The Crystal Structure of Perdeuterated Violuric Acid Monohydrate: The X-ray Diffraction Analysis

By B. M. Craven and Y. Mascarenhas*

The Crystallography Laboratory, University of Pittsburgh, Pittsburgh 13, Pa., U.S.A.

Perdeuterated violuric acid monohydrate ($C_4D_3N_3O_4.D_2O$) is orthorhombic, space group $Cmc2_1$ with cell parameters $a = 6\cdot217$, $b = 14\cdot373$, $c = 7\cdot516$ Å and with four molecules in the unit cell. The space group requires all atoms to lie in the planes $x = 0$, $\frac{1}{2}$ (parallel to a crystal cleavage plane) in a very compact hydrogen-bonded layer structure. The X-ray structure analysis has been carried out with 397 three-dimensional counter intensity data (Cu $K\alpha$ radiation) with both Fourier and least-squares refinement of atomic positional and anisotropic thermal parameters. Bond lengths and angles have been determined with e.s.d.'s of $0\cdot008$ Å and $0.6°$ respectively. The packing about the water molecules results in six coplanar interatomic approaches between oxygen atoms at distances compatible with hydrogen bonding, although only three hydrogen atoms can participate in these interactions. The unusually large B_{11} thermal parameters observed for some atoms can reasonably be interpreted in terms of random positional disordering of molecules to equal extents on each side of the crystallographic mirror planes at $x = 0$, $\frac{1}{2}$.

Introduction

Violuric acid monohydrate or 5-hydroxyiminobarbituric acid (Fig. 1) is one of a series of simple derivatives of barbituric acid the crystal structures of which are being studied in order to determine the tautomeric form of the molecule, details of the molecular structure and the nature of the hydrogen bonding.
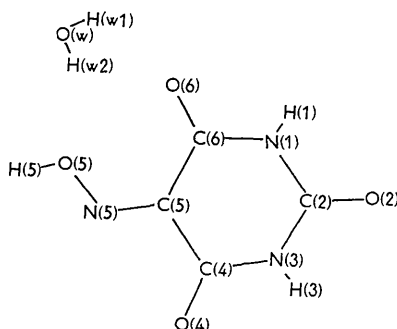

Fig. 1. Violuric acid monohydrate.

A preliminary investigation showed a similarity between the crystal structures of violuric acid monohydrate and barbituric acid dihydrate. In the crystal structure of barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961), all atoms were found to lie in mirror planes separated by $3\cdot12$ Å, giving a very compact layer structure ($D_m = 1\cdot56$ g.cm^{-3}) in which the atoms or substituent atoms at every pyrimidine ring position except C(5) take part in hydrogen bonding. An unusual feature of this structure is that each water molecule takes part in three hydrogen

---

* Present address: Escola de Engenharia de São Carlos, Universidade de São Paolo, Brazil.

bonds required to be coplanar within the experimenta limitations of the analysis.

It was readily shown that violuric acid monohydrate ($C_4H_3N_3O_4.H_2O$) also forms a layer structure with a space group which requires all atoms to lie in mirror planes separated by $3\cdot11$ Å and with a crystal density ($1\cdot72$ g.cm^{-3}) even higher than that of barbituric acid dihydrate, although there is a lower ratio (5:8) of hydrogen atoms to electronegative atoms capable of participating in hydrogen bonds than in barbituric acid dihydrate (6:7).

This structure was expected to have a greater number of close intermolecular approaches than there are hydrogen atoms available for hydrogen bonding.

Experimental

Crystals of violuric acid monohydrate grown by slow evaporation of the aqueous solution are pale orange orthorhombic bipyramids with {111} the predominant form. There is perfect cleavage parallel to (100), although otherwise the crystals are hard and brittle. Often the crystals are twinned on the cleavage plane. On standing in air, the crystals slowly lose water of crystallization as in the case of barbituric acid dihydrate. Deuterated crystals grown from 98% D_2O were given a coating film of collodion in order to prevent decomposition and isotope exchange.

The lattice parameters for perhydrogenated and perdeuterated violuric acid monohydrate were obtained by a least-squares fit based on single-crystal measurements of lattice spacings made with a G.E. XRD 3 diffractometer with Cu $K\alpha$ and Fe $K\alpha$ radiation (Table 1). Crystal densities were measured by flotation in a mixture of bromoform and chloroform.

The X-ray intensity data (Cu $K\alpha$ radiation) for the

Table 1. *The crystal data for violuric acid monohydrate*

	Hydrogenated ($C_4H_3N_3O_4 . H_2O$)	Deuterated ($C_4D_3N_3O_4 . D_2O$)
	Orthorhombic	
a =	6.224 ± 0.002 Å	6.217 ± 0.002 Å
b =	14.359 ± 0.002	14.373 ± 0.002
c =	7.508 ± 0.002	7.516 ± 0.001
U =	671.0 ± 0.3 Å³	671.6 ± 0.2 Å³
D_m =	1.726 g.cm⁻³	1.782 g.cm⁻³
D_x =	1.733	1.781
	$Z = 4$	

Systematically absent spectra:

hkl when $h+k$ odd
$h0l$ when l odd

perhydrogenated material were recorded on Weissenberg equi-inclination photographs by multiple-film techniques. The intensities of the X-ray spectra were estimated by visual comparison with a standard scale. Of the 425 non-symmetry-related hkl reflexions, which were recorded, 62 were too weak to estimate.

The X-ray intensity data for the perdeuterated material were recorded on a G.E. XRD 5 diffractometer with single-crystal orienter and scintillation counter, Cu $K\alpha$ radiation being used. The diffractometer was operated in the $\theta/2\theta$ scanning mode. A background count of 100 seconds duration was taken on both the high and low angle side of each reflexion, followed by a scan through the reflexion at a rate of $0.2°$ in 2θ per min with cumulative count. The intensity of the reflexion 0,12,0 was measured repeatedly in order to monitor the direct X-ray beam intensity. The pyramidal crystal chosen for all measurements had a crystal volume of 1.2×10^{-5} cm³ and was formed by cleaving a bipyramid. Of 412 non-symmetry-related intensities which were examined, only 10 were too weak to estimate. The intensity data were corrected for X-ray absorption by a program for the IBM 1620 computer (Craven, unpublished) based on the program by Wehe, Busing & Levy (1962) for the IBM 7090 computer. The absorption factors, as applied to the integrated intensities, ranged between 1.43 and 2.50 and were considered to be accurate to about 1%. By comparing observed intensities of certain symmetry-related reflexions and from the reproducibility of the observed intensity for a given reflexion, the standard deviation in an integrated intensity was estimated to be

$$\sigma(I) = \sigma(N) + 0.04I$$

where $\sigma(N)$ was the e.s.d. due to the counting statistics alone.

