Crystal Structure of the Perhydroanthracene Isomeride of m.p. 121°C

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Perhydroanthracene ($C_{14}H_{24}$) m.p. 121°C crystallizes in the space group $P2_1/c$ with two molecules per unit cell and $a = 5.363$ Å, $b = 9.572$ Å, $c = 12.067$ Å, $\beta = 112.7°$. The crystal and molecular structure has been determined by three dimensional X-ray methods. The molecule is centrosymmetrical and *cis-cis* as referred to the single hydrogen atoms on the central ring. Two of the C—C bond distances (1.554 Å and 1.529 Å) are significantly different from several of the others which are from 1.533 Å to 1.541 Å with the mean value 1.538 Å. The mean value of the C—H bond distances is 1.05 Å. Mean values of the bond angles are 111.5° ($\angle$ CCC), 108° ($\angle$ HCH), and 108.7° ($\angle$ CCH).

Five isomerides of perhydroanthracene may be predicted. Only two of these are centrosymmetrical. When the present investigation was undertaken, the structure of the isomer of m.p. 90°C had been determined by the X-ray methods. This molecule is centrosymmetrical and *trans-trans* as referred to the four single hydrogen atoms bonded to the central ring.[1] Some preliminary results from the work on the isomeride of m.p. 121°C have previously been published.[2] This isomer has also been investigated by the electron diffraction methods by Davis and Hassel.[3] They reported the average C—C bond distance 1.538 Å and the average CCC bond angle 112.05°.

EXPERIMENTAL

The compound used was kindly supplied by Professor Henbest. All the experimental work was done at room temperature. The density of the compound was found by the floatation method to be close to 1.12 g/cm³. Single crystals were obtained by slow evaporation of the acetone solution.

X-Ray work. X-Ray powder diagrams were obtained by a Philips wide range goniometer (type PW 1050/25) with a paper recorder. CuKα ($\lambda = 1.5418$ Å) and CuKα₁ ($\lambda = 1.5405$ Å) radiation was used. Pb(NO₃)₂ was used as internal calibration standard ($a = 7.8568$ Å). The single crystal intensity data were obtained by an equi-inclination, integrating Weissenberg camera with filtered CuKα radiation, using multiple film technique. The a-axis, approximately parallel to the longest edge of the crystal, was used

as the rotation axis, and the layer lines $0-4$ were recorded. A total of 1051 independent reflections were photometrically evaluated.

Calculations. The cell dimensions were refined by the least-squares methods using 23 diffraction lines. The intensity data were corrected for Lorentz and polarisation effects but not for absorption and extinction effects. In the structure factor calculation the atomic scattering factors were taken from a work by Hanson *et al.*[4] The structure was refined by the least-squares methods. The weight factors were chosen according to the formula: $1/w = (a + |F_o| + c|F_o|^2)^{\frac{1}{4}}$ where $a = 2|F_{o,min}|$ and $c = 2/|F_{o,max}|$.[5] For each non-observed reflection $|F_o|$ was assumed to be half of the smallest observable value. Reflections which are assumed to be affected by secondary extinction, were not included. The positional parameters obtained from the least-squares refinement were corrected for thermal motion, assuming rigid-body translation and libration with the centres of libration, gravity, and symmetry coinciding. A difference between two quantities (distances, angles) is considered to be significant when it is greater than three times the average standard deviation. Most of the calculations were performed on the UNIVAC 1107 computer. The programs used were according to the following list:

Least-squares refinement of unit cell dimensions: R. A. Sparks at the University of California at Los Angeles.

Calculations of structure factors and corrections for Lorentz and polarisation effects: Borgen *et al.*[6]

Least-squares refinement: Borgen *et al.*[7] This program is based on a program written by W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge National Laboratory, Tennessee, U.S.A.

Electron density calculation: Borgen *et al.*[8]

Rigid-body calculations: Hirshfeld *et al.*[9] The program used is based on theoretical work by Cruickshank [10] and Scheringer.[11]

Interatomic distances and angles: Borgen *et al.*[12] This program is based on a program written by W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge National Laboratory, Tennessee, U.S.A.

CRYSTAL DATA

Perhydroanthracene ($C_{14}H_{24}$) m.p. 121°C. Monoclinic, space group $P2_1/c$. $a = 5.363$ (0.006) Å, $b = 9.572$ (0.004) Å, $c = 12.067$ (0.009) Å, $\beta = 112.7°$ (0.1°). The numbers in the parentheses are the standard deviations.

Calculated density: 1.12 g/cm^3. $Z = 2$.

STRUCTURE DETERMINATION

There are two centrosymmetrical molecules per unit cell. The molecular model for the isomer of m.p. 121°C was assumed to be of the *cis-anti-cis* type [13] and accordingly to have a lower symmetry than the *trans-trans* isomer which has the lower melting point. All the rings were assumed to be in the „chair" form and the bond distances and the bond angles were assumed to be normal. Patterson and sharpened Patterson maps along [100] were calculated. The maps indicated that many intramolecular distances, and therefore also the longest ones which are of the same length as the b axis, were oriented approximately along [010]. The appropriate orientation of the molecule was tried. Although this orientation might have been expected to be inconsistent with a favourable packing of the molecules, it turned out to be the final one. A few "across-the-ring" distances were identified in the sharpened Patterson map. Bragg-Lipson charts [14] were also constructed. A trial structure was postulated and 136 structure factors were calculated. New coordinates were obtained from four successively calculated electron density maps whereby the reliability

