molecular column but are staggered alternately with an angle of 39·5°. Iodine is placed at every corner of the unit cell. In the electron micrographs presented here, no distinct image of iodine was detected. This may be due to the uncertainty of the iodine positions in a nonstoichiometric complex, such as the case studied here. The determination of the iodine position in such specimens will be made in future with a thinner specimen mounted on a low-temperature stage of an electron microscope suitable for high-resolution work. The present investigation has revealed that a small amount of doping can cause the structure change in the matrix crystal and that many disorders are introduced in the crystal. At the same time, the direct observation of molecular images by high-resolution electron microscopy has proved the possibility of the determination of molecular arrangements in reaction intermediates of organic crystals.

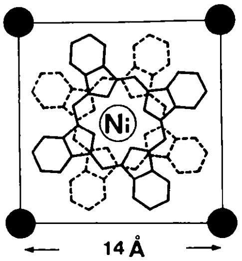

Fig. 17. A schematic representation of the crystal structure of Ni(phc).$I_{1\cdot0}$ after Schramm *et al.* (1980).

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Characterizations of the Monohydrates of the Monosodium and Dipotassium Salts of *cis–syn* Thymine Photodimer.* Crystallographic Treatments of Mixed Crystals Containing Dimers and Monomers Resulting from X-ray Cleavage of Dimers in the Solid State†‡

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Abstract

The monohydrated monosodium and dipotassium salts of *cis–syn* thymine photodimer, $Na^+.C_{10}H_{11}N_4O_4^-.H_2O$ and $2K^+.C_{10}H_{10}N_4O_4^{2-}.H_2O$, have been prepared and their structures unambiguously determined by X-ray analyses. The sodium salt ($M_r = 292\cdot233$) crystallizes in the monoclinic space group $P2_1/n$ with $a = 6\cdot555\,(1)$, $b = 29\cdot010\,(3)$, $c = 6\cdot762\,(1)$ Å, $\beta = 106\cdot028\,(6)°$, $V = 1235\cdot88$ Å^3, $Z = 4$, $D_x = 1\cdot570$, $D_m = 1\cdot53$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å, $\mu(\text{Cu } K\alpha) = 13\cdot925$ cm^{-1}, $F(000) = 608$, $T = 297$ K. The successful analysis of the structure was accomplished [final $R(F) = 0\cdot051$] with the assumption that the crystal consists of the dimers intermingled with the monomer products of their X-ray cleavage and that the gradual photomonomerization takes place as a linear function of exposure. The results of the analysis, in which monomers were treated as rigid groups, revealed

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* Sodium hydrogen 4a,4b-dimethyl-4a,4b,8a,8b-tetrahydrocyclobuta[1,2-*e*:3,4-*e*′]dipyrimidinate monohydrate and dipotassium 4a,4b-dimethyl-4a,4b,8a,8b-tetrahydrocyclobuta[1,2-*e*:3,4-*e*′]dipyrimidinate monohydrate.

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detailed configurational features of the dimer, including the geometry of the cyclobutane ring, coordination around the Na^+ ion, and intermolecular H-bonding. The potassium salt ($M_r = 346{\cdot}438$) crystallizes in the monoclinic space group Cc with $a = 7{\cdot}007$ (4), $b = 25{\cdot}97$ (2), $c = 8{\cdot}025$ (5) Å, $\beta = 99{\cdot}15$ (5)°, $V = 1441{\cdot}49$ Å^3, $Z = 4$, $D_x = 1{\cdot}595$ g cm^{-3} (D_m not measured), μ(Cu $K\alpha$) = 60·222 cm^{-1}, $F(000) = 712$, $T = 297$ K. Although the coexistence of dimers and monomers was strongly suspected because of unusually long C–C bond lengths across the cyclobutane ring in what is evidently an average structure, monomer positions could not be located and $R(F)$ was not reduced below 0·101. However, the configuration of the cyclobutadipyrimidinate ion closely resembles that in the sodium-salt crystal.

Introduction

Irradiation by UV of frozen solutions of pyrimidine or *N*-methylated pyrimidine is known to cause dimerization across 5,6-double bonds (Wang, 1960, 1961). Among the four types of photodimers (*viz cis–syn*, *trans–syn*, *cis–anti* and *trans–anti*) thus formed (Wulff & Fraenkel, 1961; Blackburn & Davies, 1966; Cohn, Leonard & Wang, 1974), the *cis–syn* type that occurs in DNA (Weinblum & Johns, 1966) is the most prevalent. To date, structures of five such photodimers have been reported: those of uracil (Adman & Jensen, 1970), 6-methyluracil (Gibson & Karle, 1971), 1,1′-trimethylene-linked thymine (Leonard, Golankiewicz, McCredie, Johnson & Paul, 1969), 1,3-dimethylthymine (Camerman & Camerman, 1970), and the monosodium salt of thymine dimer (Wei & Einstein, 1968). Because of the vulnerability of the cylobutane ring of the pyrimidine dimers to splitting by the action of X-rays (Lochmann, 1963), the structural investigations of the last three cited compounds were complicated by the problem of dealing with the coexistence of dimers and monomers in the same crystalline lattice. Thus, in the structure of 1,1′-trimethylene-linked thymine dimer (Leonard *et al.*, 1969) four monomeric sites, corresponding to cyclobutane-ring atoms, were located and were included in the refinement with 10% occupancy. In the case of 1,3-dimethylthymine photodimer (Camerman & Camerman, 1970), monomerization was also suspected, but the authors could not find the positions of minor monomer-atom sites. In addition, the disordered structure of a mixed crystal of *trans–syn* cyclobutane dimer, 4-methyl-5,6-diaza-2,4-cyclohexadien-1-one (87% occupancy), and its principal UV irradiation product (13% occupancy) has recently been reported (Karle, 1982).

We present here the analysis for the sodium salt of *cis–syn* thymine photodimer, which has led to the successful refinement of a mixed dimer–monomer model including all non-H monomer sites. In addition, some structural features are presented for the dipotassium salt of thymine dimer.

