(11) | 0.0440 | 0.0468 | 0.0521 | 1.37 |
| H(12) | 0.0470 | 0.0483 | 0.0507 | 1.45 |
| H(13) | 0.0470 | 0.0483 | 0.0507 | 1.45 |
| H(14) | 0.0722 | 0.0782 | 0.0 | 0.01 |

Table 3. *Observed and calculated structure factors*

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  L  FO  FC        L  FO  FC        L  FO  FC        L  FO  FC        L  FO  FC        L  FO  FC        L  FO  FC        L  FO  FC

H,K= 0 0        0  13  12        0   9  -8        2   7  -7        0   0  -5        6   0  -1        3   0   4        0   7   4
2 323-422       1  72  20        1  24  24        3   6  -6        1   9   8        7   0   0        4   0   1        0  26 -26
4 159 172       2  11 -10        2   8   8        4   3   4        2   5   5        8   0   1        5   0  -2        1  44  44
6  71 -70       3  15 -14        3  19 -18        5   4   3        3   0  -2      H,K= 22 2         6   0   0        2  19  20
8  29  25       4   8   6        4   7  -5      H,K= 25 1         4   0  -3        1   3   1      H,K= 21 3         3  30 -30
H,K= 2 0        H,K= 28 0        5  10  10        0   6   6        5   0   1        2  10  11        0  26  25        4  10 -10
0  81  78       0  15  11        6   3   2        1   8  -8        6   0   1        3   0  -1        1   0   3        5  16  16
1  61 -61       1   4  -2        7   3  -4        2   6  -5        7   0   0        4   5  -6        2  22 -21        6   0   3
2  63 -69       2  11 -10        8   0   0        3   5   5        H,K= 10 2       5   4  -3        3   5  -2        7   5  -7
3  51  56       H,K= 0 1        H,K= 12 1         4   0   3        0  19 -18        6   0   2        4  12  12        8   0   0
4  37  39       1  53 -54        1   4  -3      H,K= 26 1         1  15 -13      H,K= 23 2         5   0   0        H,K= 8 4
5  25 -26       3  26  27        2  30  29        0   0   2        2  11  11        0  22  23        H,K= 22 3         0  86  84
6  18 -18       5  11 -12        3   0   2        1  15 -13        3   7   7        1   8  -9        0   0   1        1   7  -8
7  10   9       7   6   5        4  16 -16        2   3  -2        4   2  -5        2  15 -17        1   5  -6        2  66 -67
8   8   8       H,K= 1 1        5   0  -1        3   7   7        5   3   1        3   3   2        2   0  -1        3   4   5
H,K= 4 0        0  85 -83        6   8   6        4   0   1        6   0   2        4   9   9        3   3   4        4  37  37
0  62 -62       1  30  30        7   0  -1        5   0  -5        7   0   0        5   0   0        4   0   1        5   0  -2
1  23 -23       2  61  63        8   0  -1        6   0   0        8   0   0        6   0  -3        H,K= 23 3         6  16 -15
2  37  38       3  18 -19        H,K= 13 1       H,K= 27 1         H,K= 11 2       7   0   0        0   0   0        7   0   0
3   0   4       4  31 -31        0  58  56        1   9   8        0  34  32        8   0   1        1   9 -11        8   4   4
4  14 -14       5   7   8        1  22  21        2   0   4        1  15  15        H,K= 24 2         2   3   0        H,K= 9 4
5   0   0       6  15  15        2  44 -43        3   7  -6        2  31 -30        0   0  -1        3   5   7        0  31  28
6   4   5       7   3  -2        3  13 -13        H,K= 28 1         3  11 -11        1   0   0        4   0   0        1  32  31
7   3   1       8   7  -7        4  25  24        0  11 -13        4  19  19        2   0   1        5   0  -3        2  22 -21
8   0  -1       H,K= 2 1        5   5   7        1   0   0        5   4   5        3   0   0        H,K= 24 3         3  20 -20
H,K= 6 0        0  16  15        6  13 -10        2  11  11        6   7  -7        4   0  -1        0   5   7        4  12  11
0  33  31       1   0  -1        7   0  -3        H,K= 29 1         7   0  -1        H,K= 25 2         1   5   9        5  10  10
1  15 -14       2   9 -10        8   0   3        0   0   3        8   0   2        0   0  -4        2   3  -6        6   6  -5
2  21 -22       3   0  -2        H,K= 14 1       1   0  -1        H,K= 12 2       1   0   0        3   3  -6        7   3  -5
3   8   8       4   3   3        0   2   3        H,K= 0 2         0  18 -17      H,K= 10 3         4   0   0        H,K= 10 4
4   9  10       5   0   1        1  21  22        0  17 -18        1  54 -51        0  11  12        H,K= 25 3         0  26 -23
5   0  -4       6   0  -1        2   0  -2        2  25  25        2  18  15        1  36 -34        0   0  -3        1  43 -44
6   3  -3       7   0   0        3  16 -15        4  18 -18        3  34  33        2  11 -12        1   3   7        2  19  19
7   0   1       8   0   0        4   0   1        6   8   7        4  10 -10        3  20  19        2   0   3        3  28  28
8   0   0       H,K= 3 1        5   6   7        8   0  -1        5  17 -17        4   7   7        3   0  -5        4  10 -10
H,K= 8 0        0  12  12        6   0  -1        H,K= 1 2         6   5   5        5  10  -9        4   0  -1        5  13 -14
0  15 -12       1  40  39        7   0  -2        0   4  -4        7   7   7        6   3  -2        H,K= 26 3         6   5   4
1  14  14       2  10  -9        H,K= 15 1       1  24 -24        8   0  -2        7   0   4        0   6  10        7   3   5
2  10   9       3   8  -9        0   0   0        2   2   4        H,K= 13 2       8   0  -3        1   0  -2        H,K= 11 4
3   4  -5       4   4   5        1  10 -10        3  10  12        0  37  36        H,K= 11 3         2   5  -8        0  29 -28
4   0  -4       5   0   2        2   3   3        4   0  -2        1  70 -69        0  15  17        3   0   1        1   0   0
5   0   2       6   0  -1        3   9   7        5   5  -4        2  27 -27        1  11   9        H,K= 27 3         2  21  20
6   0   1       7   0  -1        4   0   2        6   0   0        3  46  46        2  12 -13        0   4   4        3   0   1
7   0   0       8   0   0        5   0  -4        7   0   2        4  13  13        3   4  -5        1   0   1        4   9 -10
8   0   0       H,K= 4 1        6   0  -2        8   0   0        5  23 -23        4   6   7        2   0  -4        5   0   0
H,K= 10 0       0   0   2        7   0   1        H,K= 2 2         6   6  -5        5   0   3        H,K= 28 3         6   0   3
0  16  14       1  23  23        H,K= 16 1       0  71 -70        7   9   9        6   3  -3        0   0  -4        7   0   0
1  22  23       2   0  -1        0   2  -4        1  63  65        H,K= 14 2       7   3  -2        1   0   0        H,K= 12 4
2  17 -16       3  14 -15        1   6  -9        2  47  49        0  46 -46        H,K= 12 3         2   0   0        0   3  -2
3  16 -16       4   0   0        2   2   3        3  29 -30        1  19 -19        0  23  23        3   0   2        1   0   5
4  11  12       5   6   6        3   5   6        4  22 -22        2  40  38        1   8   6        H,K= 0 4         2   0   1
5   7   8       6   0   0        4   0  -3        5  11  11        3  14  13        2  18 -18        0  56 -54        3   0  -3
6   3  -5       7   0   0        5   3  -3        6   8   8        4  24 -23        3   2  -4        2  37  37        4   9   8
7   0  -2       8   0   0        6   0   2        7   3  -3        5   7  -7        4  10  10        4  19 -18        5   0   1
8   0   2       H,K= 5 1        7   0   0        8   0  -2        6  11  11        5   0   0        6   8   9        6   0   2
H,K= 12 0       0  61 -60        H,K= 17 1       H,K= 3 2         7   3   3        6   3  -4        8   0  -4        7   0  -2
0  44  44       1  64 -64        0  10  10        0  71 -72        8   0   3        7   0   0        H,K= 1 4         H,K= 13 4
1   4   3       2  41  42        1   0  -1        1  67 -68        H,K= 15 2       H,K= 13 3         0  28  26        0  15 -14