Table 1. Observed and calculated structure factors. The data are separated into groups having common h. The four columns in each group list values of k, l, $10|F_o|$, $10F_c$ in that order. Reflections marked with asterisks are those omitted from the three dimensional refinement because of assumed extinction.

```
h = 0
 0  2  409*  564
 0  4  383* -469
 0  6  199  -212
 0  8   20    23
 0 10   32    29
 0 12    9    12
 0 14  < 5*    4
 1  1  209   268
 1  2   77   -83
 1  3  129  -137
 1  4  204   227
 1  5  156  -174
 1  6  173   177
 1  7   81   -81
 1  8   13   -11
 1  9   24   -27
 1 10   15    -4
 1 11  < 8    -3
 1 12   41    37
 1 13   31    18
 1 14  < 6     5
 2  0  268* -346
 2  1   67   -74
 2  2   77   -90
 2  3   28   -32
 2  4   53    53
 2  5   35   -31
 2  6    9   -11
 2  7   57   -56
 2  8    9    -9
 2  9   31   -25
 2 10   21    15
 2 11   23    21
 2 12    7   -10
 2 13   32   -18
 3  1  141   163
 3  2   14   -21
 3  3   17    22
 3  4   17   -20
 3  5   40   -47
 3  6  < 6     2
 3  7   46    48
 3  8   39    39
 3  9  126   145
 3 10   35    33
 3 11   48    49
 3 12  < 7    -5
 3 13   91   -63
 4  0  227  -252
 4  1  149   162
 4  2  146  -154
 4  3   93    97
 4  4   34   -37
 4  5   24   -24
 4  6   26    23
 4  7  < 7     5
 4  8   68    71
 4  9   27    27
 4 10   59    55
 4 11  < 7     7
 4 12   23   -16
 4 13   26    18
 5  1  137  -146
 5  2  181   191
 5  3   75   -74
 5  4   28   -24
 5  5   66    70
 5  6  129  -138
 5  7   88    88
 5  8   72   -71
 5  9  < 8     1
 5 10  < 7     1
 5 11   34   -31
 5 12   23    14
 6  0  210   227
 6  1  < 6    -7
 6  2   62    61
 6  3  < 7     2
 6  4   55   -55
 6  5    8    -6
 6  6   16    14
 6  7   27   -27
 6  8   41    39
 6  9  < 8     4
 6 10   10     8
 6 11   34    20
 6 12   19   -14
 7  1   88    90
 7  2  < 7     8
 7  3   22   -20
 7  4   55    58
 7  5   84   -84
 7  6   47    45
 7  7   68   -67
 7  8   24   -23
 7  9   20   -19
 7 10   14    -9
 7 11   12     9
 8  0  < 8     2
 8  1   54    50
 8  2   39    36
 8  3   80    84
 8  4   23    23
 8  5  < 8     6
 8  6   48   -48
 8  7   71   -68
 8  8   53   -50
 8  9   65   -44
 8 10  < 6    -3
 9  1   42    34
 9  2   50    47
 9  3   50    39
 9  4  < 8    11
 9  5  < 7     1
 9  6   16   -14
 9  7   22   -14
 9  8   17    11
 9  9  < 6     5
10  0   25   -20
10  1  < 7     7
10  2   27   -23
10  3  < 7    -6
10  4   23   -21
10  5  < 8    -8
10  6    8    -6
10  7   35    24
10  8  < 5     5
11  1   49   -25
11  2   44    24
11  3   31   -17
11  4  < 6    -6
11  5   23    14
11  6   41   -32
12  0   21   -11
12  1  < 5     3
12  2   15   -10
```

```
h = 1
 0 -14    7     9
 0 -12   12   -15
 0 -10   42    27
 0  -8  138  -128
 0  -6  470  -471
 0  -4  279  -292
 0  -2  670   697
 0   0  378   636
 0   2   60   -64
 0   4   74   -78
 0   6   71   -69
 0   8   54   -44
 0  10   51    48
 0  12   75    61
 1 -14    7     7
 1 -13   20   -16
 1 -12  <11     1
 1 -11  <12   -12
 1 -10  <11    -1
 1  -9   62    55
 1  -8   88   -76
 1  -7   10    17
 1  -6   72   -65
 1  -5  100  -104
 1  -4   20    -2
 1  -3   56   -52
 1  -2  320  -343
 1  -1  302   335
 1   0  348  -359
 1   1  280   287
 1   2  193   188
 1   3  < 7     3
 1   4   90    92
 1   5  154  -153
 1   6  121  -129
 1   7  134  -135
 1   8  106  -103
 1   9   30   -29
 1  10   19    19
 1  11   31    29
 1  12   31    26
 1  13    8     9
 2 -14    7    -9
 2 -13  <10   -11
 2 -12   19   -18
 2 -11  <12     7
 2 -10  <12     3
 2  -9   36   -31
 2  -8   88    85
 2  -7   94   -93
 2  -6  134   141
 2  -5  < 8     7
 2  -4   48   -49
 2  -3  300   308
 2  -2  279  -290
 2  -1  284   294
 2   0   53    51
 2   1  183   179
 2   2  178   174
 2   3   85    86
 2   4   33   -33
 2   5   10   -10
 2   6   64   -62
 2   7  <11     8
 2   8   13    13
 2   9   52    53
 2  10  <11     7
 2  11  <10     8
 2  12   24   -21
 3 -14   33    31
 3 -13   20   -16
 3 -12  <11    -2
 3 -11   41    42
 3 -10   55   -56
 3  -9  <11     7
 3  -8   61   -57
 3  -7   35   -37
 3  -6   16   -11
 3  -5   52   -55
 3  -4   58    48
 3  -3  158  -157
 3  -2   51    53
 3  -1  118  -120
 3   0   19   -15
 3   1   40    30
 3   2   58   -55
 3   3   66   -55
 3   4   43   -38
 3   5   16    11
 3   6  < 7    11
 3   7  124   132
 3   8   23    21
 3   9  109   111
 3  10  <11     4
 3  11  <10     4
 3  12  < 9     4
 4 -14   26   -30
 4 -13  <10     7
 4 -12  <10     2
 4 -11   56   -56
 4 -10   75    74
 4  -9  <11   -17
 4  -8  132   134
 4  -7  108   111
 4  -6   90    91
 4  -5   57    51
 4  -4  131  -121
 4  -3  237  -243
 4  -2  246  -229
 4  -1  211  -209
 4   0   12   -16
 4   1   18    11
 4   2    7     7
 4   3  < 9     6
 4   4   52   -53
 4   5  <10    -6
 4   6  <11    -2
 4   7   45   -49
 4   8   63    64
 4   9   55   -57
 4  10   32    34
 4  11   19    16
 4  12   29   -28
 5 -13   46   -42
 5 -12   41   -33
 5 -11   38   -39
 5 -10  <11     7
 5  -9   81    81
 5  -8  120   120
 5  -7  129   131
 5  -6  113   111
 5  -5    9    14
 5  -4   23   -26
 5  -3   94   -87
 5  -2   48   -38
 5  -1   87   -85
 5   0   98   102
 5   1   60   -59