Experimental

Preparation

Thymine photodimer was prepared by the UV irradiation of a frozen solution of thymine according to procedures similar to those described by Blackburn & Davies (1966). Aliquots, 55 ml each, of aqueous thymine solution (400 mg l^{-1}) were frozen in a tray (12·5 × 22 cm) and were irradiated for 30 min at 5 cm distance with a UV lamp (15 W). After the conversion the average yield of the dimer was approximately 50%. The formation of *cis–syn* thymine dimer, essentially free of monomer, was established spectroscopically by UV (Ishihara, 1963) and IR (Weinblum & Johns, 1966) spectra.

Each salt, sodium or potassium, of the thymine dimer was prepared by dissolution of the dimer in a large excess of solution of base, NaOH or KOH, containing ethanol, followed by heating over a steam bath under reflux for 1–2 h. The salts were precipitated out by the addition of hot ethanol, followed by cooling at 277 K overnight. The white products were collected by filtration. The results of elemental analyses suggested that the dialkaline salts were contaminated by $NaHCO_3$ or $KHCO_3$* due primarily to insufficient washing with water. Nevertheless, the crystals used in this investigation were obtained from these products. The raw salt was suspended in boiling ethanol to which 1*N* NaOH (or KOH) was added dropwise until the solution became clear. Ethanol was then added until the solution became slightly turbid. After storage at 277 K for 1–2 weeks needle crystals eventually grew. The subsequent X-ray characterization revealed that they were the monohydrates of the monosodium and dipotassium salts of the *cis–syn* thymine dimer (hereafter designated NaHtd and K_2td, respectively).

Data collection and selection of intensity data

Crystals (0·10 × 0·07 × 0·68 mm for NaHtd, 0·16 × 0·16 × 0·28 mm for K_2td) mounted in thin-walled glass capillaries with tiny amounts of grease. Space group and approximate unit-cell parameters for each compound from Weissenberg and precession photographs. For NaHtd, nine strong reflections (2θ range 87–90°) centered with an Oak Ridge automated computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968) by use of Ni-filtered Cu $K\alpha_1$ (λ = 1·54051 Å) radiation and cell parameters

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* This deduction was substantiated by the fact that among many crystals examined later some had unit-cell parameters nearly identical with those reported for $KHCO_3$ (Nitta, Tomie & Koo, 1954).

refined by least squares. For K_2td, 11 reflections (2θ range 33–57°) were used. For both compounds, data collected by wide ω step-scans (maximum scan widths: 1·5° for NaHtd; 6° for K_2td). For NaHtd $2\theta_{\max} = 125°$ (minimum spacing 0·87 Å), for K_2td $2\theta_{\max} = 90°$ (minimum spacing 1·1 Å). Absorption corrections by the method of Busing & Levy (1957) for NaHtd (transmission factors 0·852–0·925), no corrections for K_2td. One standard reflection (2, 12, 0) measured every 30 reflections for NaHtd. For K_2td, one standard reflection ($\bar{2}21$) measured every 15 reflections at low 2θ ranges, one standard (152) measured every 15 reflections at high 2θ ranges. Variation of standards: for NaHtd (range $2\theta = 65$–100°) N(initial)/N(final) = 1·072 (within three days); for K_2td N(initial)/N(final) = 1·457.

For NaHtd the fairly large mosaic range, approximately 0·8°, and very pronounced thermal-diffuse scattering made it extremely difficult to measure accurate background intensities, especially where the longest axis (29 Å) caused problems of resolution. In addition, the unit-cell parameters changed gradually but significantly during the course of data collection, and the entire first set of data was rejected because of excessively large setting errors. The unit-cell parameters and the orientation angles were measured several times during collection of the second and final set of data. However, many reflections of the second set had to be rejected because of obvious errors caused by strong thermal-diffuse scattering or overlap from stronger neighboring reflections. Reflections considered to be in doubt were removed prior to solution of the structure through inspection of the chart record showing the ω-scan profiles of all measured reflections. The set finally accepted for all following calculations consisted of 1006 of the 1817 independent nonzero reflections [$I > 3\sigma(I)$] that had been measured.

The K_2td crystal showed much more mosaic spread and diffracted even more poorly than the NaHtd crystal. Of 580 independent reflections measured, only 523 nonzero ($I > 0$) reflections were used. Variances $\sigma^2(F_o^2)$ for use in least-squares weighting were estimated in a manner similar to that given elsewhere (Wei, Doherty & Einstein, 1972), except that the quantity $0{\cdot}05F_o^2$ was added to the variance of F_o^2 for NaHtd in order to make allowance for systematic errors (Peterson & Levy, 1957). For the K_2td data the slightly larger quantity $0{\cdot}06F_o^2$ was added similarly.

Solution and refinement of the structures

Analysis of NaHtd. The structure was readily solved by the symbolic-addition procedure with the use of programs *FAME* and *MAGIC* (Dewar & Stone, 1967). However, the initial least-squares refinement of all non-H atoms with *ORFLS* (Busing, Martin & Levy, 1962) brought $R(F)$ no lower than 0·120, even though all atoms were assigned anisotropic thermal parameters. Furthermore, the calculated C–C bond lengths across the cyclobutane ring were 1·65 (2) Å for C(5)–C(5′) and 1·63 (2) Å for C(6)–C(6′), considerably longer than the expected value for a single C–C bond length. The subsequent difference map showed peaks in proper positions for many of the H atoms, but also a number of extra, well-defined peaks about twice as strong as those for the H atoms.

A close examination of the three-dimensional model showed that several of the extra difference-Fourier peaks were in proper positions to form roughly hexagonal rings near the corresponding rings of the dimer. This finding led to the hypothesis that dimer molecules are split by X-irradiation into pairs of monomers that can fit into the same (or very nearly the same) unit cell and that we were dealing with a mixed crystal having a dimer–monomer ratio which decreased with X-ray exposure.* The hypothesis implied an unusual situation, since several atoms would be assumed to move large distances from dimer to monomer sites (see below) without causing the surrounding region to become amorphous. Nevertheless, the hypothesis was confirmed by the subsequent successful refinement of the mixed dimer–monomer model.