2  33 -34       3  29  32        2   7  -7        2  53  54        0  29 -28        0  15 -16        1  27  28        1  22  19
3   3  -6       4  19 -19        3   0   0        3  35  36        1  15 -14        1  10  10        2  13 -14        2  12  11
4  18  18       5  11 -12        4   4   4        4  28 -28        2  23  22        2  11  12        3  22 -22        3  16 -15
5   0   2       6   8   7        5   0   0        5  14 -14        3  10  10        3   5  -7        4   0   4        4   4  -6
6   7  -7       7   3   3        6   0  -2        6  12  11        4  12 -11        4   5  -7        5  10  10        5   7   8
7   0   0       8   0  -2        7   0   0        7   5   4        5   6  -5        5   5   4        6   0  -1        6   0   3
8   0   2       H,K= 6 1        H,K= 18 1       8   3  -4        6   6   4        6   0  -1        7   0  -3        7   0  -2
H,K= 14 0       0  76 -77        0  50 -49        H,K= 4 2         7   0   2        7   0   3        8   0  -1        H,K= 14 4
0  47  46       1 107 109        1  16  15        0  10  -9        H,K= 16 2       H,K= 14 3         H,K= 2 4         0  25  25
1  52  51       2  61  63        2  43  42        1  58 -58        0  29 -29        0  30  29        0  15  15        1   4  -6
2  35 -35       3  61 -62        3  11 -12        2   5   5        1  18  19        1  30 -30        1  27  28        2  20 -21
3  34 -34       4  32 -33        4  27 -26        3  32  33        2  26  24        2  25 -24        2  13 -14        3   3   3
4  18  18       5  28  27        5   6   6        4   0  -2        3  12 -12        3  20  20        4   0   4        4  13  13
5  17  16       6  13  12        6  14  13        5  14 -14        4  15 -15        4  15  14        6   0  -1        5   0   0
6   7  -7       7  11 -10        7   0  -2        6   0   1        5   6   6        5  10  -9        7   0  -3        6   5  -6
7   5  -5       8   3  -3        H,K= 19 1       7   5   4        6   9   7        6   0  -6        8   0   2        7   0   0
H,K= 16 0       H,K= 7 1        0   3   2        8   0   0        7   0  -2        7   0   0        H,K= 13 4         H,K= 15 4
0  33  31       0  30 -30        1   3  -4        H,K= 5 2         H,K= 17 2       H,K= 15 3         0  15 -14        0   6   7
1  13  -6       1  40  38        2   0  -2        0  27 -27        0  31  30        0  15  13        1  27  28        1  26  28
2  24 -25       2  23  22        3   0   3        1  74  74        1   5   5        1   7   6        2  13 -14        2   5  -5
3   6   6       3  18 -17        4   3   1        2  22  23        2  26 -25        2   4  -5        3  22 -22        3  20 -20
4  14  14       4  12 -11        5   0  -1        3  36 -39        3   5  -4        3  11 -11        4   0   4        4   0   2
5   3  -3       5   6   7        6   0   0        4  12 -13        4  16  16        4   0   3        5  10  10        5  10  10
6   6  -5       6   0   5        7   0  -2        5  14  16        5   3  -2        5   5   5        6   0  -1        6   0  -1
7   0   1       7   0  -2        H,K= 20 1       6   4   5        6   8  -9        6   0   1        7   0  -3        7   0   3
H,K= 18 0       8   3  -1        0  23 -23        7   5  -5        7   0   0        7   0  -3        8   0  -1        H,K= 16 4
0  49 -43       H,K= 8 1        1  23  22        8   6  -9        H,K= 18 2       H,K= 16 3         H,K= 4 4         0   3  -2
1  42 -43       0   2   2        2  21  20        H,K= 6 2         0   0   0        0  14 -13        0  25  25        1  20  20
2  36  35       1 142 144        3  17 -16        0  36 -36        1  10 -11        1  23 -23        1   4  -6        2   0  -3
3  30  30       2   3  -5        4  14 -13        1  56 -54        2   0   0        2  11  11        3  14 -15        3  23 -23
4  23 -21       3  83 -81        5  10   9        2  26  26        3   7   8        3  17  17        4  -5  -6        4   0   2
5  16 -16       4   2   4        6   8   7        3  31  31        4   0   0        4   5  -7        5   9   9        5  11  13
6  11   9       5  38  37        H,K= 21 1       4  14 -13        5   3  -3        5   0   9        6   0   0        6   0  -1
7   5   7       6   0  -1        0  20 -21        5  14 -14        6   0   0        6   9  10        7   0  -3        H,K= 18 4
H,K= 20 0       7  16 -14        1   8  -8        6   4   5        H,K= 19 2       7   7  -9        H,K= 5 4         0   3   4
0  16  10       8   0   0        2  17  17        7   6   5        0  10   9        H,K= 17 3         0   6   7        1  31  32
1  23  22       H,K= 9 1        3   5   5        8   0  -1        1   5   5        0   0   0        1   7  10        2   0  -3
2   7  -8       0  46 -46        4  10 -10        H,K= 7 2         2   7  -8        1  12 -13        2   9 -10        3  23 -23
3  15 -15       1  10  -9        5   0  -2        0  13  14        3   3   5        2   0   4        3   0  -2        4   0   2
4   3   4       2  30  30        6   4   4        1  10 -10        4   7   7        3   7   9        4   0   1        5  11  13
5   8   6       3   2   2        H,K= 22 1       2  14 -13        5   0  -3        4   0  -6        5   6  10        6   0  -1
6   0  -1       4  11 -13        0  12 -11        3   4   4        6   0  -5        5   0   6        6   0  -1        H,K= 19 4
H,K= 22 0       5   0  -1        1  16  16        4   9   9        H,K= 20 2       6   0  -2        7   0   0        0   7  -8
0  10   6       6   7   6        2  10   9        5   0  -3        0  11  10        H,K= 18 3         H,K= 6 4         1   0   3
1   7  -4       7   0   0        3  12 -11        6   0  -5        1  16 -15        0  33 -34        0   3  -2        2   7   7
2   3  -5       8   0  -2        4   5  -6        H,K= 8 2         2   8  -0        1   8   9        1  20  20        3   0  -2
3   3   3       H,K= 10 1       5   5   5        0  11  10        3  10  11        2  29  29        2   0   2        4   0  -3
4   0   3       0  46  46        H,K= 23 1       1  16 -15        4   5  -5        3   5  -6        3  14 -15        5   0   1
5   0  -1       1  28 -27        0   3   2        2   8  -9        5   5  -5        4  19 -19        4   4  -5        6   0   0
H,K= 24 0       2  38 -38        1  12  11        3  10  11        6   0  -2        5   0   3        5   9   9
0  14 -12       3  13  12        2   0  -2        4   5   5        H,K= 21 2       6   9  10        6   0   0
1  11   9       4  22  20        3   0  -8        5   5  -5        0   0  -2        7   7  -9        7   0  -3
2  10  10       5   3  -5        4   0   1        6   0  -2        1   5   7        H,K= 20 3         H,K= 7 4
3   6  -7       6   9  -8        5   9  -8        H,K= 9 2         2   0  -2        0   0  -4        0   6   6
4   6  -6       7   0   1        H,K= 24 1       0  11 -12        3   5  -5        1   0  -6        1   0   4
5   4   4       8   4   2        0   8   8        1  22  21        4   0   2        2   0  -4        2   3  -4
H,K= 26 0       H,K= 11 1       1   9   9        2   9   9        5   0   2                         3   0  -3
                                                 3  10 -10                                         4   0  -3
                                                 4   5  -5                                         5   0   2
                                                 5   7   7                                         6   0  -2
                                                 6   0  -1                                         7   0   0
                                                 7   0  -1                                         H,K= 8 4
```

## Table 3 (cont.)

The table lists L, FO, FC values in eight columns, grouped by H,K headings.