 5   2   50    50
 5   3   27    24
 5   4  <10     3
 5   5   46    49
 5   6   13    14
 5   7    7    12
 5   8  <11     5
 5   9  <11    -2
 5  10  <10     2
 5  11  <10     0
 5  12  < 5    17
 6 -13  < 6   -12
 6 -12   34   -32
 6 -11  <10    -6
 6 -10   12   -14
 6  -9  <11    10
 6  -8   26   -26
 6  -7   22    24
 6  -6   70   -77
 6  -5   37    38
 6  -4    9    -9
 6  -3    6     5
 6  -2  105   107
 6  -1   80   -80
 6   0   11    11
 6   1   65   -64
 6   2   54   -52
 6   3  <11     2
 6   4   31    30
 6   5  <11     8
 6   6  <12    43
 6   7  <12    -1
 6   8  <11     4
 6   9  <10     6
 6  10  <10     2
 6  11  < 8     3
 7 -12  < 7     2
 7 -11   12    12
 7 -10  <10     5
 7  -9  <11     2
 7  -8  <11    -2
 7  -7   32   -34
 7  -6   22    22
 7  -5   47   -47
 7  -4   20    15
 7  -3   24    24
 7  -2  123  -119
 7  -1  128   129
 7   0  141  -138
 7   1   93    90
 7   2   45    47
 7   3   27   -28
 7   4   74    78
 7   5   88   -94
 7   6   32   -34
 7   7   66   -70
 7   8   52   -54
 7   9  <11    10
 7  10  < 8     3
 8 -11  < 8    -3
 8 -10   27   -21
 8  -9   27    34
 8  -8   29   -25
 8  -7   26    26
 8  -6  <11     7
 8  -5  <12    -3
 8  -4   10    -6
 8  -3   13   -25
 8  -2  <11     3
 8  -1  <11    -3
 8   0   75    78
 8   1   88    86
 8   2   67    68
 8   3  100   100
 8   4   42   -44
 8   5   10    14
 8   6   68   -70
 8   7   33   -34
 8   8   12   -17
 8   9  < 8    -8
 9 -10   26   -29
 9  -9   48   -42
 9  -8   13   -11
 9  -7   38   -37
 9  -6  <11    -1
 9  -5   10     9
 9  -4   16   -23
 9  -3   13    10
 9  -2   10   -14
 9  -1   10    12
 9   0   17    18
 9   1  <11     9
 9   2  <11     9
 9   3   10   -13
 9   4  < 8     7
 9   5    9    10
 9   6   14    16
 9   7  < 8     3
10  -8   14    14
10  -7  <10     3
10  -6  <11    -2
10  -5   16    15
10  -4    6    -9
10  -3   12   -11
10  -2  <11    -3
10  -1   15   -14
10   0  <11    -2
10   1   12   -12
10   2  <10    -7
10   3    9   -12
10   4  <11    -7
10   5  <10     2
10   6  < 9    -5
10   7  < 6    -1
11  -6   19    20
11  -5   13    -9
11  -4  <10    -3
11  -3   21   -15
11  -2  <11     5
11  -1   16   -14
11   0   37    29
11   1   22   -20
11   2   30    25
11   3  < 9     1
11   4  < 8     7
11   5   12    15
12  -2    7    -9
12  -1   15   -16
12   0   37    40
12   1  < 6    -7
```

```
h = 2
 0 -14    8     5
 0 -12  <11     2
 0 -10  <11    -3
 0  -8  107  -100
 0  -6   95   -98
 0  -4   28   -37
 0  -2   21   -33
 0   0   30    32
 0   2   84    83
 0   4  123  -118
 0   6  236  -235
 0   8   77   -71
 0  10   73    72
 1 -15  < 7    -5
 1 -14   19   -16
 1 -13   40   -37
 1 -12   13    10
 1 -11  <12    -2
 1 -10   16   -14
 1  -9   35    31
 1  -8   27    25
 1  -7  < 9    -4
 1  -6   74    71
 1  -5   13   -14
 1  -4   56   -58
 1  -3   49    50
 1  -2  103  -102
 1  -1  187   188
 1   0  313   297
 1   1  256   244
 1   2  218   211
 1   3   63    50
 1   4  113  -111
 1   5   98   -97
 1   6  146  -144
 1   7   99   -65
 1   8   32   -30
 1   9   21    20
 1  10  <10     7
 1  11   28    25
 1  12   19    24
 2 -13   41    37
 2 -12   52   -47
 2 -11   54   -52
 2 -10  <11     5
 2  -9  201  -202
 2  -8  118   114
 2  -7  162  -159
 2  -6   56    56
 2  -5   70    68
 2  -4  127  -128
 2  -3  135   133
 2  -2   73   -68
 2  -1   81    50
 2   0  127   126
 2   1   53    53
 2   2  <11    39
 2   3   25   -17
 2   4  < 9     4
 2   5    9     6
 2   6   38    35
 2   7   49    44
 2   8   13    14
 2   9   12   -15
 2  10   10   -12
 2  11   14   -11
 3 -14   43    38
 3 -13  <10     6
 3 -12  <11    -4
 3 -11   27   -26
 3 -10   70   -66
 3  -9   40    36
 3  -8   80   -78
 3  -7   96    96
 3  -6  < 9    -5
 3  -5   91   -93
 3  -4  154   146
 3  -3  326  -318
 3  -2  140   130
 3  -1  101  -106
 3   0   50   -46
 3   1   63   -50
 3   2   89    73
 3   3   77   -65
 3   4   16   -12
 3   5  <11     4
 3   6  <11     2
 3   7   26    24
 3   8  <11    10
 3   9  <11     4
 3  10  <11    -4
 3  11  < 8     6
 4 -14   26   -25
 4 -13   29   -28
 4 -12  <11    -7
 4 -11   19   -17
 4 -10   64    62
 4  -9   99   101
 4  -8  107   104
 4  -7  102   104
 4  -6   21    23
 4  -5   26   -28
 4  -4  103   -93
 4  -3   59   -62
 4  -2   32   -31
 4  -1  < 8     3
 4   0   96    74
 4   1   18    17
 4   2   15    15
 4   3   34    33
 4   4  <11     5
 4   5   18   -17
 4   6   49    49
 4   7   74   -77
 4   8   61    59
 4   9   25   -26
 4  10   16    17
 4  11   16    21
 5 -14   16   -21
 5 -13   52   -47
 5 -12   33   -33
 5 -11  <11    -2
 5 -10  <11     4
 5  -9   57    56
 5  -8   37    35
 5  -7   45    45
 5  -6   21    20
 5  -5   25    26
 5  -4  <11    -8
 5  -3   16   -17
 5  -2   73   -67
 5  -1   97   -92
 5   0  115  -108
 5   1   25   -24
 5   2  < 9    -9
 5   3   55    56
 5   4   84    89
 5   5   40    42
 5   6   51    51
 5   7   36    21
 5   8  < 9   -11
 5   9   23    18
 6 -13    9    10
 6 -12   17   -18
 6 -11  <10    -2
 6 -10   19   -20
 6  -9  <11    -3
 6  -8   20   -27
 6  -7   50    56
 6  -6   16    14
 6  -5   73    77
 6  -4   29    23
 6  -3   23   -22
 6  -2   92   -82
 6  -1  124  -120
```