The disorder model consisted of four atoms (Na^+, OW and two water H atoms) with full occupancy, 29 dimer atoms (including 11 H atoms) with occupancy a_D, and two monomers (non-H only), the 18 atoms of which had occupancy a_M. The monomers were treated as two rigid groups, each having three adjustable positional, three adjustable Euler-angle parameters, and a single isotropic thermal parameter. The dimer non-H atoms, Na^+, and OW were each assigned anisotropic thermal parameters; and all H atoms had individual isotropic temperature factors.

The occupancies a_D and a_M were constrained to total 1·0 and were to the first approximation assumed to vary linearly with exposure, *i.e.* with the sequence number n of the reflection. For each reflection, a_D was calculated as $\bar{a}_D - k(n/N - 0{\cdot}5)$, where $\bar{a}_D$ represents the dimer occupancy at the halfway point of the data collection, N is the total number of measured reflections (2222), and k represents the decrease in a_D over the entire data collection. Thus, the dimer occupancies at the start and at the end of data collection were represented by $\bar{a}_D + k/2$ and $\bar{a}_D - k/2$, respectively.

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* A progressive change in structure during X-ray data collection was also indicated by the gradual change in cell parameters and was substantiated by the later refinement of a model variable representing the rate of monomerization of dimers (see below).

Starting values for the rigid-group parameters were calculated with program *RBANG*, part of the rigid-group refinement program *ORFLSD*, kindly made available to us by Dr L. F. Dahl of the University of Wisconsin–Madison. The final refinement was carried out with *ORXFLS*4 [updated version of *ORFLS* (Busing, Martin & Levy, 1962)].* In the final refinement, slack constraints were also applied to the methyl groups by assigning C–H distances of 1·0 Å and tetrahedral C–C–H and H–C–H angles of 109·5°, with assigned e.s.d.'s of 0·09 Å for the former and 5–8° for the latter (for a simple example, see Wei, 1982). After several cycles, the values of $R(F)$, $R(F^2)$ and $R_w(F^2)$ stood at 0·051, 0·077 and 0·1120, respectively, for the 1006 reflections used (number of variables: 236, data-to-variable ratio: 4·26). The standard deviation of an observation of unit weight (S) was 1·605. On the final cycle, $(\Delta/\sigma)_{\max}$ for non-H and H atoms were 0·3 for C(7) and 0·4 for H(7a); no residual $\Delta\rho$ peaks > 0·18 e Å^{-3}.

The final values for the occupancy variables $\bar{a}_D$ and k, defined above, were 0·72 (1) and 0·06 (2). Thus, the dimer occupancy a_D is calculated to have been 0·75 (1) at the start and 0·69 (1) at the end of the data collection. The value of 0·75 (1) at the beginning can be rationalized by the fact that a great deal of exposure was incurred in taking Weissenberg and precession photographs and in collecting the first, rejected set of data (see above), all done with the same crystal.† The value of k, representing the rate of change of dimers to monomers, is three times its e.s.d. and therefore of marginal significance. When another refinement was carried out with $k = 0$ and varying the average dimer occupancy, values of 0·051, 0·079 and 0·1127 were obtained for $R(F)$, $R(F^2)$ and $R_w(F^2)$, respectively, and $\bar{a}_D$ value of 0·74 (1). Applying the R-factor ratio test (Hamilton, 1965), we found $\mathcal{R} = 1·006$, as compared to $\mathcal{R}_{1,770,0·005} = 1·005$ interpolated from Hamilton's table for the 0·5% significance level for a hypothesis of one dimension and 770 degrees of freedom. Hence, the hypothesis that in the NaHtd crystal dimers monomerize as a linear function of exposure cannot be rejected at a confidence level of 0·995.

Least-squares refinements for both structures were carried out on F^2. Scattering factors used were those of Ibers (1962) for C, O, N, Na^+, and K^+; those of Stewart, Davidson & Simpson (1965) for H.

Analysis of K_2td. Heavy-atom method yielded the positions of two K^+ atoms and 19 other non-H atoms, including one water O atom, in the probable space group *Cc*. Least-squares refinement gave an $R(F)$ value of 0·139 when the two K^+ ions were assigned anisotropic temperature factors. Although the overall molecular configuration of the dimer appeared correct and was similar to that in NaHtd, the calculated bond lengths across the cyclobutane ring were 2·14 (6) Å for C(5)–C(5′) and 2·02 (5) Å for C(6)–C(6′). These values were a great deal longer than the single-bond values, yet too short to be considered as intermolecular contacts. The following difference map showed many high residual peaks. Attempts were made to identify monomer sites (as in the case of NaHtd), and the refinement was continued with the two monomers as rigid groups, by the use of program *ORFLSD*. Unlike the case of NaHtd, however, this refinement was unsuccessful, leading to an $R(F)$ value of 0·146 and no significant improvement for the two key bond lengths, C(5)–C(5′) and C(6)–C(6′), which remained at 2·02 (6) and 1·95 (6) Å, respectively. Hence, the rigid-group refinement was abandoned, and no such detailed analysis as for the NaHtd data was carried out. The results presented in this paper are based on the refinement in which all 21 non-H atoms were each assigned anisotropic thermal parameters. The final measures of fit were $R(F) = 0·101$, $R(F^2) = 0·107$, $R_w(F^2) = 0·143$, and $S = 1·598$ (number of variables: 188, data-to-variable ratio: 2·78). $(\Delta/\sigma)_{\max}$ in the last least-squares cycle = 0·59 for N(1); more than 50 residual $\Delta\rho$ peaks > 0·2 e Å^{-3} (maximum 0·34 e Å^{-3}).

The final atomic positional parameters and isotropic thermal parameters (or their equivalents) for the dimer molecules of NaHtd and two sets of group parameters are listed in Table 1; individual derived parameters for the two monomer molecules are given in Table 2. For K_2td, the positional and equivalent isotropic thermal parameters are given in Table 3.*

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* The 12 rigid-body positional and angle parameters were accommodated as 'extra' variables of the program *ORXFLS*4 and individual monomer-atom coordinates were calculated in a special version of subroutine *RESETP*. The two occupancy variables $\bar{a}_D$ and k were also treated as 'extra' variables. The occupancies a_D and a_M for each reflection were calculated in subroutine *WEIGHT* by the formula given above. Subroutine *CSTRAN*, which as furnished calculates all derivatives defined in *RESETP* (Busing, 1971), was modified to include calculation of the derivatives with respect to the occupancy variables.