The structure determination

The approximate structure parameters were first determined for the perhydrogenated violuric acid monohydrate from the photographic intensity data. Then an analysis of the structure of perdeuterated

violuric acid monohydrate by neutron diffraction methods made it advisable to complete the X-ray analysis by refinement of the structure parameters of the deuterated crystals, using the more accurate X-ray intensity data obtained on the counter diffractometer.

The initial structure determination

The presence of the cleavage plane suggested a layer structure with sheets of atoms parallel to (100). This was readily confirmed by examining the diffraction pattern, which was found to be characteristic of a structure with all atoms in planes parallel to (100) with a separation of $a/2$. Thus the intensities of corresponding reflexions in the even layers $0kl$, $2kl$, $4kl$, etc. appear to be the same, apart from a general decrease in intensity with increasing scattering angle, and similarly for the odd layers, $1kl$, $3kl$ etc.

As might be expected in this type of structure, the diffraction pattern at room temperature is notable for strong diffuse scattering. For example, normal to **a**, there are intense halos about the strong $h00$ Bragg reflexions. This diffuse scattering may arise from thermal lattice waves in a layer structure in which atomic vibrations are predominantly parallel to **a**. Alternatively, a major contribution to the diffuse scattering may arise from the disordering of the structure by small displacements or distortions of the molecules from coplanarity so that only short range order is retained. The intensities of reflexions hkl and $\bar{h}kl$ were examined carefully and were found to show no differences to indicate that the apparent mirror planes normal to **a** were only pseudosymmetrical.

Of the space groups consistent with the systematically absent spectra, the space group $Cmcm$ is not possible since it does not possess a fourfold position of suitable point symmetry to accommodate the violuric acid molecules. The space groups $Cmc2_1$ and $C2cm$ both have only one fourfold position of suitable point symmetry (m), but $C2cm$ requires the atoms to lie in mirror planes normal to **a** and this is incompatible with the structural evidence given above. The space group is thus $Cmc2_1$ with all atoms in the mirror planes at $x=0$, $\frac{1}{2}$.

The extreme compactness of the layer structure and the stereochemical requirements of hydrogen bonding severely limit the number of reasonable trial structures. A satisfactory trial structure was readily chosen which also agreed with the observed line $(0, v, \frac{1}{2})$ of the Patterson function and this structure was shown to be essentially correct by a reiterative Fourier refinement, using the programs of Shiono (1957) for the IBM 650 computer. Since the structure does not have a resolved projection, three-dimensional methods were used from the beginning, but with only the reflexions $0kl$ and $1kl$ at first, in order to minimize the computation time. The atomic scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used throughout in this analysis.

With the complete data, the refinement of the structure parameters, including anisotropic thermal parameters, was concluded by least-squares methods with a Hughes weighting scheme, the IBM 704 computer being used with the program of Busing & Levy (1959). The effect of hydrogen atom scattering was ignored. Although the final R index was 0·10 (weighted R index 0·13) with no serious discrepancies between observed and calculated structure amplitudes, and although all parameter changes had become small in terms of their e.s.d.'s, there were some features of the resulting structure which seemed chemically unreasonable. In particular, the bond lengths N(1)–C(2) and N(3)–C(2), which might be expected to be almost equal were found to be 1·42 and 1·34 Å, a difference which is very significant in terms of its e.s.d. of 0·024 Å.* Although there seemed no reason to doubt that the structure determined was essentially the solution to the phase problem, it was believed that atom C(2) particularly was

displaced from its true position as a result of a cumulative effect of errors in the intensity data, for example, those errors which might be related to the inferior quality of the crystal used in recording the data for the layers $l=0, 1, 2$ etc. and the neglect of absorption corrections. Some support for this belief was obtained from the subsequent refinement in which the more accurate data for the perdeuterated violuric acid monohydrate were used, since this gave a set of structure parameters which were chemically reasonable. However, a comparison of the two sets of observed structure amplitudes revealed no discrepancies attributable to systematic errors which might explain the differences in the corresponding derived structure parameters.†

The refinement of the structure of perdeuterated violuric acid monohydrate

Because a knowledge of the precise hydrogen atom positions about the water oxygen atom would be of

---

* This e.s.d. was calculated with allowance for the effect of the common atom C(2) and the correlation between z parameters resulting from the polar direction c (Templeton, 1960).

† Tables of the observed and calculated structure factors and the structure parameters for the refinement based on photographic intensity data are available from the authors on request.
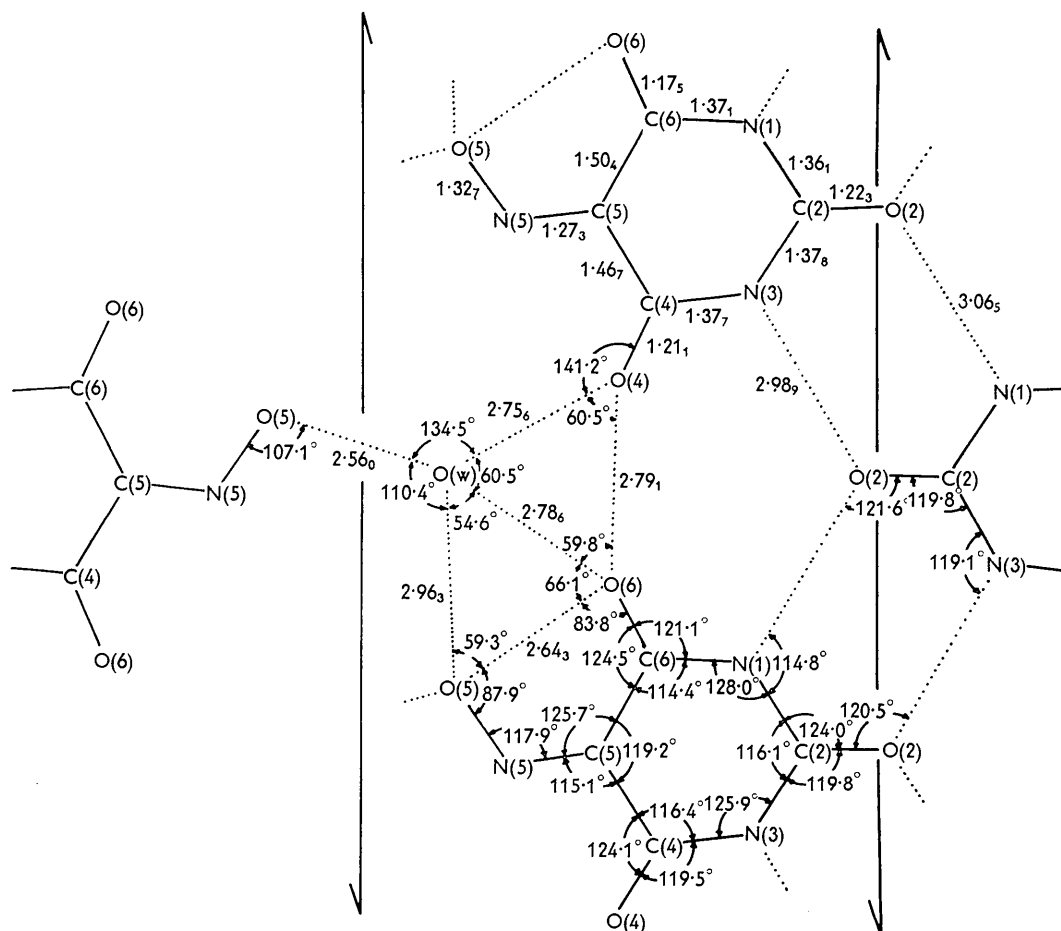

