corresponding value in the selenium derivative is much larger (90·6°). This means that the different orientation of the $-XC(NH_2)_2$ groups in the seleno- and thio-derivatives is not only due to packing requirements, but is related to the different size of selenium with respect to sulphur and to the possibility of orbital interactions concerning the $X-X$ and $X-C$ bonds.

The positions of the chlorine atoms are mainly determined by their interactions with the $NH_2$ groups; these interactions hold the whole structure together. The contacts which could be considered as hydrogen bonds and other intermolecular contacts less than 3·5 Å are listed in Table 4.

It is interesting to compare the present structure with those of the bromide and iodide derivatives which are shown in the projections in Fig. 3. The differences in these three structures are mainly due to the fact that hydrogen bonding between the $NH_2$ group and the halide ion decreases with the increase of the halogen radius: so the $N-H\cdots O$ interactions are prefered with respect to the $N-H\cdots I^-$ (or $Br^-$). Consequently the bromide and iodide derivatives crystallize as hydrates, while the chlorine derivative is anhydrous.

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# The Crystal and Molecular Structure of a Methylated Photoproduct of Thymine–Uracil, Containing Four Pyrimidine Nuclei

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The structure of a pyrimidine tetramer, $C_{24}H_{28}N_8O_6$, was determined through single-crystal X-ray diffraction analysis using diffractometer data. This molecule was produced by irradiating an aqueous solution of a thymine–uracil adduct, 6,4′-(pyrimidin-2′-one)-thymine, with relatively long-wavelength ultraviolet(UV) irradiation (310–360 nm). The adduct is itself a photoproduct isolated in minute quantities from UV-irradiated deoxyribonucleic acid (DNA). The compound crystallizes in the monoclinic space group $P2_1/c$ with three molecules of $H_2O$ per asymmetric unit. Cell dimensions are: $a=7{\cdot}117\pm0{\cdot}003$, $b=21{\cdot}348\pm0{\cdot}016$, $c=18{\cdot}237\pm0{\cdot}006$ Å and $\beta=98{\cdot}6\pm0{\cdot}2°$. The tetramer contains a 12-membered ring comprising carbon atoms from each pyrimidine ring, plus two methylene groups. The structure was solved directly by the symbolic-addition procedure.

## Introduction

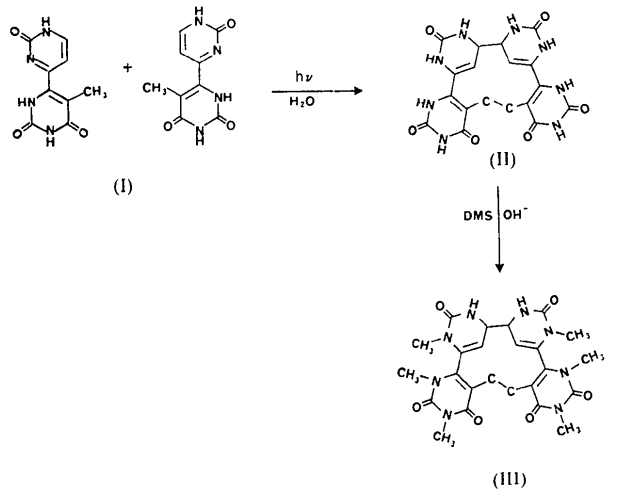
Several photoproducts derived from pyrimidine bases have now been isolated from UV-irradiated DNA both *in vivo* and *in vitro* (Wang & Varghese, 1967; Varghese & Wang, 1967). The formation of these products, and also subsequent transformations of these products by UV light, are being studied to provide a basis for understanding radiation damage in living organisms.

The simplest and most abundant photoproducts from pyrimidines are the cyclobutyl-type dimers. Many of these dimers have been characterized and their crystal structures have been reported (*e.g.* Gibson & Karle, 1971; Konnert & Karle, 1971; Camerman, Weinblum

& Nyburg, 1969; Leonard, Golankiewicz, McCredie, Johnson & Paul, 1969; Adman, Gordon & Jensen, 1968; Camerman & Camerman, 1968; Camerman, Nyburg & Weinblum, 1967; Einstein, Hosszu, Longworth, Rahn & Wei, 1967). A thymine–thymine adduct has been isolated from irradiated DNA and has been characterized through X-ray diffraction (Karle, Wang & Varghese, 1969; Karle, 1969). Trimers of uracil and thymine have been reported (Khattak & Wang, 1969; Varghese & Wang, 1968), and the crystal structure of the thymine trimer was recently analyzed (Flippen & Karle, 1971). The structure is a combination of a cyclobutyl-type dimer and an adduct.