† It would have been valuable to perform a rapid data collection from a freshly prepared crystal as a direct substantiation of our hypothesis that the photomonomerization took place as a linear function of exposure as opposed to the possibility of co-crystallization of dimers and monomers from the solution. More than 20 fresh crystals were examined for this purpose, but no suitable crystal was found, and the effort was abandoned.

* The following data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39107 (10pp.): lists of structure factors and anisotropic thermal parameters for both NaHtd and K_2td, bond angles for K_2td, one figure for NaHtd illustrating the distorted tetrahedral environment of the water O atom, two figures showing for K_2td the [001] projection of the unit cell and the environments of the K^+ ions and the water molecule. Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional, thermal, and group parameters for the monohydrated monosodium salt of cis–syn thymine dimer*

The e.s.d.'s are given in parentheses in all tables and in the text. The digits in parentheses correspond to the least significant digits of the parameters. The equivalent isotropic temperature factors for the dimer, Na, and water O atoms were calculated from the corresponding anisotropic thermal parameters and unit-cell parameters by the relation $B_{eq}=\frac{4}{3}(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2+2\beta_{13}ac\cos\beta)$ (Hamilton, 1959). An isotropic temperature factor of 8·0 Å^2 was assigned to each of the water H atoms; 5·0 Å^2 to each of the ring H atoms; and 7·0 Å^2 to each of the methyl H atoms.

	x	*y*	*z*	B_{eq} or *B* (Å^2)
Na	0·2771 (3)	0·00336 (6)	0·1218 (4)	4·83 (7)
O*W*	0·7650 (7)	0·0288 (2)	0·5571 (7)	5·4 (1)
N(1)	−0·0801 (9)	0·1150 (2)	0·2638 (10)	4·3 (2)
C(2)	0·0255 (11)	0·0841 (3)	0·1775 (13)	3·9 (2)
N(3)	0·2389 (9)	0·0818 (2)	0·2230 (12)	3·9 (2)
C(4)	0·3545 (11)	0·1149 (2)	0·3416 (13)	4·2 (2)
C(5)	0·2516 (11)	0·1593 (2)	0·3935 (12)	4.0 (2)
C(6)	0·0261 (11)	0·1498 (2)	0·4020 (13)	4·0 (2)
C(7)	0·2930 (15)	0·1971 (3)	0·2513 (16)	5.8 (3)
O(2)	−0·0844 (9)	0·0554 (2)	0·0490 (12)	5.1 (2)
O(4)	0·5533 (7)	0·1121 (2)	0·4052 (9)	4·4 (2)
N(1′)	0·1487 (11)	0·0924 (2)	0·6800 (14)	3·9 (2)
C(2′)	0·3415 (17)	0·0761 (3)	0·7746 (21)	4·6 (3)
N(3′)	0·5114 (11)	0·1059 (2)	0·8310 (14)	4·4 (2)
C(4′)	0·5111 (13)	0·1513 (2)	0·7644 (13)	4·5 (3)
C(5′)	0·3069 (10)	0·1689 (2)	0·6342 (13)	4·4 (2)
C(6′)	0·1036 (10)	0·1415 (2)	0·6371 (12)	3·6 (2)
C(7′)	0·2813 (14)	0·2201 (2)	0·6822 (16)	5·1 (3)
O(2′)	0·3725 (15)	0·0332 (2)	0·8168 (21)	4·2 (2)
O(4′)	0·6737 (9)	0·1742 (2)	0·8194 (10)	5·8 (2)
H(*a*)	0·68 (1)	0·046 (2)	0·52 (1)	8·0
H(*b*)	0·76 (1)	0·015 (2)	0·45 (1)	8·0
H(1)	−0·21 (1)	0·112 (2)	0·25 (1)	5·0
H(6)	−0·06 (1)	0·177 (2)	0·39 (1)	5·0
H(7*a*)	0·22 (1)	0·224 (2)	0·26 (1)	7·0
H(7*b*)	0·19 (1)	0·193 (3)	0·11 (1)	7·0
H(7*c*)	0·46 (1)	0·200 (2)	0·27 (1)	7·0
H(1′)	0·02 (1)	0·070 (2)	0·64 (1)	5·0
H(3′)	0·64 (1)	0·093 (2)	0·88 (1)	5·0
H(6′)	0·01 (1)	0·154 (2)	0·74 (1)	5·0
H(7*a*′)	0·14 (1)	0·230 (2)	0·59 (1)	7·0
H(7*b*′)	0·27 (1)	0·226 (2)	0·82 (1)	7·0
H(7*c*′)	0·40 (1)	0·234 (2)	0·65 (1)	7·0

Group*	x_c	y_c	z_c	φ	θ	ρ
TM1	0·178 (1)	0·1256 (3)	0·209 (1)	2·892 (5)	2·945 (7)	2·720 (6)
TM2	0·284 (2)	0·1166 (3)	0·766 (3)	−2·408 (7)	−2·820 (9)	2·790 (9)

* x_c, y_c and z_c are fractional coordinates of the origins of the rigid, planar thymine monomer groups. The rigid-body positional coordinates are defined relative to right-handed orthogonal axes x', y' and z' with each group in the $x'y'$ plane. In each of the TM1 and TM2 groups (TM stands for thymine monomer), C(4) lies on the $+x'$ axis and the $+y'$ axis intersects the midpoint of C(5)–C(6). For each group, the three angle parameters φ, θ, and ρ (in radians) define the orientation of the rigid-body system with respect to the right-handed orthogonal axial vectors $\mathbf{a}_0$, $\mathbf{b}_0$, $\mathbf{c}_0$, where $\mathbf{a}_0$ is parallel to $\mathbf{a}$, $\mathbf{b}_0$ is parallel to $\mathbf{b}$, and $\mathbf{c}_0$ is parallel to $\mathbf{a}\times\mathbf{b}$. Three successive rotations bring the crystal axes into parallel coincidence with the rigid-body axes as follows. A positive rotation φ about $\mathbf{c}_0$ brings $\mathbf{a}_0$ to $\mathbf{a}_1$ and $\mathbf{b}_0$ to $\mathbf{b}_1$; next, a positive rotation θ about $\mathbf{a}_1$ brings $\mathbf{b}_1$ to $\mathbf{b}'$ and $\mathbf{c}_0$ to $\mathbf{c}_1$; lastly, a positive rotation about $\mathbf{b}'$ brings $\mathbf{a}_1$ to $\mathbf{a}'$ and $\mathbf{c}_1$ to $\mathbf{c}'$. The rigid-body coordinates were taken from those of Gerdil (1961) and projected onto the best molecular plane.