Fig. 2. The interatomic distances and angles. These are not corrected for the effects of molecular oscillations.

Table 2. *The observed and calculated structure factors*

In successive columns are listed h, l, $100|F_o|$, $100|F_c|$, $100A_o$ and $100B_o$
Reflections omitted from the least squares refinement are indicated (*)

```
        K = 0
2  0  12025  21875              *
4  0   7411   8577  7411+     0 *
6  0   2714   2769  2714+     0
0  2   3208   4309  2671+  1840-*
2  2   3439   3348  3047+  1593-
4  2   1796   1670  1741+   440-
6  2    852    729   852+    13-
0  4   1448   1475  1448+    59-
2  4   1231   1196  1231+    12-
4  4    693    718   691+    46+
6  4    366    372   3(2+    51+
0  6   5580   6783  5190+ 21444**
2  6   5216   5422  4864+  1884+
4  6   3022   3039  2842+  1027+
6  6   1320   1391  1255+   409+
0  8    523    539   510+   118-
2  8    572    562   572+    10-
4  8    498    525   483+   121+

        K = 1
1  0   2032   2110  2032-     0
3  0   1314   1280  1314-     0
5  0    726    738   726-     0
7  0    356    378   356-     0
3  1   3156   2906   171+  3152+
5  1   1565   1402   254-  1564+
7  1    596    638    48-   596+
1  2   2202   2425  1626+  1485-
3  2   1029   1046   691+   762-
5  2    295    263   140+   260-
1  3    482    494   443-   187+
3  3    365    382   202-   305-
5  3    407    350    94-   396-
1  4    507    511   503-    68-
3  4    410    293   403-    74+
5  4    255    158   198-   159+
1  5   1135    995   744-   857-
3  5    552    544   547-    70+
5  5    529    547   319-   421+
1  6   2293   2164  2208-   618+
3  6   1599   1514  1552-   382+
5  6    826    825   810-   160+
1  7   2352   2258  1291-  1965+
3  7   1573   1573   828-  1336+
5  7    796    855   395-   692+
1  8    409    385   196-   359+
3  8    282    296   182-   215+
1  9    451    440   375-   250-

        K = 2
2  0   2768   2511  2768-     0
4  0    768    675   768-     0
6  0    269    238   269-     0
2  1   2049   2009  1047+  1762-
4  1    830    799   389+   733-
6  1    315    315   112+   294-
0  2   5121   7485  5072+   933-*
2  2   5250   5287  5210+   643-
4  2   1967   1913  1943+   303-
6  2    508    544   498+    99-
0  3   2647   2653     1-  2647+
2  3   2197   2003    53-  2196+
4  3   1213   1077   113-  1208+
6  3    562    518    96-   554+
0  4   2332   2214  2170+   853-
2  4   1826   1648  1706+   650-
4  4    915    785   858+   318-
6  4    304    296   282+   113-
0  5   2658   2548  1210-  2367-
2  5   2091   1966   967+  1854-
4  5   1072   1005   525-   934-
6  5    379    414   204-   319-
0  6   1994   1832  1684-  1067-
2  6   1518   1367  1260-   846-
4  6    706    662   556-   435-
6  6    253    276   187-   171-
0  7   1938   1764   940-  1695-
2  7   1549   1473   713-  1375-
4  7    914    897   359-   841-
0  8   2408   2342  2297+   722+
2  8   1911   1811  1837+   527+
4  8    898    894   880+   177+
0  9    959    949   559-   778+
2  9    755    811   437-   615+

        K = 3
1  0   1112    999  1112-     0
3  0    569    540   569-     0
5  0    143    160   143-     0
1  1   2032   2179  1147+  1677+
3  1    944    923   532+   780+
5  1    231    230   125+   193+
1  2   5379   5785  5320-   797-
3  2   3350   3194  3322-   429-
5  2   1465   1368  1457-   147-
7  2    496    538   494-    36-
1  3   5631   5998  1753-  5352-
3  3   2989   2774   954+  2832-
5  3    757    715   263+   709-
1  4   3959   3814  3890-   731-
3  4   2596   2398  2542-   526-
5  4   1219   1162  1185-   284-
1  5   1182   1051  1023-   589-
3  5    718    672   415-   585-
5  5    358    356    45-   356-
1  6    561    502   325+   459-

3  6    307    340   196+   235-
5  6    168    180   119+   118-
1  7    777    698   671-   392-
3  7    405    420   383-   131-
5  7    137    173   136-    13+
1  8   1003    931   901-   439-
3  8    591    701   532-   256-
1  9    335    371   230+   243-

        K = 4
0  0   1524   1511  1524+     0
2  0    870    706   870+     0
6  0    134     58   134-     0
0  1   2096   2277  1056+  1811-
2  1   1678   1618   826+  1460-
4  1    790    772   327+   719-
6  1    369    355    99+   355-
0  2   2079   2126  2053-   327+
2  2   1291   1212  1261-   272+
4  2    213    195   189-    99+
6  2     89     74    90+     6-
0  3   4820   5682  1683+  4516-
2  3   4329   4172  1460+  4075-
4  3   2153   2023   599+  2057-
6  3    907    851   217+   880-
0  4   2787   2554  2751-   125+
2  4   2096   1986  2094+    85+
4  4   1048   1046  1048+    39+
6  4    416    448   415+    20+
0  5   1841   1624   296-  1817-
2  5   1428   1279   207-  1413-
4  5    751    689    70-   747-
6  5    360    304    31-   360-
0  6   1774   1669  1774+     1+
2  6   1386   1218  1386+    25-
4  6    512    524   511+    38-
0  7    987    941   377-   912-
2  7    753    762   255-   708-
4  7    426    442    87-   417-
0  8   1347   1416  1036-   861-
0  9    634    631   293+   562-
2  9    618    577   272+   555-

        K = 5
1  0   3612   3473  3612-     0
3  0   1908   1734  1908-     0
5  0    604    510   604-     0
3  1   1369   1328   416+  1305-
3  2   1631   1597  1271-  1023+
5  2    394    436   243-   309+
1  3   2439   2270   463+  2394+
3  3   1214   1059   335+  1166+
5  3    358    372   144+   328+
1  4    456    429   448-    85+
3  4    243    253   234-    65+
5  4     50     71    44-    24+
1  5   2165   2074   741+  2034-
3  5   1041    882   396+   962-
5  5    100    100    80+    59-
1  6    463    440   260-   383-
3  6    270    269   110-   247-
5  6     50    118     4+    49-
1  7     95    196    87+    40+
3  7     95     93    70-    65+
1  8    223    192   219-    39+
3  8     42     78    12-    40+
1  9    895    773   330-   832+

        K = 6
0  0   6352   7243  6352-     0 *
2  0   6033   5977  6033-     0
4  0   2438   2258  2438-     0
6  0    728    722   728-     0
0  1    816    765   663+   475+
2  1    516    504   400+   325+
4  1    166    176   109+   124+
6  1     49     49    20+    45+
0  2   2488   2695  1452+  2020+
2  2   1771   1794   918+  1514+
4  2    482    619   110+   469+
6  2    209    185    96-   182+
0  3    177    137   105-   142-
2  3    110    100    50-    97-
4  3     51     34     8-    52-
6  3     49     37    19+    48-
0  4   1039    924   564+   870+
2  4    736    686   354+   645+
4  4    271    301    53+   265+
6  4     89    119    43-    78+
0  5    703    640   581+   396-
2  5    552    507   465+   297-
4  5    262    283   227+   129-
6  5     49    130    43+    22-
0  6   2020   2145  1806-   903-
2  6   1571   1658  1441-   685-
4  6    787    857   725-   306-
0  7   1184   1080   207+  1165+
2  7    918    893   139+   908+
4  7    521    534    45+   519+
0  8    394    416   177+   351+