**Column 1**
```
L  FO  FC
H,K= 20  4
0   9   9
1   6   6
2   7  -8
3   3  -5
4   3   5
5   0   3
H,K= 21  4
0   3  -4
1   3  -1
2   0   3
3   0   1
4   0  -2
5   0  -1
H,K= 22  4
0   9   8
1   8   8
2   5  -7
3   0  -6
4   0   4
5   0   3
H,K= 23  4
0   3  -4
1   0  -2
2   0   3
3   0   2
4   0  -2
H,K= 24  4
0   9   8
1   5  -9
2   5  -7
3   4   6
4   0   4
H,K= 25  4
0   0  -4
1   0   0
2   0   3
3   0   0
H,K= 26  4
0   4  -7
1   7  -8
2   4   6
H,K= 27  4
0   0  -1
1   0  -1
H,K= 0  5
1  66  66
3  45 -45
5  26  23
7  10 -18
H,K= 1  5
0  37 -37
1   3  -4
2  28  29
3   0   2
4  14 -15
5   0  -1
6   7   5
7   0   0
8   0   0
H,K= 2  5
0  76  72
1  25  24
2  60 -57
3  18 -18
4  32  31
5   9   9
6  13 -13
7   0  -4
8   4   4
H,K= 3  5
0   4  -5
1   8   8
2   0   5
3   0  -6
4   0  -3
5   0   3
6   0   1
7   0  -1
8   0   0
H,K= 4  5
0   9   7
1  10  10
2   6  -5
3   2  -5
4   0   3
5   0   2
6   0  -2
7   0   0
8   0   1
H,K= 5  5
0   0   2
1   0   0
2   0  -1
3   0   0
4   0   0
5   0  -1
6   0   0
7   0   0
H,K= 6  5
0  11   9
1  15 -14
2   9  -8
3   8   9
4   3  -3
5   3  -4
6   0  -2
7   0   2
H,K= 7  5
0  41 -42
```

**Column 2**
```
L  FO  FC
1  12 -13
2  32  33
3   5   7
4  19 -18
5   0  -4
6   8   7
7   0   1
H,K= 8  5
0  12 -11
1  15 -15
2   9   9
3  12  11
4   5  -6
5   6  -6
6   0   3
7   0   2
H,K= 9  5
0  11   9
1   2  -2
2   4  -7
3   0   3
4   0   3
5   0  -2
6   0  -2
7   0   1
H,K= 10  5
0  40 -36
1   2  -4
2  30  29
3   3  -2
4  18 -17
5  10   1
6   9   8
7   0   0
H,K= 11  5
0   0   4
1  20 -18
2   3  -3
3  15  14
4   3   2
5   8  -8
6   0  -1
7   0   3
H,K= 12  5
0  21 -18
1   0   4
2  16  15
3   0  -3
4   8  -9
5   0   1
6   3   4
7   0   0
H,K= 13  5
0  47 -47
1  34 -34
2  40  39
3  24  23
4  25 -24
5  12 -12
6  13  11
7   4   4
H,K= 14  5
0  11  -8
1   0  -2
2   9   7
3   0   2
4   5  -4
5   0  -1
6   0   2
H,K= 15  5
0  23 -23
1   0   0
2  20  20
3   0   0
4  14 -13
5   6   7
6   5   7
H,K= 16  5
0  21  21
1  23  23
2  16 -18
3  14 -16
4  12  11
5   5   7
6   4  -5
H,K= 17  5
0   0  -1
1   0  -6
2   0   1
3   0   0
4   5  -1
5   0   0
6   0   0
7   0   1
H,K= 18  5
0  12  13
1   6 -10
2   7 -11
3   3   7
4   0   6
5   3  -3
H,K= 19  5
0   0  -4
1   6  -7
2   3   3
3   3   5
4   0  -2
5   0  -2
H,K= 20  5
0  11 -11
1   3  -3
```

**Column 3**
```
L  FO  FC
2   6   9
3   0   2
4   3  -6
5   0   0
H,K= 21  5
0   0  -3
1   0  -3
2   0   3
3   0   3
4   0  -1
H,K= 22  5
0   0   0
1   6   9
2   0   0
3   3  -7
4   0  -1
H,K= 23  5
0   0  -3
1   3  -3
2   0   3
3   0  -1
H,K= 24  5
0   5  -6
1   0  -2
2   4   5
3   0   3
H,K= 25  5
0   4  -3
1   0  -4
2   0  -2
3   9  -6
4   5   3
5   0   4
H,K= 26  5
0   5  -7
1   0   2
H,K= 0  6
0  21 -20
2  18  16
4   8  -9
6   8   4
H,K= 1  6
0   2  -3
1  42 -41
2   4   4
3  27  27
4   0  -3
5  14 -15
6   0   1
7   3   6
H,K= 2  6
0   8  -7
1  10 -11
2   8   7
3   5   6
4   3  -5
5   3  -2
6   0   2
7   0   0
H,K= 3  6
0  19  18
1  10  12
2  14 -14
3   3  -6
4   6   8
5   0   1
6   0  -2
7   0   0
H,K= 4  6
0   0   3
1   2  -4
2   4  -3
3   0   1
4   0   1
5   0  -1
6   0   0
H,K= 5  6
0  37  37
1  33 -35
2  31 -31
3  23  24
4  18  19
5  12 -12
6  10  -9
7   4   4
H,K= 6  6
0   0  -3
1  16 -16
2   2   2
3  10  11
4   5  -1
5   5  -5
6   0   0
7   0   1
H,K= 7  6
0   0  -2
1  44 -47
2   0   1
3  31  33
4  16 -17
5   7  10
6   0   5
```

**Column 4**
```
L  FO  FC
7   4  -4
H,K= 0  6
0   4  -1
1  15 -17
2   0   1
3  13  12
4   0   0
5   5  -7
6   0   0
7   0   3
H,K= 10  6
0  18 -17
1  36  37
2  13  15
3  24 -26
4   8 -10
5  14  15
6   5   5
7   0  -6
H,K= 11  6
0  15 -15
1   4  -6
2  12  12
3   0   5
4   7  -7
5   0  -3
6   0   3
H,K= 12  6
0  13   6
1   5   8
2   3  -5
3   9  -6
4   5   3
5   0  -1
6   0  -1
H,K= 13  6
0   9  10
1   0   6
2   8  -9
3   0  -5
4   3   6
5   0   3
6   0  -2
H,K= 14  6
0   0   4
1   7  -6
2   3  -4
3   4   2
4   3   2
5   3  -1
6   0  -1
H,K= 15  6
0  12  11
1   0   0
2   7  -9
3   3  -1
4   3   5
5   0   1
6   0  -2
H,K= 16  6
0   4  -6
1   4  -6
2   3  -5
3   3   5
4   6   3
5   0  -2
H,K= 17  6
0   3  -1
1   3   1
2   0   3
3   0   0
4   3   9
5   5  -2
H,K= 18  6
0  12  11
1  21 -22
2   9  -0
3  15  16
4   7   5
H,K= 19  6
0  17  18
1   3  -4
2  12 -15
3   0   3
4   7   9
5   5  -2
H,K= 20  6
0   3  -2
1   0  -2
2   0   2
3   0   1
4   0  -1
H,K= 21  6
0  12  11
1  44 -47
2   0   1
3  31  33
4  16 -17
H,K= 22  6
```

**Column 5**
```
L  FO  FC
0   5  -7
1   4   6
2   0   6
H,K= 25  6
1   0   3
H,K= 0  7
1  19  19
3  13 -14
5   8   8
7   5  -4
H,K= 1  7
0  40  40
1  18 -18
2  34 -34
3  13  13
4  20  21
5   7  -7
6  11  -9
7   0   3
H,K= 2  7
0   0   0
1   7   7
2   0   0
3   4  -6
4   0   0
5   5   3
6   0   0
7   0  -1
H,K= 3  7
0  20  19
1  43 -42
2  17 -16
3  30  30
4  11  10
5  18 -16
6   3  -5
7   5   7
H,K= 4  7
0  18 -17
1   9   8
2  15  15
3   5  -6
4   8  -9
5   3   3
6   0   4
7   4  -1
H,K= 5  7
0   0   0
1   0   2
2   0   0
3   0   3
4   0   0
5   0  -2
6   0   0
H,K= 6  7