Table 1. Continued.

```
6  0 106 - 95      11 - 6 < 7 -  2     3 - 9 130 130      6   6  42 - 46     1 -15  13   18     4   2  15   18
6  1  71 • 67      11 - 5   9 - 11     3 - 8  88 - 88     6   7  28   27     1 -14 <11 -  6     4   3  27   29
6  2  22   21      11 - 4 < 9    2     3 - 7  59   60     7 -12 < 8 -  2     1 -13  18 - 19     4   4 <12    9
6  3  13   14      11 - 3 < 9    0     3 - 6  41   36     7 -11 <11 -  9     1 -12  46 - 44     4   5 <13   11
6  4 <12    7      11 - 2 < 9 -  1     3 - 5 107 -101     7 -10 <13    4     1 -11  47 - 45     4   6 <11 -  6
6  5  32   33      11 - 1   9 - 11     3 - 4 158  148     7 - 9  23 - 26     1 -10  52 - 49     5 -13  22 - 24
6  6  63 - 62      11   0 < 9 -  4     3 - 3  64 - 62     7 - 8  33   39     1 - 9  20   20     5 -12  41   38
6  7  17   19      11   1  10 - 11     3 - 2  76   69     7 - 7  31 - 32     1 - 8  63 - 64     5 -11  65 - 54
6  8  31 - 31      11   2 < 7    5     3 - 1  35   34     7 - 6  17   21     1 - 7  60   64     5 - 9  21   18
6 -9 < 9 -  4                          3   0  20 - 15     7 - 5 <12 - 11     1 - 6  50 - 53     5 - 8  52   58
6 10  13   18                          3   1  16   13     7 - 4  20 - 20     1 - 5  25 - 21     5 - 7  90   82
7 -12 < 8    6        h = 3            3   2 <10 -  7     7 - 3  36   37     1 - 4  33   39     5 - 6  32   38
7 -11 <11    8                         3   3  10    8     7 - 2 <12    5     1 - 3  84 - 96     5 - 5 <12    6
7 -10 <10    3      0 -14 <12    3     3   4 <12 -  5     7 - 1  66   62     1 - 2  85 - 90     5 - 4  52 - 50
7 - 9 <11 -  4      0 -12  16   16     3   5  20 - 18     7   0  23   21     1 - 1  30 - 25     5 - 3  91 - 84
7 - 8  48   51      0 -10  22   18     3   6  15 - 11     7   1  23   21     1   0  16   13     5 - 1  48 - 43
7 - 7  29 - 31      0 - 8  59   50     3   7  28 - 26     7   2 <12 -  3     1   1  27   22     5   0 <12 -  9
7 - 6  80   87      0 - 6  56   55     3   8 <12 -  6     7   3  32 - 33     1   2   7    4     5   1 <12   10
7 - 5  10 - 14      0 - 4  45 - 40     3   9 <10    8     7   4  26   28     1   3 <12    2     5   2  21   21
7 - 4  23 - 22      0 - 2  21   22     4 -14  11 - 13     7   5  31 - 35     1   4  20   19     5   3  20   20
7 - 3  73   72      0   0 255  236     4 -13 <12 - 11     7   6  46   44     1   5  32 - 28     5   4 <11    2
7 - 2 120 -118      0   2  66   63     4 -12  24 - 20     7   7 < 8 -  2     1   6  26 - 24     5   5   8   12
7 - 1 134  129      0   4 190 -188     4 -11  46   43     8 -11  24 - 28     1   7  33 - 31     6 -12  20 - 21
7   0 <11    5      0   6 149 -148     4 -10 <12    6     8 -10 <10 -  4     1   8  23 - 28     6 -11 <12   10
7   1  87   80      0   8   9    9     4 - 9  24   26     8 - 9  16 - 16     2 -14 <11 - 10     6 -10 <14 -  6
7   2  78   75      0  10  28   34     4 - 8  14   16     8 - 8   9 - 13     2 -13 <13 - 10     6 - 7  15   19
7   3  21 - 23      1 -15 < 8 -  2     4 - 7  28 - 21     8 - 7  14   13     2 -12  40 - 39     6 - 6  44   40
7   4 <12 -  3      1 -14  14   11     4 - 6  19 - 25     8 - 6  14 - 13     2 -11  42 - 43     6 - 5 <12   13
7   5  66   68      1 -13  22 - 19     4 - 5  39   34     8 - 5  14 - 14     2 -10  15 - 13     6 - 4  10 -  9
7   6  34 - 33      1 -12  21 - 20     4 - 4  70 - 70     8 - 4  15 - 13     2 - 9  30 - 29     6 - 3  24 - 23
7   7  34 - 29      1 -11  45 - 41     4 - 3  67   55     8 - 3  63 - 56     2 - 8  38   37     6 - 2  42   43
7   8 <10 -  8      1 -10  25 - 29     4 - 2  43 - 36     8 - 2  35 - 33     2 - 7  20 - 20     6 - 1  69 - 68
7   9  15   17      1 - 9  36 - 35     4 - 1  14 - 13     8 - 1  34 - 31     2 - 6  51   51     6   0  31   32
8 -11  19 - 19      1 - 8 <10 -  2     4   0 <10 -  9     8   0   7 -  8     2 - 5  39   42     6   1  46 - 44
8 -10  16 - 17      1 - 7  16   18     4   1  29   28     8   1  10   11     2 - 4  43 - 43     6   2  14 - 18
8 - 9  33 - 32      1 - 6  24 - 22     4   2  14   14     8   2  12 - 12     2 - 3 126  133     6   3  29   31
8 - 8 <11 -  3      1 - 5  12   12     4   3  50   53     8   3  18   19     2 - 2 136 -132     6   4 <12 -  4
8 - 7 <11 -  9      1 - 4  20 - 18     4   4  41   43     8   4 <12    9     2 - 1  86   80     6   5  55   58
8 - 6  13 - 18      1 - 3  64 - 69     4   5 <12    6     8   5 <10 -  3     2   0  24 - 28     7 -11 <10 -  4
8 - 5 <12    3      1 - 2 168  180     4   6  39   39     9 -10  26 - 38     2   1  13 - 27     7 -10 <12 -  3
8 - 4  13 - 19      1 - 1  33   24     4   7   7 - 11     9 - 9  28   29     2   2  82   82     7 - 9   6 -  9