2  8    269    255    55+   263+
0  9    173    169   171-    27+

        K = 7
1  0   2400   2245  2400-     0
3  0   1125   1071  1125-     0
5  0    203    201   203-     0

        K = 8
1  1   2135   1828   751+  1999-
3  1   1480   1308   367-  1434-
5  1    828    725    97-   822-
1  2   2150   2082  1762+  1215+
3  2   1178   1199   959+   684+
5  2    403    458   321-   243+
1  3    829    792   165+   812-
3  3    229    200   129-   190-
5  3    120    109    49-   109+
1  4   1075    921   381-  1005-
3  4    538    509   160-   514+
5  4    165    182    13-   164+
1  5   1264   1094   123+  1258+
3  5    494    406   172+   462+
5  5     50    122    44+    22-
1  6    506    366   461-   209-
1  7   1691   1716   868+  1451-
3  7   1133   1186   553+   989-
1  8   1133   1100  1127-   115-
3  8    753    791   747-    97-

        K = 8
0  0   5343   5662  5343+     0
2  0   4417   4024  4417+     0
4  0   1852   1717  1852+     0
6  0    580    605   580+     0
0  1   3168   3316  1728-  2655+
2  1   2503   2485  1309-  2133+
4  1   1238   1210   569-  1100+
6  1    482    480   187-   444+
0  2   1909   1925  1904-   134+
2  2   1369   1289  1359-   163+
4  2    430    446   409-   132+
0  3    915    890   727-   555+
2  3    604    628   515-   316+
4  3    187    246   187-    24+
6  3     49    134    27-    41-
0  4   1229   1111  1015-   692+
2  4    911    877   745-   532+
4  4    463    488   386-   256+
6  4    199    226   170-   104+
0  5   2663   2669   182+  2657+
2  5   2176   2108   133+  2172+
4  5   1168   1110    48+  1167+
0  6   2195   2186  2029+   839+
2  6   1713   1713  1577+   669+
4  6    886    892   806+   368+
0  7    575    624   255+   515+
2  7    487    537   191+   447+
0  8    885    849   842+   274-
2  8    557    600   539-   138-

        K = 9
1  0   2613   2369  2613-     0
3  0   1732   1564  1732-     0
5  0    823    768   823-     0
1  1    621    655   573-   238-
3  1    262    313   260-    29-
5  1    127    114   112-    61+
1  2   1084    969  1082+    58-
3  2    883    820   880+    75-
5  2    612    577   609+    60-
1  3   2578   2530  1428-  2146+
3  3   1345   1275   881+  1016+
5  3    338    398   298-   160+
1  4   1229   1222  1217-   171-
3  4   1006    938  1005+    20-
5  4    611    605   608+    66+
1  5    469    436    54+   466-
3  5    204    216    85-   185-
5  5     50    149    45-    21-
1  6   1495   1454  1492-   101+
3  6    959   1012   958-    26+
1  7    464    486    95+   454+
1  8    515    477   476+   196+

        K = 10
0  0    204    101   204-     0
2  0    193     97   193+     0
4  0    279    240   279+     0
6  0    182    144   182+     0
0  1   1540   1529   157-  1532+
2  1   1296   1247   156-  1286+
4  1    752    737   104-   745-
6  1    364    363    36-   363+
0  2   1228   1178  1076+   592-
2  2    786    759   632+   468-
4  2    205    231    33+   203-
6  2    187    150   162-    94-
0  3   5216   6183  1017-  5116-
2  3   4929   5031   924-  4842+
4  3   2904   2933   488-  2863+
6  3   1432   1375   209-  1416+
0  4   1262   1184   583-  1119-
2  4   1033    981   505-   900-
0  5   1737   1570   120+  1733+
2  5   1416   1322    68+  1415+
4  5    853    820    11-   853-
0  6    416    394   289-   298-
2  6    260    255   123-   229-
0  7    693    695   221+   657+
2  7    507    550   144+   486+
0  8    954    995   904-   305+

        K = 11
1  0   1039   1035  1039+     0
3  0    592    615   592+     0

        K = 11
5  0    201    222   201+     0
1  1    499    511   135-   481+
3  1    160    194   114-   111+
5  1     97    127    79-    56-
1  2   2245   2212  1370-  1778-
3  2   1550   1555  1122-  1070-
5  2    865    818   738-   450-
1  3   3793   3846   510+  3758-
3  3   2742   2536   355+  2719-
5  3   1316   1286   158+  1307-
1  4   2603   2436  2578-   361-
3  4   1908   1732  1880-   325-
5  4    955    951   934-   199-
1  5    775    771    10+   775+
3  5    297    330    84+   285+
1  6    318    302   289+   131-
3  6    182    206   163+    81-
1  7    149    141   148+    15+

        K = 12
2  0   1298   1140  1298+     0
4  0    300    237   300+     0
0  1    849    824   304+   792+
2  1    662    651   292+   594+
4  1    302    350   196+   230+
0  2   1876   1816  1605+   969+
2  2   1606   1566  1428+   734+
4  2   1025   1029   965+   345+
0  3   1105   1040   994+   482+
2  3    856    839   763+   388+
4  3    415    475   359+   209-
0  4   1707   1670  1704+   110-
2  4   1512   1436  1510+    80-
4  4    900    936   900+    12-
0  5    676    659     3+   676+
2  5    567    523    13+   566+
4  5    273    279    26+   272+
2  6    162    156    55-   152+
0  7    325    328   275+   173+

        K = 13
1  0   1967   1929  1967+     0
3  0   1308   1215  1308+     0
1  1   2342   2316   319+  2320-
3  1   1634   1587   225+  1618-
5  1    805    830   107+   798-
1  2    416    430   359+   209+
3  2    288    311   258+   160+
5  2     50    171    36+    36+
1  3    825    830   270+   779+
3  3    483    455   191+   443+
1  4    410    377   105-   396-
3  4    230    229   121-   195-
1  5   2506   2390   429+  2468-
3  5   1682   1578   274+  1660-
1  6    668    715   347+   571+

        K = 14
0  0   1258   1373  1258+     0
2  0   1254   1318  1254+     0
4  0    977   1033   977+     0
0  1   1680   1579   657+  1546+
2  1   1407   1317   471+  1326+
4  1    793    814   153+   778+
0  2   2090   2017  2086+   130+
2  2   1706   1601  1704+    90+
4  2    838    865   837+    24+
0  3    414    364   225+   347-
2  3    315    286   175+   262-
4  3     52    133    30+    42-
0  4   1356   1268  1336+   232+
2  4   1141   1068  1120+   216+
0  5    430    391   353-   245-
2  5    256    281   235-   101-
0  6    789    714   772+   162+

        K = 15
1  0   1468   1471  1468+     0
3  0   1064   1056  1064+     0
1  1    287    346   272+    93+
3  1    291    203   275+    93+
1  2    258    267   211+   148+
3  2    261    282   238-   107+
1  3   1460   1420   268+  1435-
3  3    783    794   146+   769-
1  4    456    410   220-   399-
3  4    239    278   157-   179-
1  5    640    644   632-   101+

        K = 16
0  0    428    455   428+     0
2  0    290    309   290+     0
0  1    245    247   236-    65-
2  1    163    186   150-    63-
0  2    475    507   426-   211+
2  2    358    362   303-   191+
0  3    817    817   200+   792-
2  3    634    672   137+   619-
0  4    334    217    28-   333-
2  4     84    161     8-    83+

        K = 17
1  0   1233   1111  1233-     0
3  0    813    791   813-     0
1  1    875    863     8-   874-
1  2    707    844   464-   532+

        K = 18
0  0    824    796   824-     0
0  1    365    380    88-   354-
0  2    763    692   612-   456+
```