0   0   0
1  10 -10
2   0   0
3   6   7
4   0   0
5   3  -3
6   0   0
H,K= 7  7
0  14  12
1  10  11
2   9  -9
3   6  -8
4   5   6
5   3   0
6   3  -3
H,K= 8  7
0  18  17
1   3  -3
2  15 -15
3   6   8
4   9   8
5   0   2
6   0  -1
H,K= 9  7
0  15  15
1  11 -10
2  12 -13
3   6   8
4   4   9
5   3  -5
6   4  -4
H,K= 10  7
0   0   2
1   9  10
2   0   0
3   7  -7
4   5   0
5   0   1
H,K= 11  7
0   0   0
1   4   6
2   7   7
3   3  -6
4   5  -4
5   3   4
6   0   0
H,K= 12  7
0   0  -2
1  11  10
2  16  16
3   8  -7
4   9  -9
5   3   0
6   0   4
```

**Column 6**
```
L  FO  FC
5   0   1
6   0   0
H,K= 13  7
0  22  22
1  11  11
2  19 -18
3   7  -7
4  10  11
5   3   3
6   0  -3
H,K= 14  7
0   4  -2
1   6  -7
2   6   5
3   6   5
4   0  -1
5   0  -3
6   0   1
H,K= 15  7
0  19  19
1  10 -10
2  17 -16
3   6   7
4   8  -8
5   0   1
6   0   3
H,K= 16  7
0   9  -6
1   6  -7
2   0  -4
3   0  -3
4   0   1
5   0   0
H,K= 17  7
0   5   2
1   5   4
2   0  -1
3   5   5
4   0  -3
5   0   0
H,K= 18  7
0   7   8
1   9   8
2   0  -1
3   6  -6
4   0  -3
5   0  -5
H,K= 19  7
0   8   7
1  11  10
2   5  -6
3   8  -4
4   0   0
5   0   1
H,K= 20  7
1   3   3
2   0   0
3   0   2
4   0   0
5   0   0
H,K= 21  7
0   8 -10
1   5   6
2   6   8
3   3  -4
4   7  -5
5   0   2
H,K= 22  7
0   7   8
1   0  -3
2   8  -6
3   4   5
4   6   6
5   0  -1
H,K= 23  7
0   0   0
1   0   0
2   0   2
3   0  -4
4   5   4
5   0   0
H,K= 0  8
0   3  -2
1   0   0
2   0   0
3   0  -1
4   0  -3
5   0   1
H,K= 1  8
0  13 -13
1   3   4
2   0  12
3   0  -3
4   0   2
5   0   1
H,K= 2  8
0  19 -19
1  11  10
2  16  16
3   8  -9
4   9  -9
5   3   0
```

**Column 7**
```
L  FO  FC
H,K= 6  8
0   9 -10
1   7  -7
2   7   8
3   6   5
4   5  -5
5   0  -2
6   0   1
H,K= 7  8
0  17 -15
1   5   5
2  11  13
3   3  -3
4   8  -8
5   0   1
6   0   3
H,K= 8  8
0   0   0
1   0   0
2   5  -1
3   6   6
4   0  -3
5   0  -3
H,K= 9  8
0   8   9
1   9   9
2   6  -8
3   6  -7
4   8   5
5   4   4
H,K= 10  8
0   0   2
1   2   5
2   5   4
3   0   0
4   0  -3
5   0   0
H,K= 11  8
0   7   8
1   9   8
2   9   8
3   0   0
4   0  -3
5   0   0
H,K= 12  8
0  20 -17
1  16  15
2  14 -14
3   4   9
4  11  -9
5   0  -2
H,K= 13  8
0   0  -1
1   0  -3
2   0   1
3   0   2
4   0  -1
5   4  -3
H,K= 14  8
0   3   7
1   7  -7
2   5  -6
3   3   5
4   4   4
5   0  -7
H,K= 15  8
1   9   8
2   9   9
3   3   5
4   4   5
5   5  -5
H,K= 16  8
0   0   3
1   0   0
2   0   1
3   0   2
4   0  -1
5   0   0
H,K= 17  8
0   0  -3
1   0   0
2   0   0
3   0  -5
4   0  -1
4   4  -3
H,K= 18  8
1   0   0
2   3   0
3   0   6
H,K= 19  8
0   9 -10
1   0  -1
2   8   9
3   0   0
H,K= 20  8
0   0  -2
1   0  -4
H,K= 21  8
0   0  -1
1   4   5
2   0  -1
3   4   4
4   4  -3
```

**Column 8**
```
L  FO  FC
H,K= 2  9
0   7  -8
1  13 -12
2   7   6
3   9   9
4   0  -3
5   4  -5
H,K= 3  9
0   0   0
1   6  -5
2   0   0
3   5   4
4   0  -3
5   0  -3
H,K= 4  9
0   0   1
1   0   0
2   5  -1
3   0   0
4   0   1
5   0   0
H,K= 5  9
0   6  -5
1  10  -8
2   3   4
3   6   6
4   0   0
H,K= 6  9
0   3  -3
1   0  -2
2   0   2
3   0  -1
4   0   1
5   0   0
H,K= 7  9
0  20 -17
1   3  -2
2  16  15
3   0   2
4  11  -9
5   0  -1
H,K= 8  9
0  12  12
1   4  -1
2   0  -2
3   0   3
4   0   1
H,K= 9  9
0   5  -2
1   0  -4
2   0   2
3   0   2
H,K= 10  9
1   3  -3
2   0  -4
3   0   0
H,K= 11  9
0   6   5
1   0   1
2   2  -4
3   0   0
H,K= 12  9
2   4  -1
3   0   0
4   0   1
H,K= 13  9
0   0   5
1   5  -6
2   0  -4
3   0   3
H,K= 14  9
0   0   3
1   0   2
H,K= 15  9
1   9   8
3   7  -6
H,K= 1  11
0   0   0
1   0   0
2   0   0
H,K= 2  11
0   0   0
1   4   3
2   0   0
H,K= 3  11
0   0   1
1   7   7
2   0  -1
H,K= 4  11
0   0   0
1   0   0
2   0  -2
H,K= 5  11
0   0   4
1  10  10
2   4  -3
H,K= 6  11
0   0   4
1   4  -5
2   0   4
H,K= 7  11
0   4   4
1   0   0
2   0  -4
H,K= 8  11
0   0  -1
1   0   3
2   0  -1
H,K= 9  11
0   0   5
-1  0  -4
```

**Rightmost column**
```
L  FO  FC
3   6   5
4   0  -2
H,K= 2  10
0   3   0
1   6   5
2   0   0
3   3  -4
4   0   0
H,K= 3  10
0  13 -13
1   5  -5
2  12  11
3   3   4
4   8  -7
H,K= 4  10
0   5   3
1   3   6
2   0  -2
3   3  -4
4   0   1
H,K= 5  10
0   0   1
1   0  -2
2   0   0
3   0  -4
4   0   1
H,K= 6  10
0  12  12
2  11 -11
3   0  -2
4   8   7
H,K= 7  10
0   0   2
1   0  -4
2   0   2
3   0   3
4   0   1
H,K= 8  10
0  12  12
1   5  -4
2   8 -10
3   5   3
H,K= 9  10
0   5  -2
1   0  -4
2   0   2
3   0   2
H,K= 10  10
1   3  -3
2   0  -4
3   0   0
H,K= 11  10
0   6   5
1   0   1
2   2  -4
3   0   0
H,K= 12  10
2   4  -1
3   0   0
4   0   1
H,K= 13  10
0   0   5
1   5  -6
2   0  -4
3   0   3
H,K= 14  10
0   0   3
1   0   2
H,K= 15  10
1   9   8
3   7  -6
```

ship, 42 signs out of 269 $hk0$ reflexions were obtained. Further sign-determinations by the use of Sayre's relation gave 38 more signs. The smallest unitary structure factor for which the sign was determined was 0·20. After the final refinement of the structure it was found that only 9 out of the 80 signs determined were incorrect. The electron density projection along the $c$ axis, as shown in Fig. 1, was then calculated by the use of these 82 reflexions. This not only revealed definitely the four chlorine atoms but also a rough image of the carbon skeleton. On the basis of this model the Patterson function was found to be reasonably interpreted.