8 - 3  45 - 45      1   0 248  239     4   8  27   24     9 - 8  36 - 33     2   3  50 - 53     7 - 8   7 -  9
8 - 2  68   62      1   1 103   95     4   9  14   12     9 - 7  12   17     2   4  32   32     7 - 7   7 - 11
8 - 1  39 - 35      1   2  27   20     5 -13  17 - 16     9 - 6  23   21     2   5  49 - 45     7 - 6   5 -  8
8   0  91   86      1   3   9   14     5 -12 <12    4     9 - 5  15 - 13     2   6  41 - 40     7 - 4   7   10
8   1  55   51      1   4  45 - 45     5 -11  34 - 33     9 - 4  57   52     2   7  39 - 35     7 - 3 <12 -  5
8   2 <12 -  5      1   5  46 - 42     5 -10  22   21     9 - 3 <11 -  4     3 -14  26   28     7 - 2  28 - 25
8   3  61   60      1   6 <12 -  3     5 - 9  17 - 16     9 - 2  19   17     3 -13 <12 -  7     7 - 1 <12 -  5
8   4  44 - 42      1   7  28 - 25     5 - 8  30   31     9 - 1 <11    4     3 -11  27   27     7   0  63 - 60
8   5  16   18      1   8   9 - 10     5 - 7  67   62     9   0 <11 -  2     3 -10  80 - 79     7   1  14 - 16
8   6 <11 - 10      1   9 <11    7     5 - 6  22   31     9   1 <12    6     3 - 8  61 - 62     7   2 <13    4
8   7  11 - 10      1  10  10 - 10     5 - 5  79   65     9   2  16   16     3 - 7  23 - 23     7   3  33 - 30
8   8 < 7 -  6      2 -15  57   65     5 - 4  54 - 44     9   3 <11    9     3 - 6  32   30     7   4  57   61
9 -10  26 - 29      2 -14  16 - 14     5 - 3  80 - 80     9   4 < 9    7     3 - 5  28   24     8 -10 < 8    7
9 - 9  23 - 21      2 -13  26   26     5 - 2 180 -177     10 - 8  14 - 18     3 - 4  81   83     8 - 9  14   13
9 - 8  25 - 25      2 -12  61 - 58     5 - 1 125 -113     10 - 7  26 - 28     3 - 3  45   45     8 - 8 <12    2
9 - 7  11   12      2 -11 113 -111     5   0 129 -130     10 - 6  25 - 25     3 - 2  43   45     8 - 7   6   11
9 - 6 <10 -  3      2 -10 <12 -  8     5   1 <11    5     10 - 5  40   36     3 - 1  21   18     8 - 6   6   10
9 - 5 <11    5      2 - 9 131 -132     5   2  27   30     10 - 4  13 - 14     3   0 <11 -  6     8 - 5 <11    3
9 - 4  34   27      2 - 8  47   47     5   3  47   48     10 - 3  71   59     3   1  51   42     8 - 4 <11    5
9 - 3  47 - 44      2 - 7  28 - 25     5   4  43   49     10 - 2 <11 -  4     3   2  25 - 27     8 - 3 <11    7
9 - 2  26   23      2 - 6  22   19     5   5  28   30     10 - 1  13   13     3   3  49   44     8 - 2  22 - 21
9 - 1  34 - 31      2 - 5  19   21     5   6  15 - 15     10   0  13   10     3   5 - 15   17     8 - 1 <13    8
9   0 <11 -  9      2 - 4  34 - 39     5   7  14   16     10   1 < 9 -  5     3   5 <12    7     8   0 <13 -  7
9   1 <11 -  9      2 - 3 < 8    9     5   8  15 - 17     10   2 < 8    8     3   6 <11 -  9     8   1 <12    7
9   2 <11 -  3      2 - 2  60 - 68     6 -13  13   13                        3   7 <10    6     8   2  23   17
9   3 <10 -  1      2 - 1  45   26     6 -12 <11 -  8        h = 4           4 -13  26   24     8   3 < 9    4
9   4  18   18      2   0  53 - 50     6 -11 <10 -  3                        4 -12  21 - 17     9 - 8  22 - 29
9   5 <11    3      2   1  36 - 32     6 -10 <11 -  2     0 -14   9    9     4 -11 <12 -  8     9 - 7   7 -  7
9   6 < 9 -  4      2   2  38   39     6 - 9  18   19     0 -12 <12 -  4     4 -10  18 - 15     9 - 6  21   21
9   7  12 - 15      2   3  50 - 54     6 - 8  56   53     0 -10  10    7     4 - 9  55 - 52     9 - 5   9    9
10 - 8 < 8    2     2   4  77   79     6 - 7  64   69     0 - 8  40   43     4 - 8 <12 -  4     9 - 4  42   39
10 - 7 <10    3     2   5  36 - 34     6 - 6  79   79     0 - 6   9    9     4 - 7 <12 -  2     9 - 3  37   15
10 - 6  10 - 10     2   6 <12 -  8     6 - 5  47   49     0 - 4   7 -  4     4 - 6 <10 -  7     9 - 2  21   21
10 - 5   8   11     2   7  36 - 32     6 - 4 <12 -  8     0 - 2 123  131     4 - 5 <12 -  8     9 - 1 <11    5
10 - 4 <10 -  3     2   8  35 - 33     6 - 3  41 - 39     0   0 128  118     4 - 4  39   29     9   0 <10    6
10 - 3  31   28     2   9  31 - 26     6 - 2  57 - 48     0   2  35 - 33     4 - 3  43 - 36     9   1  14   17
10 - 2  14   12     3 -14  38   35     6 - 1  83 - 84     0   4  51 - 48     4 - 3  50 - 48
10 - 1  21   18     3 -13  26 - 27     6   0  41   44     0   6 <11    4     4 - 2  60 - 58
10   0  21   19     3 -12 <11 -  9     6   1  39 - 41     0   8 < 8    8     4 - 1  51 - 47
10   1 <12 -  6     3 -11  21   20     6   2  30   27                        4   0  24 - 24
10   2  17   16     3 -10  83 - 84     6   3  25   23                        4   1  23   24
10   3 <10 -  2                        6   4  57 - 60
10   4   8    8                        6   5  49   54
```