Table 2. *Derived parameters of group atoms for* NaHtd

Single isotropic temperature factors of 5·2 (3) and 4·8 (3) Å^2 were obtained for the groups TM1 and TM2, respectively.

Group		*x*	*y*	*z*
TM1	N(1)	−0·0286	0·1401	0·1235
	C(2)	0·0099	0·0941	0·1259
	N(3)	0·2153	0·0816	0·2115
	C(4)	0·3844	0·1112	0·2942
	C(5)	0·3323	0·1597	0·2866
	C(6)	0·1285	0·1722	0·2018
	C(7)	0·5058	0·1940	0·3727
	O(2)	−0·1310	0·0656	0·0558
	O(4)	0·5618	0·0943	0·3662
TM2	N(1)	0·1327	0·0828	0·6960
	C(2)	0·3343	0·0688	0·7859
	N(3)	0·4775	0·1034	0·8518
	C(4)	0·4356	0·1504	0·8351
	C(5)	0·2172	0·1629	0·7376
	C(6)	0·0749	0·1287	0·6721
	C(7)	0·1580	0·2130	0·7132
	O(2)	0·3852	0·0278	0·8070
	O(4)	0·5834	0·1774	0·9027

Table 3. *Positional and equivalent isotropic thermal parameters for the monohydrated dipotassium salt of cis–syn thymine dimer*

	x	*y*	*z*	B_{eq} (Å^2)
K(1)	0·25	−0·0020 (5)	0·25	8·8 (3)
K(2)	0·771 (1)	−0·0278 (3)	0·472 (1)	6·8 (2)
O*W*	0·347 (4)	0·091 (1)	0·101 (3)	12 (1)
N(1)	0·892 (7)	0·139 (2)	0·349 (6)	14 (2)
C(2)	0·931 (6)	0·093 (2)	0·401 (7)	10 (2)
N(3)	0·977 (4)	0·067 (2)	0·561 (5)	8 (1)
C(4)	0·982 (6)	0·107 (2)	0·693 (9)	9 (2)
C(5)	0·945 (7)	0·162 (2)	0·649 (5)	10 (2)
C(6)	0·832 (5)	0·175 (2)	0·445 (5)	10 (2)
C(7)	1·087 (5)	0·198 (2)	0·730 (6)	12 (2)
O(2)	0·928 (4)	0·054 (1)	0·290 (3)	10 (1)
O(4)	1·034 (4)	0·087 (1)	0·848 (4)	11 (1)
N(1′)	0·507 (5)	0·124 (2)	0·465 (4)	11 (2)
C(2′)	0·513 (6)	0·085 (3)	0·559 (7)	9 (3)
N(3′)	0·534 (4)	0·088 (1)	0·741 (5)	7 (1)
C(4′)	0·595 (6)	0·132 (2)	0·792 (4)	8 (2)
C(5′)	0·664 (8)	0·179 (2)	0·696 (4)	14 (2)
C(6′)	0·569 (6)	0·175 (2)	0·493 (6)	12 (2)
C(7′)	0·657 (9)	0·239 (2)	0·731 (7)	18 (3)
O(2′)	0·456 (3)	0·040 (1)	0·528 (4)	7 (1)
O(4′)	0·632 (3)	0·148 (1)	0·948 (4)	9 (1)

Discussion

Structure of NaHtd

This structure analysis appears to be the first one for a mixed crystal of photodimers and their monomer cleavage products in which the *refined* model contains all non-H monomer atoms. In two of the previous analyses of pyrimidine dimers, monomer atoms were located: four sites in the 1,1′-trimethylene-linked thymine dimer (Leonard *et al.*, 1969) and all ten sites in the *trans–anti* 1-methylthymine dimer (Wei & Einstein, 1981). The successful refinement of monomer parameters in the present case undoubtedly depended on the large occupancy values.

Bond lengths, bond angles, and their e.s.d.'s were calculated with the program *ORFFE*4 (Busing, Martin & Levy, 1964) and are given in Table 4. Shown in Fig. 1, prepared with the program *ORTEP*II (Johnson, 1976), is a stereoscopic view of the NaHtd dimer molecule, looking down upon the cyclobutane ring. The cyclobutane ring is buckled: the angle formed by two planes consisting of C(5′), C(5), C(6) and C(5′), C(6′), C(6) is 152·2 (7)°, and the torsion angle C(5′)–C(5)–C(6)–C(6′) is −19·8 (5)°. The buckling results in a twisting of the two saturated pyrimidine rings, as shown by the torsion angles of 28·6 (8)° for C(4)–C(5)–C(5′)–C(4′) and 27·7 (8)° for N(1)–C(6)–C(6′)–N(1′). Despite the structural disorder, the geometry found for the cyclobutane ring is closely similar to that reported for uracil dimer (Adman & Jensen, 1970) and to that in the 1,3-dimethylthymine dimer (Camerman & Camerman, 1970) (for reviews, see Karle, 1976).

Fig. 1 also shows that neither pyrimidine ring is planar. Plane calculations reveal that N(1), C(2), N(3) and C(4) are within 0·032 (5) Å of their least-squares plane but that C(5) and C(6) deviate from this plane by 0·39 (1) and 0·06 (1) Å in opposite directions; N(1′), C(2′), N(3′) and C(4′) are within 0·051 (5) Å of their plane, with C(5′) and C(6′) located 0·14 (1) and 0·26 (1) Å away from the plane in opposite directions. The angle between the two four-membered planes is 54·0 (6)°.