This work concerns a pyrimidine tetramer which is easily formed in the laboratory by irradiating a uracil–thymine adduct comparable in structure to the thymine–thymine adduct mentioned above. The adduct, 6-4′-(pyrimidin-2′-one)-thymine (I), undergoes a head-to-head (*syn*) dimerization upon UV irradiation (313–360 nm) in an aqueous solution to form a large-ring compound, (II). Methylation of (II) with dimethyl sulfate produced a hexamethyl derivative, (III), which could be crystallized. The present paper describes the determination of the structure of this derivative.

The methylene bridge in (II) is formed during the photoreaction from the usually non-reactive thymine methyl groups. Thus, this photoreaction gives credence to earlier suggestions (Alcantara & Wang, 1965; Wang & Alcantara, 1965; Wang, Patrick, Varghese & Rupert, 1967; Varghese, 1970) that hydrogen abstraction from the methyl group of thymine may be important in photochemistry and photobiology at these wavelengths.



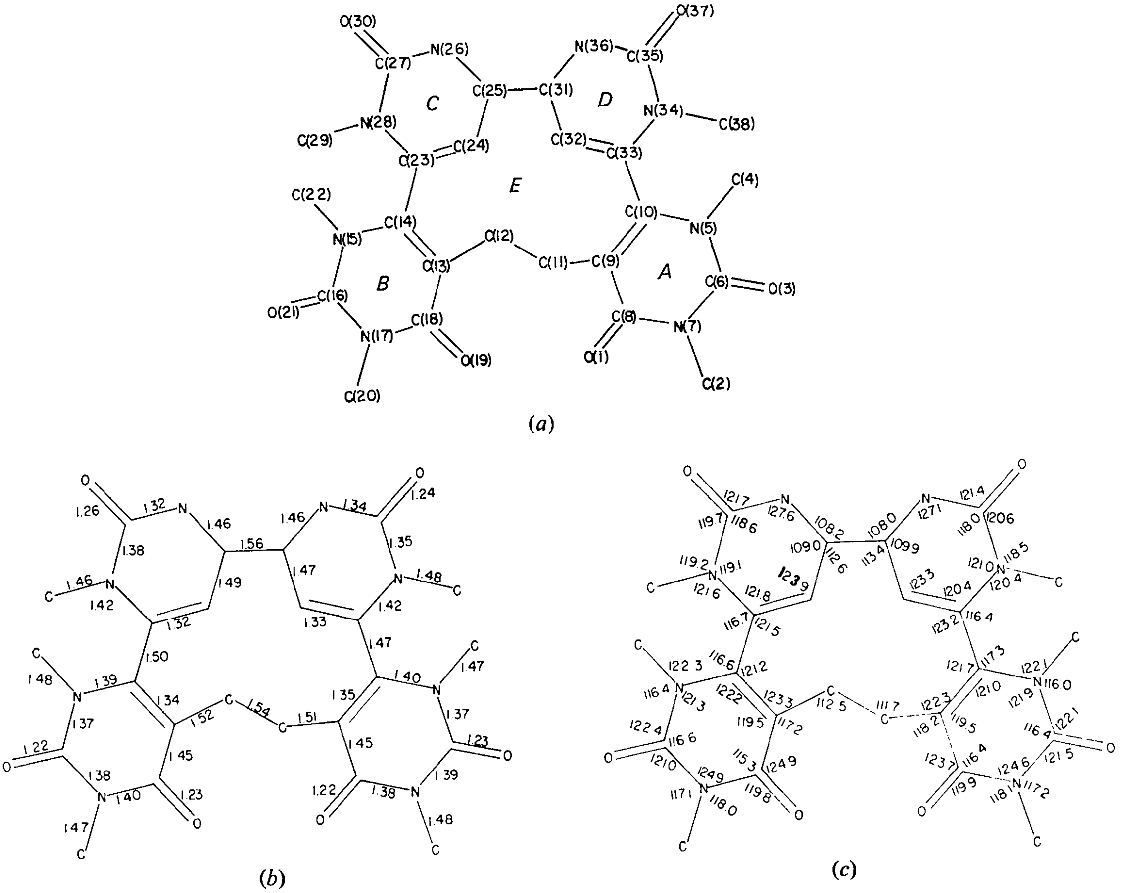


Fig. 1. Bond distances and angles and the numbering scheme for the pyrimidine tetramer. Standard deviations estimated from the least-squares refinement are ±0·008 Å (C–C bonds), ±0·007 Å (C–N or C–O bonds), and ±0·5° for angles.