Table 3. *The atomic parameters with their e.s.d.'s*

Atom	y	$\sigma(y) \times 10^4$	z	$\sigma(z) \times 10^4$	U_{11}	$\sigma(U_{11}) \times 10^3$	U_{22}	$\sigma(U_{22}) \times 10^3$	U_{33}	$\sigma(U_{33}) \times 10^3$	U_{23}	$\sigma(U_{23}) \times 10^3$
C(2)	0·4282	4	0	—	0·044	2	0·018	2	0·021	2	−0·001	2
C(4)	0·2847	4	0·1774	12	0·055	4	0·021	3	0·027	3	−0·001	2
C(5)	0·2302	3	0·0121	14	0·045	2	0·019	2	0·018	2	0·005	2
C(6)	0·2803	4	−0·1639	10	0·049	4	0·022	3	0·016	3	−0·002	2
N(1)	0·3755	3	−0·1506	14	0·063	3	0·017	3	0·018	3	0·002	2
N(3)	0·3801	4	0·1588	12	0·053	3	0·020	3	0·017	2	0·003	2
N(5)	0·1422	4	0·0333	13	0·058	2	0·026	2	0·045	5	0·001	2
O(2)	0·5133	2	0·0008	12	0·064	2	0·018	2	0·024	2	0·001	2
O(4)	0·2508	3	0·3251	11	0·145	5	0·024	2	0·016	2	0·003	2
O(5)	0·0890	3	−0·1112	12	0·092	3	0·021	2	0·025	2	−0·002	2
O(6)	0·2432	3	−0·3034	13	0·138	5	0·025	2	0·014	2	−0·007	2
O(w)	0·0805	3	0·4945	12	0·089	12	0·013	2	0·037	2	−0·005	2
D(1)	0·407		−0·276		0·063		0·013					
D(3)	0·420		0·266		0·053		0·034					
D(5)	0·020		−0·077		0·058		0·032					
D(w1)	0·137		0·402		0·089		0·051					
D(w2)	0·111		0·617		0·089		0·042					

Note:　(i) Coordinates y and z are fractional. Mean square atomic displacements U_{ij} are in Å^2 and are referred to the crystallographic axes.

(ii) Cell origin defined by setting $z(C(2)) = 0$.