In this structure, the monoanion of thymine dimer exists in the N(3)-deprotonated form, in contrast to the N(1)-deprotonated potassium thyminate trihydrate (Lock, Pilon & Lippert, 1979). The intra-annular angle of 118·7 (7)° at N(3) is significantly smaller than the angles 125·1 (7), 122·4 (6) and 123·5 (6)°, respectively, at N(3′), N(1) and N(1′) (see Table 4*c*), in accordance with the finding of Singh (1965) and Hodgson (1977) that when an N atom of a pyrimidine or purine ring is deprotonated its valence angle becomes significantly smaller. The two methyl carbons in the molecule are separated by only 3·01 (1) Å. As pointed out by Karle (1976), this crowding of the methyl groups creates a strain that facilitates the cleavage by X-rays of the cyclobutane ring of *cis–syn* photodimers.

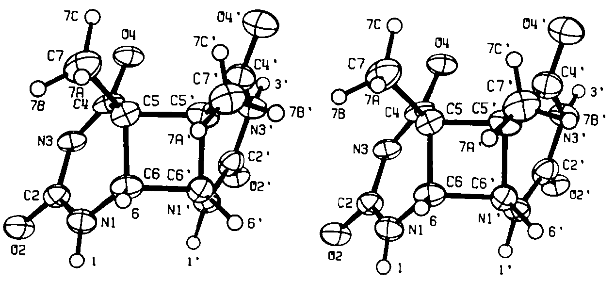

Fig. 1. Stereoscopic view of the cyclobutadipyrimidinate ion in the structure of NaHtd, looking down upon the cyclobutane ring. Each thermal ellipsoid for non-H atoms encloses 30% probability. All atoms are numbered. The buckling of the cyclobutane ring and the non-planarity of the pyrimidine ring are clearly seen.

Table 4. *Molecular parameters for* NaHtd

(*a*) Bond lengths (Å) for dimer molecules

N(1)–C(2)	1·359 (9)	N(1′)–C(2′)	1·336 (10)
C(2)–O(2)	1·275 (9)	C(2′)–O(2′)	1·279 (9)
C(2)–N(3)	1·349 (8)	C(2′)–N(3′)	1·377 (10)
N(3)–C(4)	1·342 (9)	N(3′)–C(4′)	1·393 (9)
C(4)–O(4)	1·258 (8)	C(4′)–O(4′)	1·223 (9)
C(4)–C(5)	1·539 (9)	C(4′)–C(5′)	1·475 (10)
C(5)–C(7)	1·530 (11)	C(5′)–C(7′)	1·538 (10)
C(5)–C(6)	1·520 (9)	C(5′)–C(6′)	1·557 (10)
C(6)–N(1)	1·421 (10)	C(6′)–N(1′)	1·469 (8)
N(1)–H(1)	0·83 (7)	N(1′)–H(1′)	1·01 (7)
C(6)–H(6)	0·97 (7)	N(3′)–H(3′)	0·92 (7)
C(7)–H(7*a*)	0·93 (7)	C(6′)–H(6′)	1·11 (7)
–H(7*b*)	0·99 (7)	C(7′)–H(7*a*′)	1·01 (8)
–H(7*c*)	1·11 (7)	–H(7*b*′)	0·99 (8)
		–H(7*c*′)	0·93 (7)
C(5)–C(5′)	1·591 (11)	O*W*–H(*a*)	0·72 (7)
C(6)–C(6′)	1·549 (11)	–H(*b*)	0·84 (7)

(*b*) Separations (Å) of corresponding atoms in dimer and monomer. For each dimer atom, numbering of the corresponding monomer partner is omitted. TM1 and TM2 designate monomers derived by cleavage from the nonprimed and primed atoms of the dimer, respectively.

N(1)···TM1	1·311 (6)	N(1′)···TM2	0·327 (6)
C(2)···TM1	0·444 (7)	C(2′)···TM2	0·233 (9)
N(3)···TM1	0·153 (6)	N(3′)···TM2	0·303 (7)
C(4)···TM1	0·433 (7)	C(4′)···TM2	0·778 (8)
C(5)···TM1	1·007 (7)	C(5′)···TM2	1·045 (7)
C(6)···TM1	1·790 (7)	C(6′)···TM2	0·505 (7)
C(7)···TM1	1·412 (10)	C(7′)···TM2	0·913 (9)
O(2)···TM1	0·437 (5)	O(2′)···TM2	0·197 (8)
O(4)···TM1	0·589 (5)	O(4′)···TM2	0·927 (6)