Table 1. *Physical data*

| | |
|---|---|
| Molecular formula | $C_{24}N_8O_6H_{28}.3H_2O$ |
| M.W. | 578·56 |
| Habit | Rectangular prism |
| Crystal size | 1 mm (mounting axis) × 0·4 mm × 0·5 mm |
| Space group | $P2_1/c$ |
| $a$ | 7·117 ± 0·003 Å |
| $b$ | 21·348 ± 0·016 |
| $c$ | 18·237 ± 0·006 |
| $\beta$ | 98·62 ± 0·10° |
| Volume | 2741·53 Å$^3$ |
| Density (calc) | 1·40 g.cm$^{-3}$ |
| Molecules per unit cell | 4 |
| Radiation | Cu $K\alpha$ ($\lambda$ = 1·54178), Ni filter |
| Number of independent reflections measured | 4350 |
| Maximum sin $\theta/\lambda$ | 0·557 |
| Linear absorption coefficient ($\mu$) | 9·30 cm$^{-1}$ |

Table 2. *Fractional coordinates and thermal parameters for the pyrimidine tetramer*†

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 0·8598 | 0·3319 | 0·2066 | 6·38 | 4·01 | 2·21 | −1·68 | 0·56 | −0·31 |
| C(2) | 1·0331 | 0·4419 | 0·2451 | 5·51 | 3·64 | 3·77 | −1·20 | 1·32 | 0·46 |
| O(3) | 1·0015 | 0·4796 | 0·3848 | 5·07 | 2·73 | 4·03 | −1·20 | −0·10 | −0·46 |
| C(4) | 0·8495 | 0·4167 | 0·4889 | 5·51 | 3·46 | 2·47 | −0·12 | 0·36 | −0·31 |
| N(5) | 0·8396 | 0·3931 | 0·4125 | 3·05 | 2·37 | 2·34 | −0·06 | −0·25 | −0·15 |
| C(6) | 0·9280 | 0·4290 | 0·3657 | 2·57 | 2·55 | 3·12 | −0·06 | −0·41 | 0·00 |
| N(7) | 0·9362 | 0·4042 | 0·2961 | 2·95 | 2·55 | 2·34 | −0·48 | −0·05 | 0·31 |
| C(8) | 0·8506 | 0·3489 | 0·2699 | 3·56 | 2·73 | 2·08 | −0·24 | −0·41 | 0·15 |
| C(9) | 0·7531 | 0·3142 | 0·3208 | 2·95 | 2·37 | 2·47 | −0·18 | −0·56 | −0·00 |
| C(10) | 0·7516 | 0·3364 | 0·3899 | 2·63 | 2·37 | 2·47 | 0·18 | −0·36 | 0·46 |
| C(11) | 0·6567 | 0·2537 | 0·2943 | 3·82 | 2·55 | 2·86 | −0·78 | −0·51 | −0·15 |
| C(12) | 0·7986 | 0·1990 | 0·2986 | 3·54 | 2·91 | 2·99 | −0·60 | 0·15 | −0·31 |
| C(13) | 0·7020 | 0·1368 | 0·2780 | 3·37 | 2·55 | 2·86 | −0·24 | 0·20 | −0·15 |
| C(14) | 0·6635 | 0·0949 | 0·3280 | 3·03 | 2·37 | 3·25 | −0·06 | −0·36 | −0·31 |
| N(15) | 0·5767 | 0·0380 | 0·3078 | 3·35 | 2·37 | 2·86 | −0·30 | −0·25 | 0·15 |
| C(16) | 0·5166 | 0·0235 | 0·2352 | 3·21 | 3·10 | 3·38 | −2·16 | −2·03 | −0·15 |
| N(17) | 0·5521 | 0·0672 | 0·1835 | 4·06 | 2·91 | 2·73 | −0·84 | −0·25 | −0·15 |
| C(18) | 0·6495 | 0·1234 | 0·1998 | 3·84 | 2·73 | 2·86 | −0·24 | 0·20 | −0·46 |