(iii) All atoms listed are in the plane $x = 0$. Also, $U_{12} = U_{13} = 0$.

(iv) Hydrogen atom y, z, and U_{22} parameters assumed from neutron diffraction study. It is also assumed that for hydrogen atoms $U_{22} = U_{33}$ and $U_{23} = 0$.

great. interest, it was decided to determine these positions by means of a neutron diffraction study of the deuterated material. Since the neutron intensity data were collected only for the zone $0kl$ and thus would not allow an independent complete structure determination, it was decided to assume carbon, nitrogen and oxygen parameters from the X-ray analysis. Thus it became necessary to determine the structure of the deuterated material using counter intensity data and including absorption corrections for improved accuracy in the results.

The values of structure parameters which were obtained in the previous X-ray analyses were initial values in the refinement of the structure parameters of perdeuterated violuric acid monohydrate based on the X-ray counter data. Three cycles of full-matrix least-squares refinement using the Busing & Levy program (1959) for the IBM 704 computer were sufficient to produce negligible parameter changes. In this refinement, the function minimized was

$$R = \Sigma w(|F_o| - |F_c|)^2$$

in which the weights were based on the e.s.d.'s in the integrated intensities as described above. Atom C(2) was assigned $z = 0$ in order to define the cell origin.

The deuterium atoms were assumed to have the positional and isotropic thermal parameters as determined from an initial refinement using the neutron data. In the final least-squares cycle, deuterium atoms were assumed to have the same B_{11} parameters as the oxygen or nitrogen atoms to which they are bonded. Six intense reflexions were considered to be seriously affected by extinction and were given zero weight in the least-squares refinement. These are

marked by (*) in the table of observed and calculated structure factors (Table 2). The final R index (excluding the six reflexions indicated) was 0·059 with a weighted R index 0·095. The final structure parameters are listed in Table 3 with their standard deviations as estimated from the least-squares inverse matrix. The interatomic distances and angles shown in Fig. 2 are based on these parameters. The e.s.d. in a bond length is 0·006 Å when normal to c or 0·008 Å when approximately at an angle of 60° to c. The e.s.d. in a bond angle is 0·6°. A final three-dimensional difference Fourier map showed a maximum electron density of 0·2 e.Å^{-3} which is not significant in terms of the e.s.d. of 0·14 e.Å^{-3} (Cruickshank & Rollett, 1953).

Discussion of the thermal vibrations and the coplanarity of the molecular sheets

The space group $Cmc2_1$ adopted in this analysis requires all atoms to lie in the mirror planes $x = 0$, $\frac{1}{2}$ so that the violuric acid molecule and the hydrogen bonds about a water molecule are coplanar. However, the observed U_{11} parameters for O(4), O(6), O(5) and O(w) are large, corresponding to thermal motion with r.m.s. amplitudes 0·38, 0·37, 0·30 and 0·30 Å respectively, so that it is also possible to consider the structure in terms of a disordering of each atom over two symmetry-related positions, slightly displaced from the mirror plane. This description might be favoured since a displacement of the water oxygen atom and its donor or acceptor neighbours by about 0·45 Å in opposite senses gives rise to hydrogen bonding in a nonplanar configuration at approximately tetrahedral angles, as is commonly observed in crystal structures of hydrates. Also, there is evidence

from the observed bond lengths and bond angles, that the violuric acid molecule is subjected to strain arising from non-bonding intramolecular interactions, and this could be relieved by some distortion of the molecule from coplanarity.

In examining the alternatives of an ordered or disordered structure, a row of oxygen atoms with periodicity 6·217 Å was assumed to be irradiated by Cu $K\alpha$ X-radiation. The atoms were given the form factor of Berghuis et al. (1955) and allowed to vibrate along the line of centers with an r.m.s. amplitude of 0·38 Å, corresponding to the observed U_{11} parameter for O(4). A similar row was set up but with each atom divided into half atoms slightly displaced along the line of centres. By trial and error, it was found, for example, that if the half atoms were displaced by 0·4 Å and allowed to vibrate with r.m.s. amplitude of 0·22 Å, then the calculated electron density for these hypothetical structures could be matched with a maximum discrepancy of only 0·077 e.Å^{-3}.

It was concluded that the experimental intensity data could not allow a distinction between an ordered structure with considerable anisotropic thermal motion and a disordered nonplanar structure. At lower temperatures, with reduction in the atomic thermal vibrations, such a distinction might become possible, and in fact, the diffraction effects from a single crystal at 90 °K under a liquid nitrogen drip do provide some evidence for an ordered structure with a greater degree of coplanarity. Thus Laue photographs showed a great reduction in the diffuse X-ray scattering on cooling to 90 °K, particularly in the intense halo surrounding the Bragg reflexion 200. Also, counter diffractometer measurements showed that on cooling

from 300 °K to 90 °K, the interlayer spacing decreased from 3·109 ± 0·001 Å to 3·009 ± 0·001 Å and the integrated intensity of the Bragg reflexion 600 (after corrections for angle factors) increased by a factor of 2·8.

From the values of the thermal parameters U_2 and U_3 (Fig. 3), it is not possible to describe the molecular motion in terms of the rigid body approximation. Thus the outermost atoms of the violuric acid molecule appear to be undergoing rotational oscillations about a molecular axis parallel to **a**, but this is not the case for the atoms of the ring.

This makes it difficult to determine reliable corrections for the shortening in observed bond lengths due to molecular rotational oscillations (Cruickshank, 1956). However, corrections have been applied to the positions of the extra-annular atoms and one half the appropriate bond lengthening has been added to the e.s.d. in each affected bond length (Table 4). Such corrections were not applied to intermolecular distances so that the values of these distances must be regarded as lower limits.

Table 4. *Bond lengths corrected for molecular oscillations*

Bond	d (before correction)	Δd (estimated correction)	d (after correction)	$\sigma(d)$ (after correction)
N(1)–C(2)	1·361 Å	0 Å	1·361 Å	0·008 Å
C(2)–N(3)	1·378	0	1·378	0·008
N(3)–C(4)	1·377	0	1·377	0·006
C(4)–C(5)	1·467	0	1·467	0·008
C(5)–C(6)	1·505	0	1·505	0·008
C(6)–N(1)	1·371	0	1·371	0·006
C(2)–O(2)	1·223	0·007	1·230	0·009
C(4)–O(4)	1·211	0·020	1·23	0·02
C(6)–O(6)	1·175	0·020	1·20	0·02
C(5)–N(5)	1·274	0·007	1·284	0·009
N(5)–O(5)	1·327	0·008	1·335	0·012

Discussion of the structure

The violuric acid molecule

In aqueous solution, the molecule of violuric acid possesses three mobile hydrogen atoms, as is shown by the ease with which they may be exchanged for deuterium atoms. Although there was no attempt to locate the hydrogen atoms in the X-ray analysis, the C–O bond lengths which were determined (1·20, 1·23, 1·23 Å) confirm the results of the neutron analysis (Craven & Takei, 1964) in showing that in the crystals of the monohydrate, the molecule exists in the triketo form (5-isonitrosopyrimidine-2,4,6-trione). The triketo form (pyrimidine-2,4,6-trione) is also adopted in the crystals of barbituric acid (Bolton, 1963) and barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961).