A two-dimensional Fourier synthesis, based on the coordinates of the four chlorine atoms and the ten carbon atoms of the calicene skeleton and two $\alpha$-methylenes, clearly gave the other four carbon atoms of the propyl groups. Further refinements of the parameters were therefore made by the block-diagonal matrix least-squares method, all $hkl$ reflexions being included. Anisotropic temperature factors, in the form $\exp \{ - (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl) \}$, were assigned to the chlorine atoms, while the carbon atoms were treated as undergoing isotropic thermal motion. After three cycles of refinement the discrepancy index, $R = \Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|$, was reduced to 0·134 for the observed reflexions. The next refinements were performed by taking account of anisotropic temperature factors for all the non-hydrogen atoms. After two

cycles the $R$ value was 0·123. At this stage, a difference synthesis revealed the approximate positions of all the hydrogen atoms. All of the hydrogen atoms were then included in further least-squares refinements, with all of the observed and unobserved reflexions except the strongest, 002, which appeared to suffer from extinction; the positions and individual isotropic temperature factors of the hydrogen atoms were allowed to vary. After three cycles no significant changes in parameters were observed and the $R$ value reached to 0·073 for the observed reflexions, excluding the strongest reflexion. When this is included, $R = 0·078$.

The atomic scattering factors used in the calculations were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and the temperature factors are given in Table 1, and their standard deviations in Table 2. The observed and calculated structure factors are listed in Table 3. The final three-dimensional electron density distribution calculated with signs based on these parameters is shown in Fig. 2.

The computations were done on an NEAC 2101 computer at the Institute for Protein Research of Osaka University with the programs written by Dr T. Takano and Mrs Y. Nishi, and on a HITAC 5020E computer at the University of Tokyo with the programs written by one of the authors (T. A.).

### Validity of the space group

The consistency of equivalent bond lengths and angles and the trend of parameter standard deviations and anisotropic temperature factors suggest the centrosymmetric structure to be correct. But there are some unusual short intermolecular approaches in the crystal as will be discussed later, so that the possibility of a non-centrosymmetric space group cannot be completely ruled out. The statistical tests for centrosymmetry mentioned in the preceding paragraph are not necessarily decisive in the present case, in which the atomic distribution shows pseudosymmetry and is not random. The refinement on the basis of the space group symmetry $Pna2_1$ was then tried by the block-diagonal matrix least-squares method. It resulted in very large error estimates and drastic shifts in the $z$ coordinates of all carbon and chlorine atoms. Almost the same results were obtained when the full-matrix least-squares refinement was applied in which the correlation matrix clearly indicates strong interactions among the $z$ coordinates of all atoms. Similar experience has also been reported with chromium hexacarbonyl (Whitaker & Jeffery, 1967). The most suitable refinement techniques for this type of problem have not yet been determined (Rae & Maslen, 1963).

In an alternative attempt, the propyl groups were artificially displaced from the mirror plane in order to avoid unusual intermolecular short contacts, and the structure factors for this model were calculated. The $R$ value was rather large, 0·178. At the next stage a
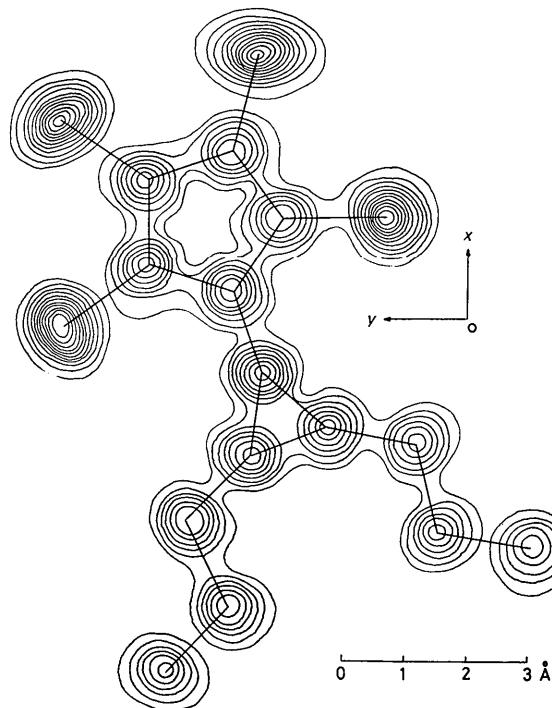


Fig. 2. Final electron density distribution on a section at $z = 0·25$. The contours of carbon atoms are at intervals of 1·0 e.Å$^{-3}$, and those of chlorine atoms are at intervals of 2·0 e.Å$^{-3}$, the lowest being 1·0 e.Å$^{-3}$.

difference synthesis was made, assuming $Pna2_1$ symmetry, based on the four chlorine atoms and eight carbon atoms in the calicene nucleus. The resulting map clearly showed six carbon atoms on the mirror plane with reasonable peak heights. From this re-examination of the symmetry, it can be concluded that even if the molecule deviates from planarity, the deviations must be very small and the molecule must lie on the crystallographic mirror plane within the accuracy of the analysis. The discussion in the following section will be based on the centrosymmetric structure.