| O(19) | 0·6839 | 0·1575 | 0·1493 | 6·20 | 3·64 | 2·60 | −1·14 | 0·25 | 0·31 |
| C(20) | 0·4793 | 0·0535 | 0·1053 | 7·62 | 5·10 | 2·60 | −2·22 | −0·61 | −0·77 |
| O(21) | 0·4357 | −0·0257 | 0·2162 | 4·89 | 2·91 | 4·16 | −1·26 | −0·61 | −0·77 |
| C(22) | 0·5365 | −0·0087 | 0·3631 | 5·09 | 2·73 | 4·03 | 0·30 | 0·15 | 1·08 |
| C(23) | 0·7094 | 0·1079 | 0·4095 | 3·41 | 2·55 | 2·99 | −0·24 | −0·10 | 0·31 |
| C(24) | 0·5849 | 0·1348 | 0·4464 | 3·50 | 2·91 | 3·12 | 0·24 | 0·25 | 0·31 |
| C(25) | 0·6291 | 0·1513 | 0·5265 | 4·46 | 2·55 | 2·99 | 0·54 | 0·30 | 0·31 |
| N(26) | 0·8154 | 0·1261 | 0·5564 | 5·11 | 3·83 | 2·73 | 1·74 | −0·25 | 0·46 |
| C(27) | 0·9441 | 0·1024 | 0·5190 | 4·79 | 3·10 | 3·25 | 1·08 | −0·71 | 0·00 |
| N(28) | 0·8953 | 0·0927 | 0·4440 | 3·74 | 3·83 | 2·73 | 1·02 | −0·56 | −0·46 |
| C(29) | 1·0331 | 0·0638 | 0·4028 | 4·10 | 5·46 | 4·55 | 1·74 | 0·20 | −0·77 |
| O(30) | 1·1089 | 0·0893 | 0·5502 | 5·68 | 5·46 | 4·68 | 2·34 | −2·13 | −0·77 |
| C(31) | 0·6328 | 0·2233 | 0·5399 | 3·72 | 2·91 | 2·60 | 0·42 | 0·15 | 0·15 |
| C(32) | 0·7336 | 0·2582 | 0·4879 | 2·85 | 2·91 | 2·86 | 0·30 | −0·15 | 0·00 |
| C(33) | 0·6530 | 0·3033 | 0·4436 | 2·77 | 2·91 | 2·60 | 0·18 | −0·10 | −0·15 |
| N(34) | 0·4625 | 0·3219 | 0·4466 | 2·83 | 3·64 | 4·29 | 1·08 | 0·56 | 1·39 |
| C(35) | 0·3573 | 0·2930 | 0·4925 | 3·29 | 4·19 | 3·51 | 0·18 | 0·51 | 0·00 |
| N(36) | 0·4366 | 0·2451 | 0·5337 | 3·39 | 3·28 | 4·16 | 0·60 | 1·12 | 0·77 |
| O(37) | 0·1932 | 0·3108 | 0·4965 | 3·17 | 5·46 | 6·51 | 1·44 | 1·42 | 1·23 |
| C(38) | 0·3701 | 0·3703 | 0·3950 | 4·73 | 6·92 | 7·42 | 2·64 | 0·66 | 4·62 |
| *W*(1) | 0·0696 | 0·1996 | 0·1375 | 6·69 | 6·01 | 6·11 | −0·78 | 0·71 | 0·15 |
| *W*(2) | 0·2780 | 0·3178 | 0·1527 | 6·00 | 6·74 | 6·51 | 1·08 | 1·22 | −0·92 |
| *W*(3) | 0·1331 | 0·0890 | 0·2238 | 9·05 | 4·37 | 6·90 | 2·10 | 1·73 | 1·39 |
| | | | | Average e.s.d.'s | | | | | |
| C | 0·0008 | 0·0002 | 0·0003 | 0·24 | 0·18 | 0·26 | 0·18 | 0·20 | 0·15 |
| N, O | 0·0006 | 0·0002 | 0·0002 | 0·20 | 0·18 | 0·13 | 0·18 | 0·15 | 0·15 |
| *W* | 0·0010 | 0·0003 | 0·0004 | 0·38 | 0·36 | 0·39 | 0·24 | 0·25 | 0·31 |

† Thermal parameters are of the form

$$T=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right]\cdot$$

The $B_{ij}$ values are in Å$^3$ units.