The observed point symmetry of the pyrimidine-trione ring is nearly 2*mm* but with small distortions, which are considered to arise from the effects of the 5-hydroxyimino substituent and the intermolecular
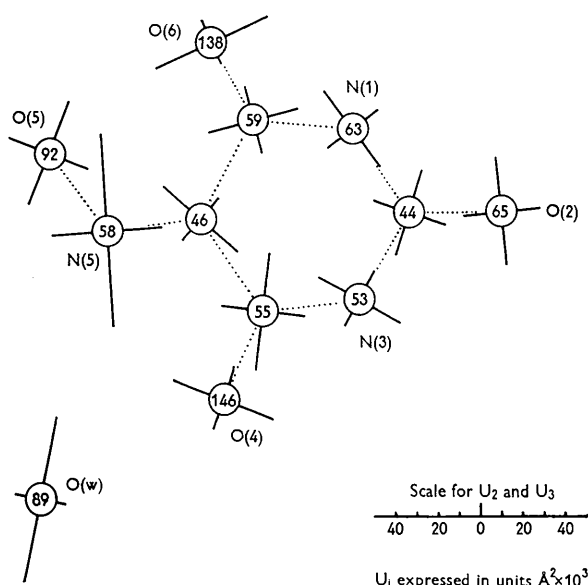

Fig. 3. The orientations and lengths of principal axes for each atomic thermal vibration ellipsoid. The parameters given are U_2, U_3 lying in the plane (100) and U_1 perpendicular to this plane.

hydrogen bonding. Thus there are significant differences between the ring bond angles at C(4) and C(6) (116·4°, 114·4°) and N(1) and N(3) (128·0°, 125·9°). However, the ring bond angles including those at C(2) and C(5) (116·1°, 119·2°) have approximately the values predicted by Pauling & Corey (1956).

The C–N bond lengths are consistent with a point symmetry of 2mm for the ring since there are no significant differences between the lengths C(4)–N(3) and C(6)–N(1) (1·377 and 1·371 Å) and between the lengths C(2)–N(3) and C(2)–N(1) (1·378 and 1·361 Å). Furthermore, as in the case of barbituric acid dihydrate, there are no significant differences between these pairs of bond lengths, so that all four bond lengths may be said to have approximately the same double bond character. This result might be expected from an inspection of the valence bond contributors to the structure of the violuric acid molecule.

The difference of 0·038 Å between the bond lengths C(4)–C(5) and C(5)–C(6) is significant in terms of its e.s.d. of 0·014 Å. The C(4)–C(5) bond length (1·467 Å) agrees closely with the central C–C bond length in acrolein (1·472 Å, Costain & Cherniak, 1961) and may be described as a bond between two trigonally hybridized carbon atoms of covalent radius 0·74 Å (Lide, 1962) with a slight shortening due to double bond character. The greater length of the C(5)–C(6) bond (1·505 Å) is attributed to the intramolecular non-bonding repulsions involving the hydroxyimino group which are more effective towards the C(6)–O(6) carbonyl than the C(4)–O(4) carbonyl.* The effect of such repulsions is also seen in the opening of the angles C(5)C(6)O(6) (124·5°), C(6)C(5)N(5) (125·7°) and C(5)C(4)O(4) (124·1°).

In the crystal structure of the red form of 5-methoxy-2-nitrosophenol, Bartindale, Crowder & Morley (1959) have shown that the molecule exists as the o-quinone monoxime, so that the carbonyl group and the hydroxyimino group including the hydrogen atom, are analogous to the C(4)–O(4) carbonyl group and the hydroxyimino group of the violuric acid molecule. Thus, there is a striking similarity in the N(5) · · · O(4) distance in perdeuterated violuric acid monohydrate (2·69 Å) and the corresponding distance in the o-quinone monoxime (2·70 ± 0·02 Å). In perdeuterated violuric acid monohydrate, the N(5)···O(6) distance is much greater (2·92 Å) than the N(5)···O(4) distance and this is further evidence of the non-bonding repulsive effects, particularly between O(5) of the hydroxyimino group and the C(6)–O(6) carbonyl group.

It is noted that the observed N(5) · · · O(4) and O(5) · · · O(6) distances (2·69 Å and 2·64 Å) are intermediate between the values obtained from the sums of the 'hard sphere' radii (2·27 Å and 2·26 Å) proposed

by Bartell (1960) for non-bonding intramolecular interactions, and the sums of the van der Waals radii (2·9 Å and 2·8 Å) given by Pauling (1960).

The bond lengths C(5)–N(5) and N(5)–O(5) and the bond angle C(5)N(5)O(5) observed in violuric acid monohydrate (1·284 Å with e.s.d. 0·009 Å, 1·335 Å with e.s.d. 0·012 Å, 117·9° with e.s.d. 0·6°) agree reasonably well with the corresponding values for 5-methoxy-o-benzoquinone monoxime (1·22 Å, 1·36 Å, 117° Bartindale et al., 1959) as determined by crystal structure analysis in projection. Hamilton (1961) has tabulated and discussed the results of eight other structure analyses of oximes by various workers, and again these results are reasonably compatible with the present results.

In perdeuterated violuric acid monohydrate the C(4)–O(4) and C(6)–O(6) bond lengths are 1·23 Å, 1·20 Å, but with an e.s.d. of 0·02 Å the difference is not significant. Together with the C(2)–O(2) length (1·231 Å with e.s.d. 0·009 Å), these are typical of carbonyl bond lengths as tabulated by Spencer (1959) for pyrimidines and related compounds.