## Discussion

### Molecular geometry

The intramolecular bond lengths and angles are illustrated in Figs. 3 and 4, respectively, and are listed in

Table 4, with their estimated standard deviations. It is noted that there are no significant differences between chemically equivalent bond lengths and angles. Therefore, the point group symmetry of the molecule, of which planarity has been mentioned already, can be concluded to be $mm2$.

### Structure of the calicene nucleus

Dewar & Gleicher (1965) and Nakajima, Kohda, Tajiri & Karasawa (1967) have made theoretical investigations for calicene itself by the semi-empirical self-consistent field molecular orbital method. In Table 5, the bond lengths predicted by these workers are compared with those observed in the calicene nucleus in the present molecule, the observed values being the average ones assuming the above mentioned molecular symmetry. It may be generally stated that the agreement

Table 4. *Bond lengths and angles with their e.s.d.'s*

| | Length | e.s.d. | | Angle | e.s.d. |
|---|---|---|---|---|---|
| C(1)—Cl(1) | 1·714 Å | 0·007 Å | C(8)—C(1)—Cl(1) | 125·2° | 0·5° |
| C(2)—Cl(2) | 1·703 | 0·007 | C(2)—C(1)—Cl(1) | 125·3 | 0·5 |
| C(3)—Cl(3) | 1·697 | 0·008 | C(2)—C(1)—C(8) | 109·6 | 0·6 |
| C(4)—Cl(4) | 1·702 | 0·007 | C(1)—C(2)—Cl(2) | 127·0 | 0·6 |
| C(1)—C(2) | 1·360 | 0·009 | C(3)—C(2)—Cl(2) | 125·2 | 0·5 |
| C(2)—C(3) | 1·451 | 0·010 | C(1)—C(2)—C(3) | 107·8 | 0·6 |
| C(3)—C(4) | 1·353 | 0·010 | C(2)—C(3)—Cl(3) | 124·3 | 0·6 |
| C(4)—C(8) | 1·447 | 0·009 | C(4)—C(3)—Cl(3) | 127·7 | 0·6 |
| C(1)—C(8) | 1·423 | 0·009 | C(2)—C(3)—C(4) | 108·0 | 0·6 |
| C(7)—C(8) | 1·370 | 0·009 | C(3)—C(4)—Cl(4) | 126·7 | 0·6 |
| C(5)—C(7) | 1·391 | 0·009 | C(8)—C(4)—Cl(4) | 124·3 | 0·5 |
| C(6)—C(7) | 1·390 | 0·009 | C(3)—C(4)—C(8) | 109·0 | 0·6 |
| C(5)—C(6) | 1·320 | 0·009 | C(4)—C(8)—C(7) | 126·9 | 0·6 |
| C(5)—C(9) | 1·466 | 0·009 | C(1)—C(8)—C(7) | 127·5 | 0·6 |
| C(9)—C(10) | 1·501 | 0·010 | C(1)—C(8)—C(4) | 105·6 | 0·6 |
| C(10)-C(11) | 1·513 | 0·011 | C(8)—C(7)—C(5) | 150·2 | 0·6 |
| C(6)—C(12) | 1·467 | 0·009 | C(5)—C(7)—C(6) | 56·7 | 0·5 |
| C(12)-C(13) | 1·526 | 0·010 | C(6)—C(7)—C(8) | 153·2 | 0·6 |
| C(13)-C(14) | 1·510 | 0·011 | C(7)—C(5)—C(9) | 148·7 | 0·6 |
| C(9)—H(2) | 0·98 | 0·05 | C(6)—C(5)—C(9) | 149·7 | 0·7 |
| C(10)-H(4) | 1·00 | 0·05 | C(6)—C(5)—C(7) | 61·7 | 0·5 |
| C(11)-H(6) | 0·99 | 0·06 | C(5)—C(6)—C(12) | 152·3 | 0·6 |
| C(11)-H(7) | 0·94 | 0·08 | C(7)—C(6)—C(12) | 146·0 | 0·6 |
| C(12)-H(9) | 0·99 | 0·05 | C(5)—C(6)—C(7) | 61·7 | 0·5 |
| C(13)-H(11) | 0·98 | 0·05 | C(5)—C(9)—C(10) | 114·0 | 0·6 |
| C(14)-H(13) | 0·98 | 0·05 | C(9)—C(10)-C(11) | 114·0 | 0·6 |
| C(14)-H(14) | 1·00 | 0·08 | C(6)—C(12)-C(13) | 113·4 | 0·6 |
| | | | C(12)-C(13)-C(14) | 111·8 | 0·6 |
| | | | C(5)—C(9)—H(2) | 108 | 3 |
| | | | C(10)-C(9)—H(2) | 109 | 3 |
| | | | H(1)—C(9)—H(2) | 109 | 6 |
| | | | C(9)—C(10)-H(4) | 110 | 3 |
| | | | C(11)-C(10)-H(4) | 107 | 3 |
| | | | H(3)—C(10)-H(4) | 108 | 6 |
| | | | C(10)-C(11)-H(6) | 108 | 3 |
| | | | C(10)-C(11)-H(7) | 112 | 5 |
| | | | H(6)—C(11)-H(7) | 109 | 6 |
| | | | H(5)—C(11)-H(6) | 110 | 6 |
| | | | C(6)—C(12)-H(9) | 108 | 3 |
| | | | C(13)-C(12)-H(9) | 109 | 3 |
| | | | H(8)—C(12)-H(9) | 109 | 6 |
| | | | C(12)-C(13)-H(11) | 106 | 3 |
| | | | C(14)-C(13)-H(11) | 111 | 3 |
| | | | C(13)-C(14)-H(13) | 108 | 3 |
| | | | C(13)-C(14)-H(14) | 111 | 5 |
| | | | H(13)-C(14)-H(14) | 110 | 5 |
| | | | H(12)-C(14)-H(13) | 110 | 6 |

is fairly good, but in the three-membered ring the observed bond lengths are systematically shorter than the predicted ones.

The C–C double-bond length in three- membered ring, 1·320 Å, is longer than that in cyclopropene, 1·300 Å (Kasai, Myers, Eggers & Wiberg, 1959). The C–C single-bond lengths, 1·390 Å and 1·391 Å, are longer than those (1·370 Å, 1·373 Å and 1·376 Å) in the three-membered ring of sym-triphenylcyclopropenium perchlorate (Sundaralingam & Jensen, 1966) which is a fully conjugated 2π-electron system. These values seem to suggest that the π-electrons in the three-mem-

bered ring of the present compound are partially delocalized.

It should be noted that the single bonds adjacent to the three-membered ring are shortened, in accordance with generally observed trends(Bent, 1961).The average value of the C(5)–C(9) and C(6)–C(12) bonds is 1·467Å, which is significantly shorter than the C($sp^3$)–C($sp^2$) length of 1·499 Å (Dewar & Schmeising, 1960). The lengths of these C–C bonds should be indicative of the hybridization of the carbon orbitals which form them. This hybridization of C(5) and C(6) orbitals could be calculated to be about $sp^{1·2}$ from the plot of bond lengths versus mean percentage s-character of carbon for C–C single bonds (Dewar & Schmeising, 1960). This seems to be consistent with the rehybridization (from $sp^2$) expected for the 'bent' bonds in the three-membered ring (Coulson & Moffitt, 1949).