## Experimental

One crystal of the tetramer was supplied to us Drs D. F. Rhoades and S. Y. Wang of the Johns Hopkins University. Intensity data were collected at room temperature on a fully automatic computer-controlled 4-circle diffractometer using the $\theta$–$2\theta$ technique with a $2\cdot2° + 2\theta(\alpha_2)$–$2\theta(\alpha_1)$ scan over $2\theta$. The cell constants and other physical properties of the crystal are listed in Table 1. The intensity data were corrected for Lorentz and polarization factors and were placed on an absolute scale by means of a $K$ curve (Karle & Hauptman, 1953). Normalized structure-factor magnitudes $|E|$, as well as structure-factor magnitudes $|F|$, were derived.

## Structure determination and refinement

The structure was solved by the symbolic-addition procedure (Karle & Karle, 1966) for obtaining phases directly from the structure-factor magnitudes. An $E$ map computed with 600 phases contained 40 peaks of approximately equal weight that were identified as the non-hydrogen atoms of the tetramer molecule plus the oxygen atoms of two $H_2O$ molecules. The third $H_2O$ molecule was located later in a difference map.

To conserve computing time, data having $5\cdot0 > |F_o| > 50\cdot0$ were omitted from the refinement. This reduced the number of reflections from 4350 to 3035 This treatment greatly reduces refinement time yet retains all data collected under optimal (diffractometer) conditions. Coordinates and thermal factors were refined with a full-matrix three-dimensional least-squares program (Busing, Martin & Levy, 1962) on the reduced data set. The function minimized was $\sum(F_o - F_c)^2$. For the anisotropic refinement not all parameters could be varied simultaneously, due to limitations in the capacity of the computer; hence, parameters for different atoms were held constant in each refinement cycle. Ten of the 34 hydrogen atoms were located in a difference map. Methyl hydrogen atoms and those on the $H_2O$ molecules were not found. The final $R$ value for the 3035 data used in the refinement was 0·085. For all data $R$ was 0·094. Fractional coordinates and thermal parameters for the C, N, and O atoms are listed in Table 2, approximate coordinates for the hydrogen atoms are listed in Table 3, and bond lengths and angles are shown in Fig. 1. Observed and calculated values for the structure faors arcte listed in Table 4.

Table 3. *Approximate coordinates for hydrogen atoms located in a difference map*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(11*A*) | 0·450 | 0·744 | 0·176 |
| H(11*B*) | 0·400 | 0·757 | 0·263 |
| H(12*A*) | 0·156 | 0·695 | 0·144 |
| H(12*B*) | 0·104 | 0·699 | 0·233 |
| H(24) | 0·461 | 0·157 | 0·426 |
| H(25) | 0·462 | 0·871 | 0·441 |
| H(26) | 0·155 | 0·878 | 0·380 |
| H(31) | 0·318 | 0·776 | 0·404 |
| H(32) | 0·145 | 0·750 | 0·016 |
| H(36) | 0·360 | 0·277 | 0·063 |

## Discussion

The conformation of the molecule is shown in the stereodiagram in Fig. 2. Head-to-head and tail-to-tail (*syn*) dimerization of the thymine–uracil adduct to form the tetramer was accomplished by the formation of a dimethylene bridge, from the $CH_3$ groups on C(9) in ring *A* and C(13) in ring *B*, and by a *trans* junction between atoms C(25) and C(31) of rings *C* and *D*, respectively. An approximate twofold axis in the molecule passes through the centers of the C(25)–C(31) and C(11)–C(12) bonds; however, the *pseudo* twofold symmetry does not extend to the environment around the molecule.

The plane through ring *A* is nearly perpendicular to the plane through ring *D*. The same relationship exists between rings *B* and *C*. This is indicated by the torsion angles about the C(33)–C(10) and C(23)–C(14) bonds, which are 87·0 and 90·7°, respectively. Torsion angles (Table 5) indicate that the six-membered rings are not quite planar. Ring *C* exhibits the most distortion with deviations from the best least-squares plane through it being ±0·050 Å. Maximum deviations for rings *B* and *D* are ±0·025 and ±0·020 Å for ring *A*. The methyl carbon atom on N(5) is 0·11 Å from the plane through ring *A*, and the methyl carbon atom on N(17) is 0·12 Å out of the plane through ring *B*. Other methyl