factor decreased from 57 % to 24 %. Normal values had been assumed for the temperature parameters. The hydrogen atoms were omitted at this stage. After having postulated some trial structures a reasonable electron density projection also along [101] was found. The structure was refined by the least-squares methods. In the three dimensional refinement the positional and anisotropic temperature parameters of the carbon atoms and the positional parameters of the hydrogen atoms were refined. The isotropic temperature parameters of the hydrogen atoms were kept constant. In Table 1 1051 ex-

Table 2. Positional·parameters of the carbon atoms with standard deviations. The co-ordinates are given as fractions of the cell edges. All numbers have been multiplied by 10^4. The coordinates in the second row for each atom are corrected for rigid-body libration.

	x	y	z
C(1)	−95 (5)	1235 (2)	754 (2)
	−97	1238	757
C(2)	2787 (6)	1765 (3)	1462 (2)
	2796	1769	1468
C(3)	3128 (7)	3271 (3)	1119 (2)
	3137	3278	1124
C(4)	2430 (6)	3389 (3)	−234 (2)
	2437	3396	−235
C(5)	−423 (6)	2864 (3)	−950 (2)
	−427	2870	−953
C(6)	−905 (5)	1368 (2)	−620 (2)
	−909	1371	−622
C(7)	528 (6)	274 (2)	−1085 (2)
	530	274	−1089

Table 3. Temperature parameters of the carbon atoms with standard deviations. The numbers are multiplied by 10^4. The temperature factor is of the form $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	329 (14)	105 (3)	60 (2)	16 (4)	64 (3)	−3 (1)
C(2)	375 (15)	118 (3)	64 (2)	−7 (4)	47 (4)	−3 (2)
C(3)	448 (17)	120 (3)	81 (2)	−37 (5)	51 (4)	−11 (2)
C(4)	424 (17)	112 (3)	88 (2)	−26 (5)	73 (5)	5 (2)
C(5)	365 (15)	109 (3)	75 (2)	2 (4)	53 (4)	10 (2)
C(6)	285 (13)	100 (3)	64 (2)	8 (4)	59 (3)	5 (1)
C(7)	369 (15)	113 (3)	62 (2)	4 (4)	77 (4)	4 (2)

perimental and calculated structure factors are listed. Six reflections assumed to be affected by secondary extinction were not included in the calculation of the reliability factor which is 7 % for the observed reflections and 10 % when also 241 non-observed reflections ($F_o = 0$) are included. The positional parameters obtained from the three dimensional least-squares refinement were corrected for thermal motions. Cruickshank [10] has shown that this may be done by assuming the anisotropic vibrations of the atoms to arise primarily from rigid-body oscillations of the molecule and calculating the rigid-body libration and translation from the anisotropies of the various atoms. The final atomic parameters with standard deviations are listed in Tables 2, 3, and 4. Fig. 1 shows the final composite electron density map as seen along the a axis with the positions of the carbon atoms. Fig. 2 shows a composite partial difference Fourier synthesis with the positions of the hydrogen and carbon atoms indicated. The atomic positions are the ones obtained from the least-

Table 4. Final hydrogen atom positional parameters with standard deviations multiplied by 10^3. The coordinates in the second row for each atom are corrected for rigid-body libration. The isotropic temperature parameters were assumed equal ($B = 4.7$) and were not refined.

	x	y	z
H(1)	−135 (9)	191 (4)	101 (4)
	−136	192	101
H(2)	433 (8)	108 (4)	124 (3)
	435	108	124
H(3)	311 (9)	166 (4)	235 (4)
	312	166	236
H(4)	517 (9)	355 (4)	157 (4)
	519	356	158
H(5)	184 (8)	402 (4)	144 (3)
	184	403	145
H(6)	387 (8)	276 (4)	−39 (3)
	388	276	−39
H(7)	252 (8)	434 (5)	−44 (3)
	253	435	−44
H(8)	−92 (9)	288 (4)	−184 (4)
	−93	289	−185
H(9)	−185 (9)	351 (4)	−90 (4)
	−186	352	−90
H(10)	−291 (9)	117 (5)	−111 (4)
	−292	117	−111
H(11)	267 (9)	51 (5)	−71 (4)
	268	51	−71
H(12)	−21 (8)	35 (4)	−198 (4)
	−21	35	−199

Table 5. Direction cosines of the axes L, M, N of the molecular coordinate system referred to crystal axes.

	a	b	c
L	−0.2908	−0.9518	0.0223
M	−0.0124	0.1063	−0.9125
N	−0.9567	0.2880	0.4085

Table 6. Matrix transforming the coordinates x, y, z given in fractions of cell edges to the coordinates L, M, N given in Ångström units and referred to the orthogonal molecular coordinate system.

−1.55972	−9.11056	0.26876
−0.06662	1.01704	−11.01054
−5.13075	2.75628	4.92992

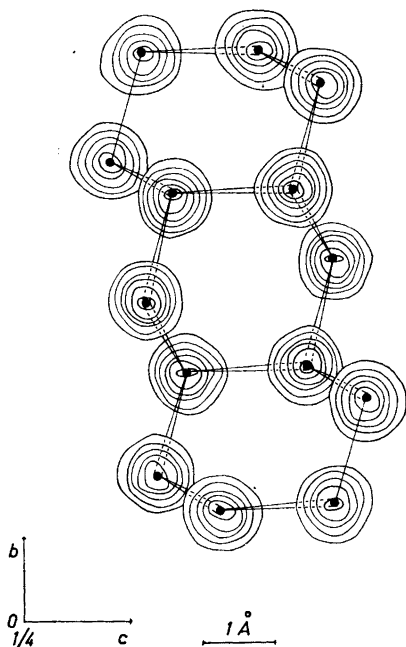**Fig. 1.** Composite electron density map viewed down along the *a* axis. Contours are drawn at 2, 3...eÅ⁻³. The positions of the atoms were taken from the least-squares refinement.
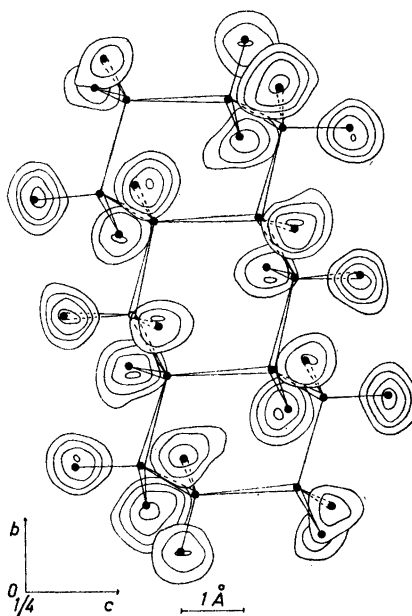