As shown in Table 5, the observed C(7)–C(8) distance apparently agrees very well with that predicted, but the predicted value does not include an allowance for the shortening effect of bonds attached to the three membered ring. If the shortening of 0·032 Å, expected from the above-mentioned results,is taken into account, the theoretical length should be equal to 1·329–1·343 Å, so that the observed value, 1·370 Å, is significantly longer than the predicted one for calicene itself. Moreover, in the five-membered ring, the lengths of the C–C single bonds adjacent to the intercyclic double bond are shorter than the others, contrary to the prediction, as shown in Table 5. This tendency is the same as that observed in 8,8-dicyanoheptafulvene which has a large contribution from the dipolar resonance form (Shimanouchi, Ashida, Sasada, Kakudo, Murata & Kitahara, 1966). On the other hand, in perchlorofulvalene (Wheatley, 1961) and 1,2,3,4-tetrachlorobenzo[g]sesquifulvalene (Nishi, Sasada, Ashida & Kakudo, 1966), the two C–C single bonds adjacent to the exocyclic double bond are significantly longer than the others. In these molecules the two ring-systems make an angle by twisting the C=C bond, and the dipolar structure is negligible. Thus it may be concluded that the present compound has a greater contribution from the dipolar form than has calicene itself. This result is consistent with the interpretation of the observed high dipole moment (7·56 D in benzene at 25 °C), nuclear magnetic resonance and electronic spectra.
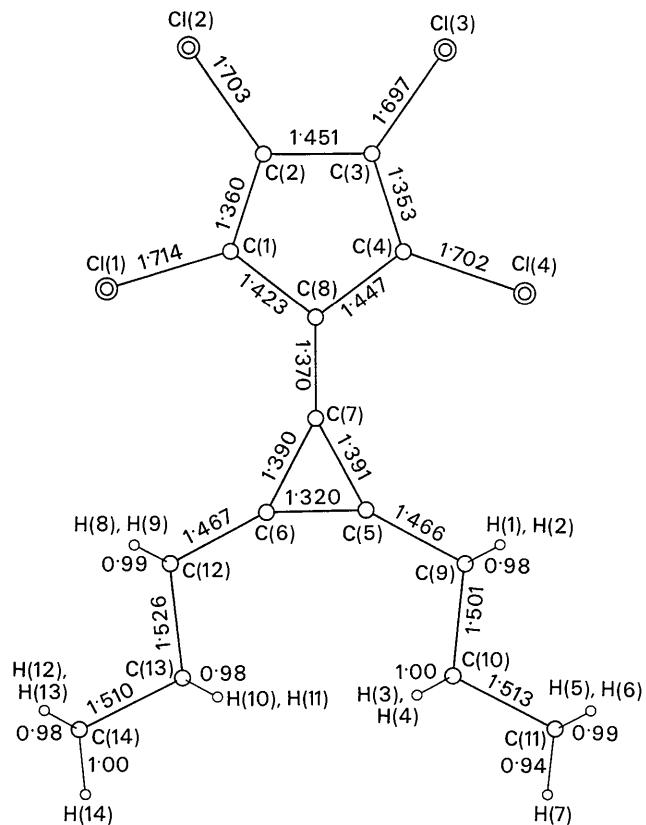


Fig. 3. Bond lengths (Å).

Table 5. Comparison of theoretical and observed values of bond lengths (Å)
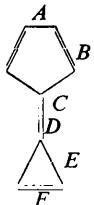


| | | Theoretical | | Observed |
|---|---|---|---|---|
| $A = 1·446$ * | (1·455) * | 1·454 † | 1·451 ‡ |
| $B = 1·361$ | (1·355) | 1·355 | 1·357 |
| $C = 1·451$ | (1·460) | 1·455 | 1·435 |
| $D = 1·370$ | (1·361) | 1·375 | 1·370 |
| $E = 1·469$ | (1·476) | 1·454 | 1·391 |
| $F = 1·349$ | (1·345) | 1·355 | 1·320 |
| | PPP | SPO | |

* Dewar & Gleicher (1965).
† Nakajima, Kohda, Tajiri & Karasawa (1967).
‡ Present work.
    PPP denotes the Pariser Parr Pople method. SPO denotes the split p-orbital method.

*Contraction of bond length in the cyclopropenylidene ring*

As pointed out above, in the three-membered ring the observed bond distances are considerably shorter than the predicted ones. These predicted values do not include the allowance for possible shortening of the bonds in the three-membered ring. The C–C bonds in three-membered rings are generally shorter than usual and vary with substituents, as listed in Table 6. By analogy with these data the shortening is about 0·02 Å. Even if this is taken into account, the bond lengths in the three-membered ring are considerably shorter than the theoretical values. This result may be interpreted as follows.

Recent precise structure analyses of *cis*-1,2,3-tricyanocyclopropane (Hartman & Hirshfeld, 1966) and 2,5-dimethyl-7,7-dicyanonorcaradiene (Fritchie, 1966) have shown by difference synthesis that the gross presence of the 'bent' bonds (Coulson & Moffitt, 1949) seems certain and a limit of $20 \pm 10°$ for bending of the cyclopropane bonds seems reasonable. If this is the case the extent of bending in the present compound should be larger than that in cyclopropane, because of the larger s-characters of the carbon orbitals in the former. The repulsions in such a deformed $\sigma$ framework may not be so much increased with shortening of the C–C distance, because the limit on approach of adjacent carbon atoms may result from repulsive interactions involving $\sigma$-bonding electrons (West, Sado & Tobey, 1966). The shortening of the C–C distance undoubtedly results in increasing overlap of the carbon p-orbitals. The expected reduction in $\sigma$-bond strength may be compensated for by this increased $\pi$-bonding in the present molecule.

The shortening of the C–C bonds in the three-membered ring of the present compound may be partly ascribed to the decreased covalent radii of positively charged carbon atoms. In fact, in 1,1'-tetramethylethyleneferrocene (Laing & Trueblood, 1965), $\alpha$-keto-1,1'-trimethyleneferrocene (Jones, Marsh & Richards, 1965) and diferrocenyl ketone (Trotter & McDonald, 1966) the mean C–C bond lengths in the negatively charged five-membered rings (1·44, 1·424 and 1·43 Å, respectively) are apparently longer than the C–C lengths in benzene, which is electrically neutral.

The reason for the exceptionally high frequency, 1865 cm⁻¹, in the infrared absorption spectrum of the present compound (Kitahara, Murata, Ueno, Sato & Watanabe, 1966) is not yet fully understood, but it may be associated with an unusually short C–C distances in the three-membered ring.

*Other bond lengths*

The C–Cl distances average 1·704 Å and are significantly shorter than the normal $C(sp^2)$–Cl bond length of 1·736 Å (Dewar & Schmeising, 1960) and the C–Cl length in 2-chlorotropone, 1·73 Å (Forbes, Gregory, Hamor & Watkin, 1966). This shortening and the exocyclic angles larger than 120° around the carbon atoms C(1), C(2), C(3) and C(4) may be the result of the fact that in the orbitals (pointing toward the chlorine atoms) of the carbon atoms the s-character is larger than that of the usual $sp^2$-hybridized orbital (Mislow, 1965). By the use of the plot of bond lengths *versus* percentage s-character of carbon for C–Cl bonds (Dewar & Schmeising, 1960), the mean hybridization of the carbon orbitals which form these bonds could be calculated to be about $sp^{1·6}$.

It is interesting that the C(1)–Cl(1) and C(4)–Cl(4) separations are slightly longer than the C(2)–Cl(2) and C(3)–Cl(3) lengths. While this tendency is consistent with that of the endocyclic angles around the carbon atoms bonding to the chlorine atoms, this may be partly a result of the omission of the corrections for libration and partly a result of the intermolecular repulsions, as will be discussed later.

In the propyl groups the mean C–C bond length, 1·513 Å, is shorter than the usual $C(sp^3)$–$C(sp^3)$ distance, 1·534 Å (Dewar & Schmeising, 1960) and those of the zigzag carbon chains (Hirokawa & Ashida, 1962; Brown, 1966; Dumbleton & Lomer, 1965). This result may also be ascribed to the intermolecular repulsions.