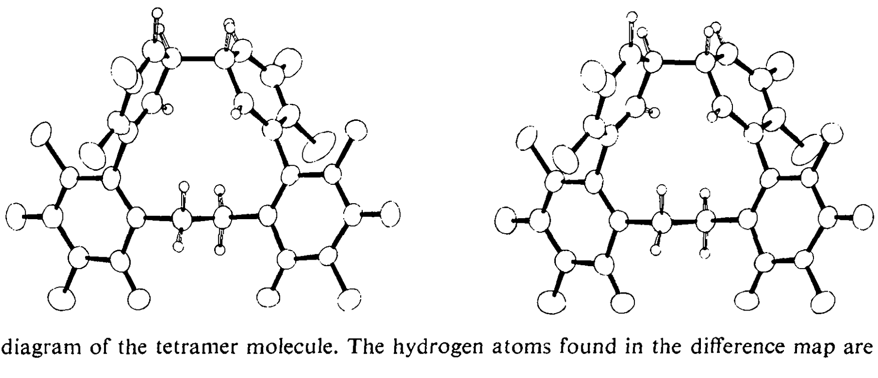


Fig. 2. Stereodiagram of the tetramer molecule. The hydrogen atoms found in the difference map are also shown.

Table 4. *Observed and calculated structure factors*

Column headings are index $k$, $F_o \times 10$, and $F_c \times 10$.

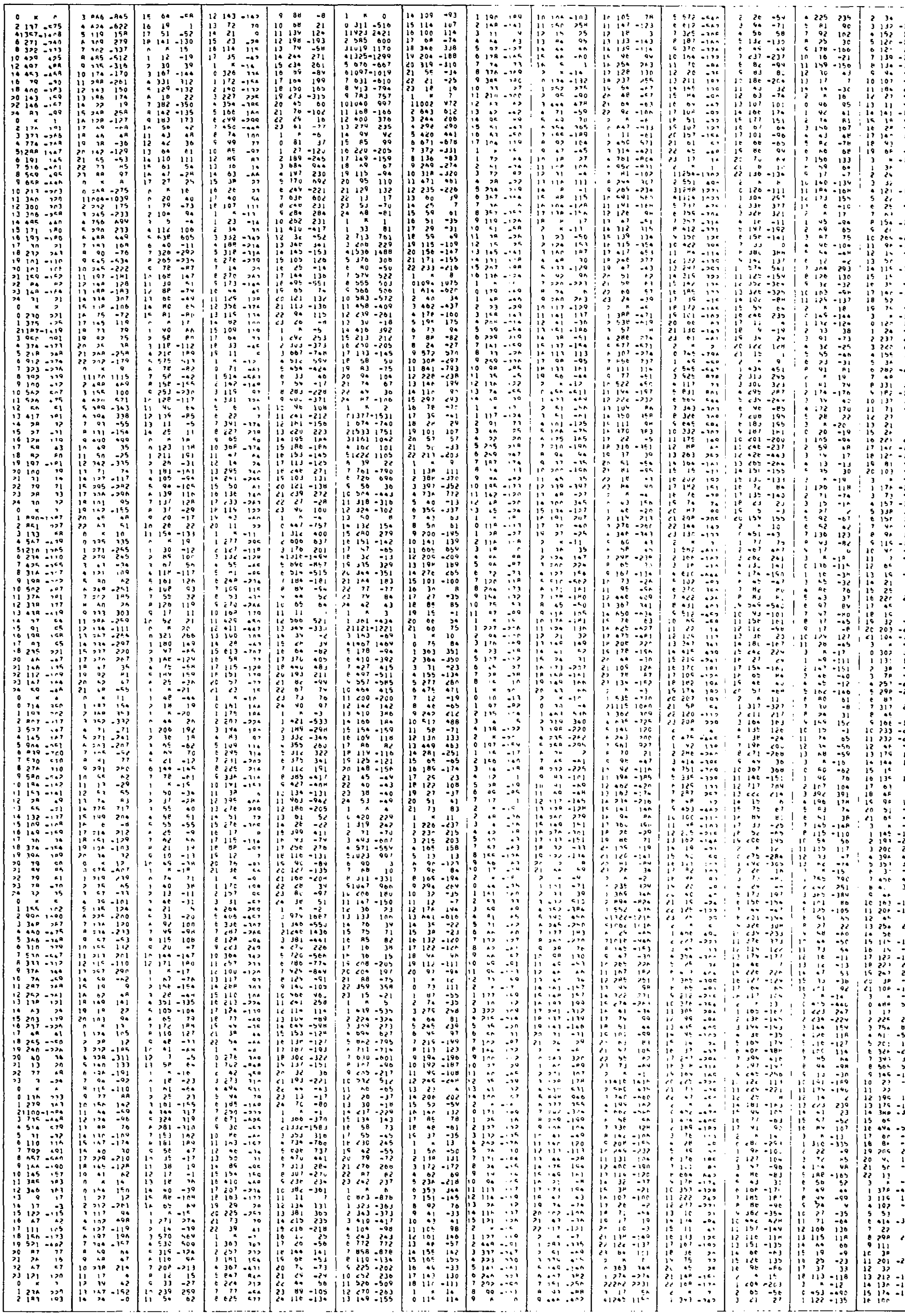


Table 4 (*cont.*)

[illegible]

carbon atoms, as well as the carbonyl oxygen atoms are within 0·09 Å of the plane through the rings to which they are bonded.