The opening of the angle N(1)C(2)O(2) to 124·0° would not be expected for an isolated violuric acid molecule, but in the crystal structure this can probably be attributed to the intermolecular hydrogen bonding requirements, since without such distortion, the N(1) · · · O(2) hydrogen bonding distance would be about 3·17 Å, corresponding to an exceptionally weak interaction.

The molecular packing and the hydrogen bonding

The violuric acid molecules pack in sheets (Fig. 4) which correspond to the crystallographic mirror planes $x = 0, \frac{1}{2}$ so that the greatest length of the molecule
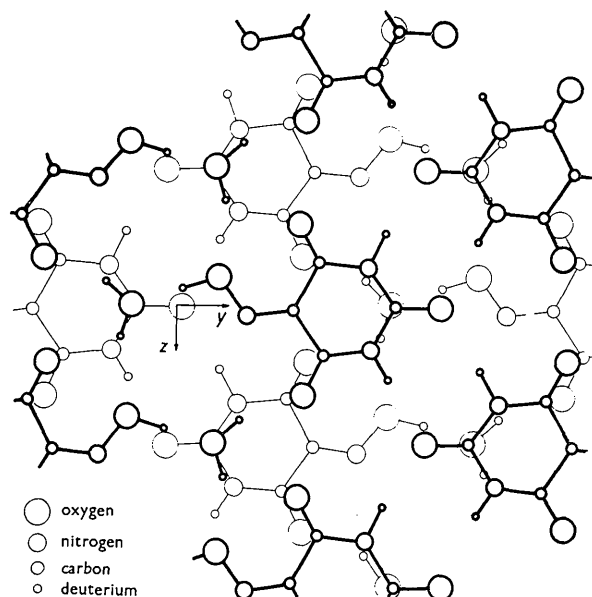
---

* The structure analysis based on the neutron diffraction data (Craven & Takei, 1964) shows that there is no intramolecular hydrogen bond O(5)–D(5) · · · O(6).

○ oxygen
○ nitrogen
○ carbon
o deuterium

Fig. 4. The molecular packing.

$(N(5) \cdots C(5) \cdots C(2) \cdots O(2))$ is almost parallel to **b**. Within a sheet, the molecules are associated by means of two separate hydrogen bonding systems and these zigzag along alternate twofold screw axes parallel to **c** and in the planes $x=0$, $\frac{1}{2}$. The first of these systems links both the imine groups to the carbonyl oxygen atom O(2) of neighbouring molecules. Although both the N $\cdots$ O(2) distances are long (2·989 Å, 3·065 Å), corresponding to quite weak interactions, they are of conventional type. The second hydrogen bonding system is complex and involves the remaining carbonyl oxygen atoms O(4) and O(6), the hydroxyimino atoms O(5) and D(5) and the water molecule. Each water molecule is associated with three violuric acid molecules in the same sheet, giving rise to six approaches among four oxygen atoms which are compatible with hydrogen bonding interactions (2·560, 2·643, 2·756, 2·786, 2·791 and 2·963 Å) but with only three deuterium atoms available for hydrogen bonds. The detailed discussion of the hydrogen bonding in this structure is given in the following paper which describes the results of the neutron diffraction analysis (Craven & Takei, 1964).

The intersheet distance, which was directly determined as one half the a translation (3·109 ± 0·001 Å at 300 °K, 3·009 ± 0·001 Å at 90 °K) is less than the intersheet distance in graphite (3·40 Å), in uracil (3·34 Å; Parry, 1954) and in barbituric acid dihydrate (3·20 Å). In the crystal structure of perdeuterated violuric acid monohydrate, adjacent sheets of molecules stack with a relative translation of $b/2$ so that the pyrimidine ring carbon atoms C(2), C(4) and C(6) are almost directly opposite the oxygen atoms O(w), O(6) and O(4) respectively, in neighbouring sheets. The intermolecular distances C(2)$\cdots$O(w), C(4)$\cdots$O(6) and C(6) $\cdots$ O(4) are 3·113, 3·137, and 3·151 Å. It is considered that the weak polar interactions between oppositely oriented carbonyl groups in neighbouring sheets contribute to the compactness of this crystal structure. Somewhat similar intermolecular interactions between carbonyl groups have been reported in chloranil (Chu, Jeffrey & Sakurai, 1962) and parabanic acid (Davies & Blum, 1955), although in these structures the intermolecular C $\cdots$ O distances are considerably shorter (2·85 Å and 2·77 Å respectively)

than in violuric acid monohydrate, and also the molecular packing is quite different, being of the 'herring bone' type, with each short C–O $\cdots$ C intermolecular approach approximately colinear with the carbonyl bond, rather than perpendicular to it as in violuric acid mononydrate.

References

BARTINDALE, G. W. R., CROWDER, M. M. & MORLEY, K. A. (1959). *Acta Cryst.* **12**, 111.

BARTELL, L. S. (1960). *J. Chem. Phys.* **32**, 827.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BOLTON, W. (1963). *Acta Cryst.* **16**, 166.

BUSING, W. R. & LEVY, H. A. (1959). Oak Ridge National Laboratory, Central Files No. 59-4-37.

CHU, S. S. C., JEFFREY, G. A. & SAKURAI, T. (1962). *Acta Cryst.* **15**, 661.

COSTAIN, C. C. & CHERNIAK, E. (1961). Reported by STOICHEFF, B. P. (1962). Tetrahedron, **17**, 135.

CRAVEN, B. M. & TAKEI, W. J. (1964). *Acta Cryst.* **17**, 415.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.

CRUICKSHANK, D. W. J. & ROLLETT, J. S. (1953). *Acta Cryst.* **6**, 705.

DAVIES, D. R. & BLUM, J. J. (1955). *Acta Cryst.* **8**, 129.

HAMILTON, W. C. (1961). *Acta Cryst.* **14**, 95.

JEFFREY, G. A., GHOSE, S. & WARWICKER, J. O. (1961). *Acta Cryst.* **14**, 881.

LIDE, D. R. (1962). Tetrahedron, **17**, 125.

PARRY, G. S. (1954). *Acta Cryst.* **7**, 313.

PAULING, L. & COREY, R. B. (1956). *Arch. Biochem. Biophys.* **65**, 164.

PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

SHIONO, R. (1957). Technical Report No. 2, Computation and Data Processing Center, University of Pittsburgh, Pa., U.S.A.

SPENCER, M. (1959). *Acta Cryst.* **12**, 59.

TEMPLETON, D. H. (1960). *Z. Kristallogr.* **113**, 234.

WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). Oak Ridge National Laboratory, Report No. ORNL-TM-229.