(*c*) Bond angles (°) for dimer molecules

C(2)–N(1)–C(6)	122·4 (6)	C(2′)–N(1′)–C(6′)	123·5 (6)
C(2)–N(1)–H(1)	121 (5)	C(2′)–N(1′)–H(1′)	119 (4)
C(6)–N(1)–H(1)	116 (5)	C(6′)–N(1′)–H(1′)	117 (4)
N(1)–C(2)–N(3)	123·6 (7)	N(1′)–C(2′)–N(3′)	119·7 (7)
N(1)–C(2)–O(2)	117·7 (6)	N(1′)–C(2′)–O(2′)	121·5 (7)
N(3)–C(2)–O(2)	118·6 (6)	N(3′)–C(2′)–O(2′)	118·8 (7)
C(2)–N(3)–C(4)	118·7 (6)	C(2′)–N(3′)–C(4′)	125·1 (7)
N(3)–C(4)–C(5)	121·6 (6)	C(2′)–N(3′)–H(3′)	116 (4)
N(3)–C(4)–O(4)	121·2 (6)	C(4′)–N(3′)–H(3′)	116 (4)
C(5)–C(4)–O(4)	117·0 (7)	N(3′)–C(4′)–C(5′)	116·2 (7)
C(4)–C(5)–C(6)	110·4 (5)	N(3′)–C(4′)–O(4′)	119·5 (7)
C(4)–C(5)–C(5′)	113·0 (6)	C(5′)–C(4′)–O(4′)	124·3 (6)
C(4)–C(5)–C(7)	106·9 (6)	C(4′)–C(5′)–C(6′)	117·0 (6)
C(6)–C(5)–C(5′)	86·7 (5)	C(4′)–C(5′)–C(5)	117·6 (6)
C(6)–C(5)–C(7)	119·7 (6)	C(4′)–C(5′)–C(7′)	110·0 (6)
C(5′)–C(5)–C(7)	119·1 (6)	C(6′)–C(5′)–C(5)	88·2 (5)
N(1)–C(6)–C(5)	114·1 (6)	C(6′)–C(5′)–C(7′)	110·3 (6)
N(1)–C(6)–C(6′)	121·8 (6)	C(5)–C(5′)–C(7′)	112·2 (6)
N(1)–C(6)–H(6)	110 (4)	N(1′)–C(6′)–C(5′)	111·8 (5)
C(5)–C(6)–C(6′)	91·1 (6)	N(1′)–C(6′)–C(6)	110·2 (6)
C(5)–C(6)–H(6)	114 (4)	N(1′)–C(6′)–H(6′)	108 (3)
C(6′)–C(6)–H(6)	105 (4)	C(5′)–C(6′)–C(6)	86·9 (5)
C(5)–C(7)–H(7*a*)	111 (4)	C(5′)–C(6′)–H(6′)	119 (4)
–H(7*b*)	108 (4)	C(6)–C(6′)–H(6′)	120 (4)
–H(7*c*)	110 (4)	C(5′)–C(7′)–H(7*a*′)	106 (4)
H(7*a*)–C(7)–H(7*b*)	88 (6)	–H(7*b*′)	115 (4)
H(7*b*)–C(7)–H(7*c*)	120 (6)	–H(7*c*′)	104 (4)
H(7*c*)–C(7)–H(7*a*)	117 (6)	H(7*a*′)–C(7′)–H(7*b*′)	104 (6)
		H(7*b*′)–C(7′)–H(7*c*′)	113 (6)
H(*a*)–O*W*–H(*b*)	97 (8)	H(7*c*′)–C(7′)–H(7*a*′)	116 (6)

When a dimer is split into monomers, the C(5)–C(5′) and C(6)–C(6′) bonds are cleaved and the pyrimidine rings separate, leaving two nearly parallel monomer planes (dihedral angle 3·59°) separated by approximately 3·6 Å, as shown in Fig. 2. Some atoms move from their original dimer positions by as much as 1·790 (7) Å for C(6), while some move as little as 0·153 (6) Å for N(3) (Table 4*b*). The consequence of the splitting of the dimer can best be illustrated by the [100] projection of the unit cell. The dimers lie in layers perpendicular to the *b* axis as shown in Fig. 3(*a*). A pair of dimer layers is interleaved by a layer of Na^+ ions and water molecules. Each dimer is connected to Na^+ and is H-bonded to water. When the monomerization takes place, the resulting monomers are arranged as shown in Fig. 3(*b*). The closest intermolecular contact between non-H atoms of the dimer (excluding those involved in H-bonding) is 3·22 (2) Å for O(2′)···O(2′), and that between non-H and H atoms is 2·46 (8) Å for O(4′)···H(6′). Between monomers, two closest contacts are 2·787 Å for N(1)TM1···O(4)TM2 and 2·781 Å for O(2)TM1···N(3)TM2, suggesting that H-bonding similar to that in the structure of potassium thyminate trihydrate (Lock, Pilon & Lippert, 1979) exists between neighboring monomers. Although as noted above, individual dimer atoms move as much as 1·790 (7) Å for C(6) when the dimer is split into monomers, the monomers fit well into the environment of surrounding dimers. No intermolecular contact between non-H atoms of monomers and surrounding dimers is smaller than 3·138 (6) Å for N(3)TM2···O(2), except for the N(1)TM1···O(4′), O(2)TM1···N(3′), O(4)TM1···N(1) and N(1)TM2···O*W* distances of 2·608 (6), 2·685 (7), 2·692 (6) and 2·810 (4) Å, respectively. The last three distances indicate that these H-bonds are retained upon splitting of the dimer (see below). The first distance appears to represent a new H-bond by monomers to dimers. Furthermore, C(6), which has moved the furthest from its dimer position, has O(4′) as its closest non-H dimer neighbor at the distance of 3·364 (7) Å.

Table 5. H-*bonds* (*A*–H···*B*) *in the structure of* NaHtd

A	H	*B*	*A*···*B*	*A*–H	H···*B*	∠*A*–H···*B*
N(1)	H(1)	$O(4)^{i}$	2·822 (8) Å	0·83 (7) Å	2·09 (7) Å	147 (7)°
N(1′)	H(1′)	OW^{i}	3·045 (8)	1·01 (7)	2·03 (7)	177 (6)
N(3′)	H(3′)	$O(2)^{ii}$	3·031 (9)	0·92 (7)	2·13 (8)	166 (6)
O*W*	H(*a*)	O(4)	2·835 (7)	0·72 (7)	2·16 (7)	157 (8)
O*W*	H(*b*)	$O(2')^{iii}$	3·03 (1)	0·84 (7)	2·24 (7)	157 (6)

Symmetry code: (i) $x-1, y, z$; (ii) $1+x, y, 1+z$; (iii) $1-x, -y, 1-z$.

All H atoms of the cyclobutadipyrimidinate ion and the water molecule appear to be involved in N–H···O or O*W*–H···O bonds with neighboring dimers. The three NH groups serve as H-bond donors, resulting in N–H···O and N–H···O*W* bonds, while O(2), O(2′) and O(4) act as acceptors in the formation of N(3′)–H(3′)···O(2), O*W*–H(*b*)···O(2′) and O*W*–H(*a*)···O(4) bonds, respectively. Only O(4′) is not involved in H-bonding. Complete information regarding the H-bonds is listed in Table 5.