Fig. 2. Composite difference electron density map where the contributions from the carbon atoms are subtracted, viewed down along the *a* axis. Contours are drawn at 0.3, 0.4...eÅ⁻³.
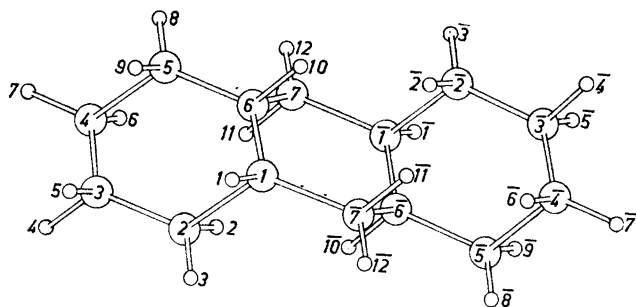

Fig. 3. A model representing the molecule. For each type of atoms n and $\bar{n}$ ($n = 1, 2...$) are labels of atoms which are related by a centre of symmetry.

squares refinement. Fig. 3 shows the labelling of the atoms. Table 5 gives the direction cosines of the axes of inertia L, M, N, of the rigid molecule. These axes are chosen as the molecular coordinate system. Table 6 gives the matrix of transformation of the coordinates. Rigid-body translation and libration parameters are listed in Table 7. Principal components of the rigid-body

Table 7. Rigid-body translation parameters T_{ij} and libration parameters ω_{ij}.

	LL	MM	NN	LM	MN	LN
T (Å²)	0.0482	0.0411	0.0356	0.0004	0.0020	−0.0008
ω (rad²)	0.00582	0.00252	0.00174	−0.00059	0.00042	−0.00003

Table 8. Principal components of rigid-body vibrations with direction cosines.

	L	M	N
$T_1{}^2 = 0.0483$ Å²	0.994	0.103	−0.033
$T_2{}^2 = 0.0418$	0.017	−0.950	−0.311
$T_3{}^2 = 0.0349$	0.067	−0.312	0.948
$\omega_1{}^2 = 0.0059$ rad²	0.983	−0.175	−0.062
$\omega_2{}^2 = 0.0026$	0.167	0.887	0.431
$\omega_3{}^2 = 0.0015$	0.052	0.424	−0.904

Table 9. Components of atomic vibration tensors **V** in Å² as found by least-squares refinement (exp) and as calculated from rigid-body parameters (RB). The values are multiplied by 10^4.

		V_{LL}	V_{MM}	V_{NN}	V_{LM}	V_{MN}	V_{LN}
C(1)	(exp)	512	448	421	−10	41	38
	(RB)	510	465	424	−9	51	19
C(2)		538	476	590	−33	−19	−1
		517	484	613	−45	−19	−8
C(3)		512	609	753	−75	−39	−20
		496	618	740	−49	−42	−8
C(4)		487	641	663	38	−15	−46
		495	632	656	47	−25	−53
C(5)		509	539	575	47	−57	−7
		515	542	586	59	−41	8
C(6)		470	466	395	31	1	−12
		498	449	416	19	−7	1
C(7)		530	455	479	39	74	−5
		529	445	440	16	70	−11
H(1)	(RB)	584	620	477	−13	116	72
H(2)		540	559	543	−14	−103	−63
H(3)		586	476	852	−78	6	15
H(4)		526	739	939	−74	−144	−82
H(5)		535	719	878	−87	34	104
H(6)		549	701	604	72	10	−123
H(7)		501	748	836	79	−51	−58
H(8)		572	529	763	103	−48	−13
H(9)		552	684	633	67	−106	73
H(10)		540	511	464	24	−77	−1
H(11)		568	571	406	38	84	−39
H(12)		597	448	636	22	118	−6

vibrations and their direction cosines with respect to molecular axes are given in Table 8. Table 9 gives the atomic vibration tensors as found by the least-squares refinement and as calculated from the rigid-body parameters referred to the molecular coordinate system.

DISCUSSION

The agreement between the two sets of values of the atomic vibration tensors listed in Table 9 indicate that the assumption of a rigid molecule is acceptable. According to the values in Table 8 the amplitudes of translational motion in directions of the principal axes L, M, and N are 0.22, 0.20, and 0.19 (Å), respectively, and the amplitudes of libration along the same axes are 4.3, 2.8, and 2.3 (°), respectively. The largest amplitudes are along the L axis. This might be expected as the molecule has its smallest moment of inertia along this axis which runs approximately along [010] (Table 5).

Bond distances with standard deviations are listed in Table 10. For comparison also those calculated from the uncorrected coordinates in Tables 2 and 4 are listed. The corrected C—C bond distances are from 0.003 to 0.008 (Å)

Table 10. Bond distances (Å) corrected and uncorrected for rigid-body libration. Standard deviations in the parentheses.