Ring *E*, the central 12-membered ring created by the dimerization, has four double bonds with two *cis* and two *trans* conformations. In each C=C–C=C segment, the torsion angle about the central C–C bond is near 90°. There are eight independent hydrogen bonds involving the tetramer and the three water molecules. These bonds, along with their lengths, are listed in Table 6. Each $H_2O$ molecule is the donor to two hydrogen bonds, while *W*(2) is also the acceptor of one and *W*(1) is the acceptor of two additional hydrogen bonds. Hydrogen atoms on the water molecules were not found in the difference map; however, their approximate locations can be deduced from the angles in which the central atom is the donor: O(37)–*W*(1)–O(19) = 117·5, *W*(1)–*W*(2)–O(30) = 112·2, and *W*(1)–*W*(3)–O(3) = 105·2°. Of all the N and O atoms available for hydrogen bonding only O(21) does not participate;

Table 5. *Torsion angles*

| Ring *A* Bond | | Ring *B* Bond | | Ring *C* Bond | | Ring *D* Bond | | Ring *E* Bond | |
|---|---|---|---|---|---|---|---|---|---|
| C(6)–N(5) | −4·0° | C(13)–C(14) | 1·0° | C(23)–C(24) | 0·1° | C(31)–C(32) | 1·0° | C(12)–C(11) | 175·4° |
| N(5)–C(10) | 1·1 | C(14)–N(15) | −3·7 | C(24)–C(25) | −7·0 | C(32)–C(33) | 2·4 | C(11)–C(9) | −98·7 |
| C(10)–C(9) | 1·3 | N(15)–C(16) | 2·0 | C(25)–N(26) | 11·6 | C(33)–N(34) | −2·2 | C(13)–C(12) | −99·9 |
| C(9)–C(8) | −0·6 | C(16)–N(17) | 2·3 | N(26)–C(27) | −8·3 | N(34)–C(35) | −1·7 | C(9)—C(10) | −0·9 |
| C(8)–C(7) | −2·6 | N(17)–C(18) | −4·7 | C(27)–N(28) | −0·4 | C(35)–N(36) | 5·8 | C(14)–C(13) | 1·8 |
| N(7)–C(6) | 4·8 | C(18)–C(13) | 2·2 | N(28)–C(23) | 4·3 | N(36)–C(31) | −5·3 | C(10)–C(33) | 87·0 |
| | | | | | | | | C(23)–C(14) | 90·7 |
| | | | | | | | | C(33)–C(32) | −177·7 |
| | | | | | | | | C(24)–C(23) | −176·8 |
| | | | | | | | | C(32)–C(31) | 121·9 |
| | | | | | | | | C(25)–C(24) | 113·1 |
| | | | | | | | | C(31)–C(25) | −43·8 |