The Na^+ ion is surrounded by N(3), O*W* and four O atoms of different dimer molecules. These atoms are all within 2·8 Å of the Na^+ ion, forming a distorted octahedron with N(3) and a symmetry-related O(2) $(-x, -y, -z)$ at the apical sites (Fig. 4). The most pronounced distortion of the octahedron is the N(3)–Na–O(2) [O(2) related to the reference one by $-x$,

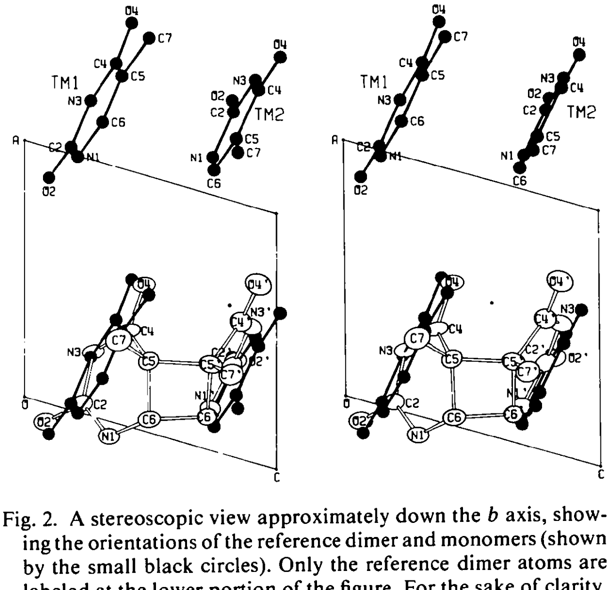

Fig. 2. A stereoscopic view approximately down the *b* axis, showing the orientations of the reference dimer and monomers (shown by the small black circles). Only the reference dimer atoms are labeled at the lower portion of the figure. For the sake of clarity, the monomer atoms are labeled for those monomers (TM1 and TM2) translated in the **a** direction. The unit-cell lines are not included except for the *ac* plane passing through the origin. The cleavage of the dimer results in two monomers which are nearly parallel (dihedral angle 3·59°) and are separated by approximately 3·6 Å.

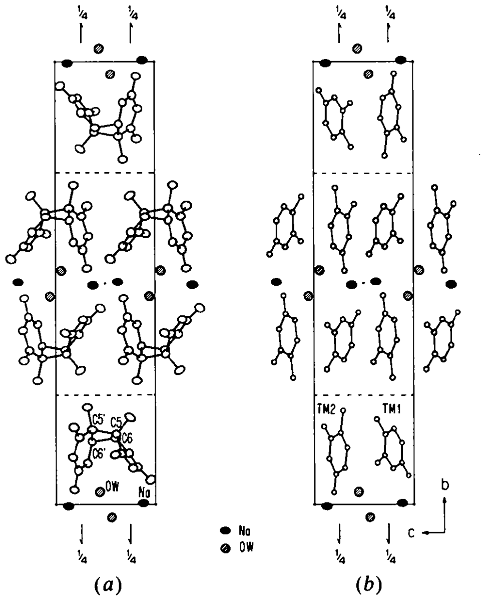

Fig. 3. Two [100] projections of the unit cell of NaHtd, showing separately the arrangements of (*a*) dimers and (*b*) monomers. In (*a*) only Na^+, O*W*, and the cyclobutane ring atoms of the reference molecule are labeled. In (*b*) TMI and TM2 designate thymine monomers resulting from non-primed and primed dimer atoms.

−y, −z] angle of 140·9 (2)°. The average of the six distances between Na^+ and the coordination sites is 2·461 (3) Å. The oxygen of the water molecule displays a distorted tetrahedral coordination, Na^+, N(1′), O(2′) and O(4) being located at the four apices.

Structure of K_2td

The technique which led to the successful refinement of the structure of NaHtd failed to yield satisfactory results for K_2td, probably because of excessive monomerization and more complex disorder, and because of the poor quality and the small number of data.

Because the structure determination yielded only average (dimer–monomer) atomic positions, as reflected by the unrealistically long C(5)–C(5′) and C(6)–C(6′) bond lengths calculated, detailed descriptions of the structure of K_2td appear to be of little value. Still, a few structural features are worth noticing. The configuration of the cyclobutadipyrimidinate ion is shown in Fig. 5. It appears that both N(3) and N(3′) are deprotonated, as substantiated (Singh, 1965) by the fact that intra-annular angles at N(3) and N(3′) are 106 (4) and 111 (4)°, decisively smaller than those of 123 (5) and 133 (4)° at N(1) and N(1′), respectively.

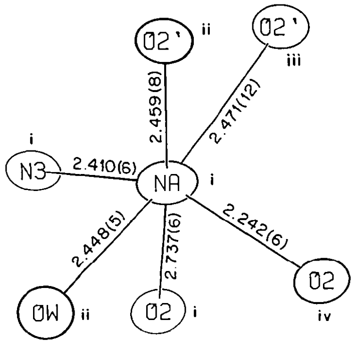

Fig. 4. The coordination around the Na^+ ion, showing a distorted octahedral arrangement. Symmetry codes: (i) x, y, z; (ii) 1 − x, −y, 1 − z; (iii) x, y, z − 1; and (iv) −x, −y, −z. (Distances in Å.)

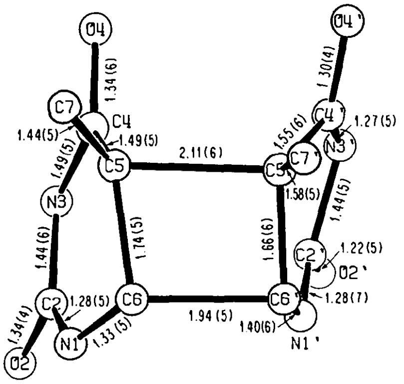

Fig. 5. Molecular configuration of the cyclobutadipyrimidinate ion in the structure of K_2td. (Distances in Å.)

The K(1) ion is surrounded by five O atoms (including a water oxygen) and two N atoms at distances ranging from 2·70 (2) to 3·00 (3) Å; the K(2) ion is surrounded by four O and two N atoms at distances 2·70 (3)–2·89 (2) Å. The two K^+ ions are joined by a bridging O(2′) and a bridging symmetry-related N(3′) atom (x, −y, z − ½) equally shared between the K^+ ions. The coordination of the water O atom is that of a distorted tetrahedron with K(1), N(1′), O(4) and O(4′) located at its four apices, similar to that in the structure of NaHtd. The three closest intermolecular distances of 2·74 (4), 2·91 (3) and 3·08 (4) Å for O*W*···O(4), O*W*···O(4′) and O*W*···N(1′), respectively, appear to represent H-bonds. However, no N···O contacts suggestive of N–H···O H-bonding were found in this structure.

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