*Crystal structure*

The packing diagram of the crystal viewed along the c axis is shown in Fig. 5, together with the short intermolecular distances. The unusual short intermolecular contacts, 3·39 Å and 3·59 Å, are found between Cl(2) in molecule A and C(14) in molecule D, and between Cl(3) in molecule A and C(13) in molecule E, respectively. These values are considerably smaller than the sum of the van der Waals radii of the chlorine atom and the methyl group given by Pauling (1960). But the corresponding Cl···H contacts are 3·17 Å, 3·21 Å and 3·28 Å, which are nearly equal to the sum of the van der Waals radii.

Table 6. *C–C distances in some three-membered rings*

| Compound | C=C | C–C | Reference |
|---|---|---|---|
| Cyclopropane | | 1·510 Å | Bastiansen, Fritsch & Hedberg (1964) |
| Chlorocyclopropane | | 1·514 | Schwendeman, Jacobs & Krigas (1964) |
| *cis*-1,2,3-Tricyanocyclopropane | | 1·518 | Hartman & Hirshfeld (1966) |
| 1,1-Dichlorocyclopropane | | 1·533 | Flygare, Narath & Gwinn (1962) |
| | C=C | C–C | |
| Cyclopropene | 1·300 Å | 1·515 Å | Kasai, Myers, Eggers & Wiberg (1959) |
| 1,2,3,4-Tetrachloro-5,6-di-n-propylcalicene | 1·320 | 1·391 | Present work |
| *sym*-Triphenylcyclopropenium perchlorate | | 1·373 | Sundaralingam & Jensen (1966) |
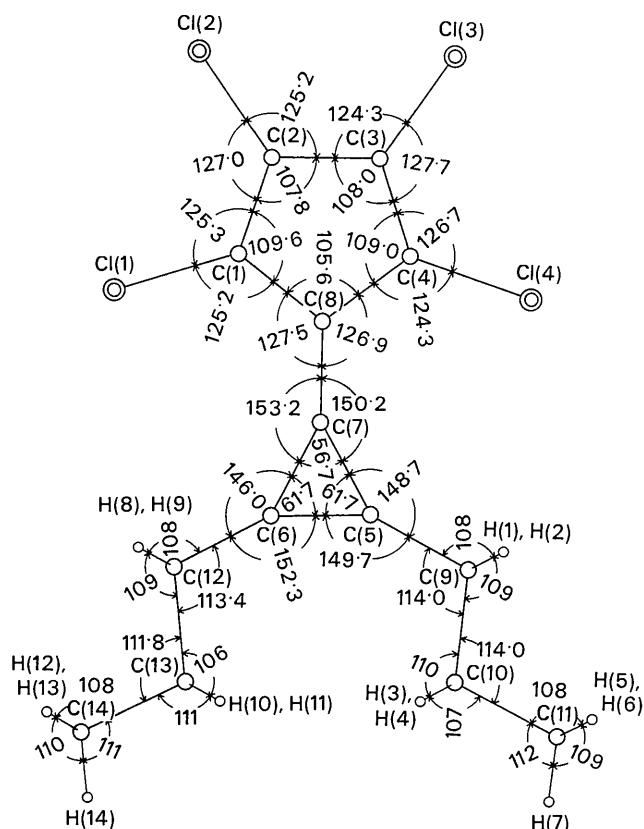
Fig. 4. Bond angles (degrees).

The shortest intermolecular Cl...Cl distance is 4·18 Å, far from the sum of the van der Waals radius, suggesting a repulsion between the negatively charged five-membered rings. The short intermolecular C···C contacts between the propyl groups are 3·65 Å and 3·78 Å, somewhat shorter than the sum of the van der Waals radii of the two methyl groups. The two methyl or methylene carbon atoms may be able to come closer than 4·0 Å if the C–H bond direction deviates from the C···C direction. In fact, the shortest distance between hydrogen atoms is 2·69 Å, far from the sum of the van der Waals radii.

The shortest non-bonding distance between atoms in adjacent layers is 3·54 Å, between the formally negative carbon atom in the five-membered ring and the positive carbon atom in the three-membered ring.

The shortest contact between chlorine and ring carbon atoms is 3·70 Å. The intermolecular spacing is directly determined as one half of the c translation to be 3·51 Å.

The arrangement of the molecules in the crystal appeared to be favourable for interacting with one another by the high dipole moment.

The molecule lies on the crystallographic mirror plane, so that all the chlorine and carbon atoms are entirely coplanar. This symmetry of molecular packing is extremely uncommon in organic crystals, apart from the crystals in which the molecules pack together in sheets by hydrogen bonding, such as barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961), violuric acid monohydrate (Craven & Mascarenhas, 1964) and metanilic acid (Hall & Maslen, 1965). In crystals (with
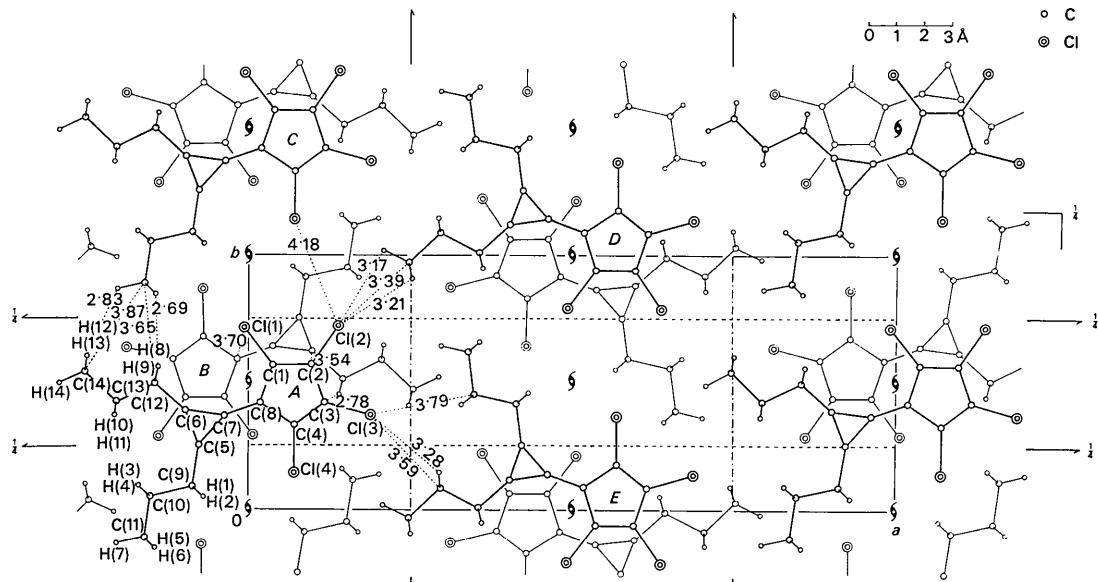


Fig. 5. Crystal structure viewed along the c axis, and short intermolecular distances (Å). Molecule A is at (x,y,z), B at (x̄, 1 − y, ½ + z), C at (x, 1 + y, z), D at (½ + x, 3/2 − y, z) and E at (½ + x, ½ − y, z).

the same space group) of *p*-chloroaniline (Palm, 1966) and carbazole (Kurahashi, Fukuyo, Shimada, Furusaki & Nitta, 1966) the molecular planes are perpendicular to the mirror plane. The unusual symmetry of the present compound may come from balancing the dipolar interactions not only within the molecular layers but also between molecules in adjacent layers.

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