C(1)—C(2)	1.541	1.536	(0.004)
C(2)—C(3)	1.533	1.530	(0.004)
C(3)—C(4)	1.539	1.531	(0.004)
C(4)—C(5)	1.529	1.524	(0.005)
C(5)—C(6)	1.538	1.535	(0.003)
C(6)—C(7)	1.533	1.528	(0.003)
C(1)—C(6)	1.554	1.548	(0.003)
C(1)—C(7̄)	1.543	1.539	(0.003)
C(1)—H(1)	1.07	1.06	(0.04)
C(2)—H(2)	1.17	1.17	(0.04)
C(2)—H(3)	1.03	1.02	(0.04)
C(3)—H(4)	1.06	1.05	(0.04)
C(3)—H(5)	1.17	1.16	(0.04)
C(4)—H(6)	1.06	1.05	(0.04)
C(4)—H(7)	0.95	0.94	(0.05)
C(5)—H(8)	1.01	1.00	(0.04)
C(5)—H(9)	1.01	1.00	(0.04)
C(6)—H(10)	1.03	1.03	(0.04)
C(7)—H(11)	1.09	1.09	(0.04)
C(7)—H(12)	1.00	1.00	(0.04)

longer than the uncorrected ones. Absolute values of the differences between the various C—C bond distances divided by the average standard deviation are listed in Table 11. C(4)—C(5) (1.529 Å) is the shortest of the C—C distances; it is significantly shorter than C(1)—C(2), C(1)—C(7̄), and C(1)—C(6). C(1)—C(6) (1.554 Å) is significantly longer than most of the other C—C bond

Table 11. Absolute values of the differences between the various C—C bond distances divided by the average standard deviation 0.004.

	C(1)—C(2)	C(2)—C(3)	C(3)—C(4)	C(4)—C(5)	C(5)—C(6)	C(6)—C(7)	C(1)—C($\bar{7}$)
C(2)—C(3)	2.0						
C(3)—C(4)	0.5	1.5					
C(4)—C(5)	3.0	1.0	2.5				
C(5)—C(6)	0.8	1.3	0.3	2.3			
C(6)—C(7)	2.0	0	1.5	1.0	1.3		
C(1)—C($\bar{7}$)	0.5	2.5	1.0	3.5	1.3	2.5	
C(1)—C(6)	3.3	5.3	3.8	6.3	4.0	5.3	2.8

Table 12. Bond angles (°) with and without rigid-body corrections and with standard deviations.

C(6)—C(7)—C($\bar{1}$)	113.5	113.6	(0.2)
C(2)—C(1)—C($\bar{7}$)	112.6	112.7	(0.2)
C(2)—C(1)—C(6)	112.1	112.0	(0.2)
C(5)—C(6)—C(7)	112.6	112.7	(0.2)
C(4)—C(5)—C(6)	113.1	113.2	(0.2)
C(1)—C(6)—C(7)	111.4	111.3	(0.2)
C(1)—C(2)—C(3)	111.1	111.1	(0.2)
C(2)—C(3)—C(4)	110.6	110.6	(0.2)
C(3)—C(4)—C(5)	111.0	111.1	(0.3)
C(5)—C(6)—C($\underline{1}$)	110.4	110.4	(0.2)
C(6)—C(1)—C($\bar{7}$)	110.3	110.3	(0.2)
C(6)—C(1)—H(1)	108	109	(2)
C($\bar{7}$)—C(1)—H(1)	109	109	(2)
C(2)—C(1)—H(1)	105	104	(2)
C(1)—C(2)—H(2)	110	110	(2)
C(1)—C(2)—H(3)	106	106	(2)
C(3)—C(2)—H(2)	107	107	(2)
C(3)—C(2)—H(3)	113	113	(2)
C(2)—C(3)—H(4)	108	108	(2)
C(2)—C(3)—H(5)	110	110	(2)
C(4)—C(3)—H(4)	108	108	(2)
C(4)—C(3)—H(5)	112	112	(2)
C(3)—C(4)—H(6)	105	105	(2)
C(3)—C(4)—H(7)	109	110	(2)
C(5)—C(4)—H(6)	111	111	(2)
C(5)—C(4)—H(7)	108	108	(2)
C(4)—C(5)—H(8)	113	114	(2)
C(4)—C(5)—H(9)	113	113	(2)
C(6)—C(5)—H(8)	107	107	(2)
C(6)—C(5)—H(9)	111	111	(2)
C(5)—C(6)—H(10)	105	106	(2)
C(1)—C(6)—H(10)	114	114	(2)
C(7)—C(6)—H(10)	103	103	(2)
C(6)—C(7)—H(11)	108	108	(2)
C(6)—C(7)—H(12)	108	107	(2)
C($\bar{1}$)—C(7)—H(11)	109	109	(2)
C($\bar{1}$)—C(7)—H(12)	108	108	(2)
H(2)—C(2)—H(3)	110	110	(3)
H(4)—C(3)—H(5)	108	108	(3)
H(6)—C(4)—H(7)	113	113	(3)
H(8)—C(5)—H(9)	99	99	(3)
H(11)—C(7)—H(12)	110	110	(3)

Table 13. Shortest intramolecular distances between hydrogen atoms which are "axial" with respect to the rings to which they are bonded. Standard deviations in the parentheses.

H(2)—H(11)	2.25 (0.06) (Å)
H(2)—H($\overline{10}$)	2.27 (0.06)
H(6)—H(11)	2.24 (0.06)
H(11)—H($\overline{10}$)	2.69 (0.06)
H(2)—H(6)	2.49 (0.06)
H(1)—H(5)	2.57 (0.06)
H(5)—H(9)	2.81 (0.06)
H(1)—H(9)	2.70 (0.06)

distances. This might be expected if "non-bonding" repulsions are assumed, as C(1) and C(6) and their symmetrical equivalents are the only atoms each bonded to three carbon atoms. C(4)—C(5) and C(1)—C(6) were not considered for the calculation of the average C—C bond distance with standard deviation: 1.538 Å (0.0014 Å). The mean of the C—H bond distances with standard deviation is 1.05 Å (0.012 Å).

Bond angles with standard deviations are listed in Table 12, from which the corrections of the bond angles may be seen to be negligible. Table 13 gives the shortest intramolecular distances between hydrogen atoms which are "axial" with respect to the carbon rings to which they are bonded. The distances between H(2) and H(11), H(2) and H($\overline{10}$), and H(6) and H(11) are significantly shorter than the others and greater repulsions between these hydrogen atoms might be expected. Taking the "non-bonding" repulsions into account it is reasonable that certain CCC angles (the five first of the angles listed in Table 12) are significantly larger than the others. The mean of the values of the bond angles with standard deviations are: $\angle$ CCC: 111.5° (0.07°), $\angle$ HCH: 108° (1.3°), $\angle$ CCH: 108.7° (0.4°).

The shortest intermolecular distances are normal, being 2.44 Å (H—H), 3.06 Å (C—H), and 3.78 Å (C—C).

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2272 K. E. HJORTAAS

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