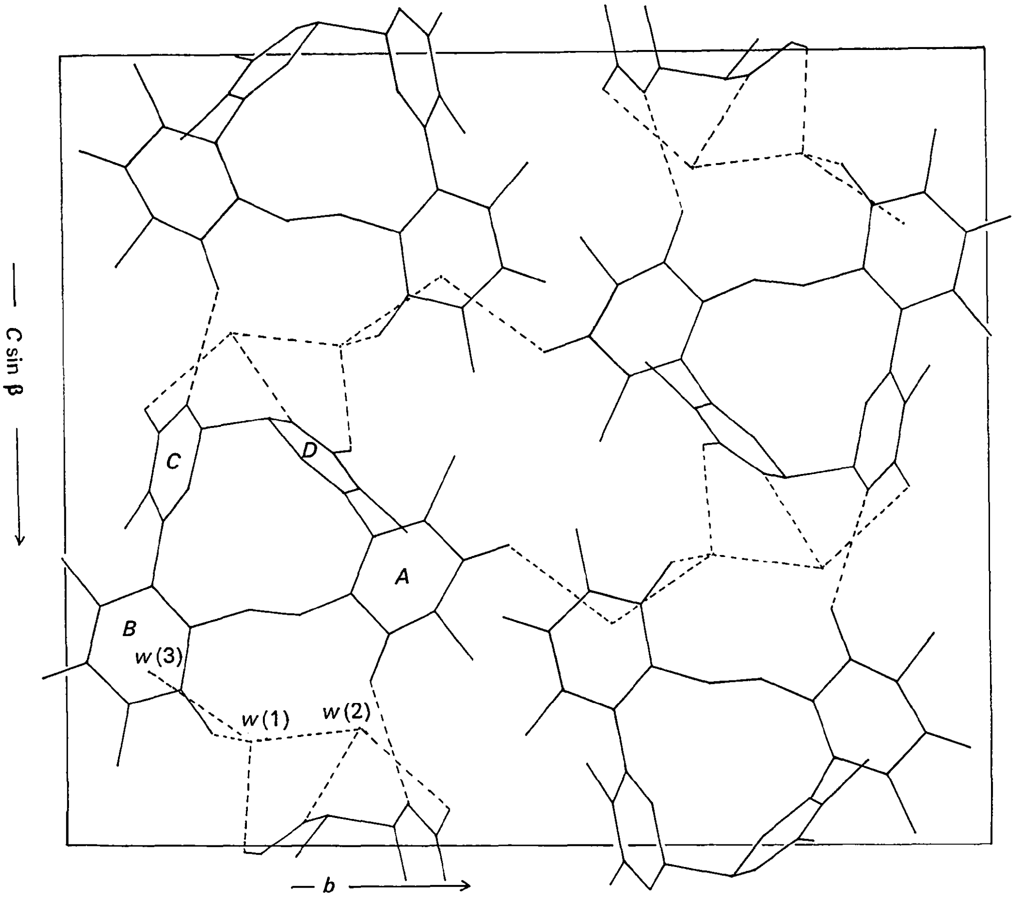


Fig. 3. Contents of one unit cell. Hydrogen-bonding network linking tetramer and $H_2O$ molecules is shown by dotted lines.

however, it is involved in two close intermolecular approaches (see Table 6). The hydrogen bonding, which is illustrated in Fig. 3, holds these bulky molecules closely together and accounts for the relatively high density: 1·40 g.cm$^{-3}$.

Table 6. *Hydrogen bond lengths and other close intermolecular approaches*

Hydrogen bonds*

| Donor | Acceptor | Distance | Symmetry of acceptor | | |
|---|---|---|---|---|---|
| $W$(1) | O(19) | 2·93 Å | $x$ | $y$ | $z$ |
| $W$(1) | O(37) | 2·85 | $x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |
| $W$(2) | $W$(1) | 2·92 | $x$ | $y$ | $z$ |
| $W$(3) | $W$(1) | 2·83 | $x$ | $y$ | $z$ |
| $W$(2) | O(30) | 2·86 | $x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |
| N(36) | $W$(2) | 2·92 | $x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |
| $W$(3) | O(3) | 3·12 | $\bar{x}$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
| N(26) | O(1) | 2·86 | $x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |

Close intermolecular approaches (< 3·2 Å)

| Atom (1) | Atom (2) | Distance |
|---|---|---|
| O(21) | C(6) | 2·95 |
| O(21) | N(7) | 3·02 |
| $W$(3) | C(16) | 3·05 |

* Standard deviations estimated from least-squares refinements are ±0·01 for distances involving water oxygen atoms, and ±0·007 for other distances.

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# The Crystal Structure of 9,10-Diazaphenanthrene

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9,10-Diazaphenanthrene, $C_{12}H_8N_2$, forms monoclinic crystals of space group $P2_1/c$ with four molecules in the unit cell of dimensions $a=6\cdot945$, $b=11\cdot938$, $c=11\cdot802$ Å and $\beta=110\cdot84°$. The molecules are arranged in pairs, 3·49 Å apart. They are only approximately planar; two C–C bonds in each benzene ring are shorter than the other four.

## Introduction

De Vries Reilingh, Rettschnick & Hoytink (1971) have investigated the fluorescence and fluorescence excitation spectra of 9,10-diazaphenanthrene in solution. From these spectra they deduce the existence of dimers in solution in 3-methylpentane with a stabilization enthalpy of 3·6 kcal.mole$^{-1}$. A determination of the crystal structure was undertaken in order to throw additional light on the interpretation of the spectra.

## Experimental

Crystals of suitable size and quality were provided by de Vries Reilingh. These crystals were yellow needles along an axis which was subsequently called [100].