benzene ($\delta = 85{\cdot}0°$) (Cox, Cruickshank & Smith, 1958) and 2-aminophenol ($\delta = 87{\cdot}7°$) (Ashfaquzzaman & Pant, 1979; Haisa *et al.*, 1980). The second H of the amino group is free from any hydrogen bond, the shortest contact involving the H being 2·66 (2) Å for C(3)···H(3^{v}). The sheets are stacked along **b** by weak van der Waals interactions in accordance with the morphology of the crystals.

The modes of hydrogen bonding, the sheet formation and the sheet stacking are the same as those in 2-aminophenol. However, a change in the mode of sheet stacking is found in 2-amino-4-chlorophenol, where the symmetry operation for the sheet stacking is changed from 2_1 along **b** to an **a** translation. Thus, the space group descends to $P2_1/c$, a maximal subgroup of *Pbca*. Such a descent in space group is found between benzene (*Pbca* form) and some if its derivatives; *e.g.* the $P2_1/c$ form of benzene (Mighell, Weir & Block, 1969), naphthalene ($P2_1/a$, Cruickshank, 1957) and biphenyl ($P2_1/a$, Charbonneau & Delugeard, 1977).

In 3- and 4-aminophenols (de Rango, Brunie, Tsoucaris, Declercq & Germain, 1974; Brown, 1951), centrosymmetric pairing of the molecules through hydrogen bonds between the amino and hydroxy groups is prohibited by packing requirements, the only possible mode of hydrogen bonding being the formation of endless chains of the molecules. Thus, the crystals of 3- and 4-aminophenols adopt non-centrosymmetric space groups ($Pca2_1$ and $Pna2_1$, respectively). It should be noted that both of these space groups are also subgroups of *Pbca*.

The authors thank the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the facility.

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Structure of Hypoxanthine

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(*Received* 16 *October* 1987; *accepted* 4 *January* 1988)

Abstract. 1,7-Dihydro-6*H*-purin-6-one, $C_5H_4N_4O$, $M_r = 136{\cdot}11$, triclinic, $P\bar{1}$, $a = 7{\cdot}102\,(2)$, $b = 9{\cdot}759\,(2)$, $c = 10{\cdot}387\,(2)$ Å, $\alpha = 58{\cdot}85\,(2)$, $\beta = 67{\cdot}64\,(2)$, $\gamma = 72{\cdot}00\,(2)°$, $V = 564{\cdot}0\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}60$, $D_m = 1{\cdot}60$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}78$ cm^{-1}, $F(000) = 280$, room temperature, $wR = 4{\cdot}6\%$ for 2916 observed unique reflections. Hypoxanthine exhibits a layered structure of N–H···O and N–H···N hydrogen-bonded molecules, the mean stacking distance between molecules of adjacent layers being 3·25 Å. There are two crystallographically independent molecules in the structure; in both of them the 1*H*,9*H* tautomer (lactam configuration) is the predominant form.

Introduction. Hypoxanthine occasionally occurs as a constituent of the nucleoside inosine in minor amounts in transfer RNA (Hurst, 1980), and it is an intermediate product of purine metabolism formed by degradation of nucleic acids. Hypoxanthine is oxidized to xanthine and uric acid in man, these reactions being catalyzed by the molybdenum- and iron-containing

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0108-2701/88/040732-05$03.00

enzyme xanthine oxidase. As a result of metabolic errors crystalline hypoxanthine or xanthine may be deposited in muscle tissue (Hesse & Bach, 1982); xanthine, in addition, occasionally crystallizes as a constituent of urinary calculi (Bastian, 1974).

Enzymes attack purines at preferred positions, and therefore the tautomerization of the substrate molecules may play an important role. These tautomerism processes have been the subject of different experimental studies in aqueous solutions, but little information is available on the crystalline state. The crystal structures of hypoxanthine hydrochloride monohydrate (Sletten & Jensen, 1969) and of hypoxanthine nitrate monohydrate (Rosenstein, Oberding, Hyde, Zubieta, Karlin & Seeman, 1982) have been reported, but in both compounds no neutral hypoxanthine molecules are observed, only N(7)/N(9)-protonated hypoxanthinium cations. Crystallographic data of hypoxanthine–metal complexes, where the ligand usually adopts its non-protonated neutral form, have recently been reviewed (Dubler, Hänggi & Bensch, 1987; Dubler, Hänggi & Schmalle, 1987).

Based on previous crystallographic, thermoanalytical and spectroscopic investigations of hypoxanthine–metal complexes, we have crystallized neutral hypoxanthine and solved its structure in order to obtain the accurate ligand geometry and to verify the tautomeric form in the crystalline state. This information is also of interest in view of the changes in bond angles and lengths of the ring system effected by either protonation or coordination of one of the imidazole N atoms.

Experimental. Crystals of hypoxanthine, suitable for X-ray investigations, were grown from a 0·25 *M* H_2SO_4 solution at 313 K. Composition: calculated for $C_5H_4N_4O$: C 44·12, H 2·96, N 41·16%; observed C 44·02, H 2·96, N 41·40%. A transparent plate-shaped crystal of approximate dimensions 0·98 × 0·62 × 0·29 mm was selected for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Density measured by flotation. Cell dimensions were determined by least-squares refinement of θ values of 25 reflections in the interval $10 < \theta < 18°$. Intensities of 6292 reflections (including standards) in the θ range 1–30° were collected using the ω–2θ-scan technique, zigzag mode and variable scan speeds between 4·0 and 6·7° min^{-1}. The index range was $-9 \le h \le 7$, $-13 \le k \le 13$, $-14 \le l \le 14$. Four standard reflections were measured every 3 h during data collection, 3·5% loss of intensities was observed and corrected for in data reduction. Orientation was controlled using five standard reflections at an interval of every 250 reflections. Data reduction ($R_{int} = 2·8\%$) led to 3277 unique reflections. The data were corrected for Lorentz and polarization effects and a numerical absorption correction was applied (min. and max. transmission factors 0·980 and 0·992 respectively). The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976), minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for the non-H atoms.

After refinement of the C, N and O atoms using 2604 reflections with $I \ge 3\sigma(I)$ ($R = 6·8\%$, $wR = 8·1\%$, $w = 1$), all H atoms could be localized in the difference Fourier maps [H(1*A*) = 0·57, H(2*A*) = 1·00, H(8*A*) = 0·79, H(9*A*) = 0·45, H(1*B*) = 0·93, H(2*B*) = 0·76, H(8*B*) = 0·94 and H(9*B*) = 0·83 e $Å^{-3}$]. Final refinements included 2916 reflections with $I \ge 0·5\sigma(I)$ and 213 variable parameters. H atoms were refined with free positional and isotropic temperature factors. Reflection 111 has been omitted because secondary extinction was suspected. The weighting scheme was $w = K/\sigma^2(F)$ (K = refined to 2·24), and the refinement converged with a maximum shift-to-e.s.d. ratio of 0·014 to $R = 5·7\%$ and $wR = 4·6\%$. The maximum and minimum heights in the final difference Fourier synthesis were 0·35 and −0·39 e $Å^{-3}$. Further electron density peaks could be observed at N(7) with 0·23 (distance 0·95 Å), at O(6) with 0·20 (distance 0·86 Å), at N(3) with 0·15 e $Å^{-3}$ (distance 0·94 Å) in molecule *A* and at O(6) with 0·19 (distance 0·90 Å) and at N(3) with 0·17 e $Å^{-3}$ (distance 0·78 Å) in molecule *B*. Calculations were performed on Hitachi AS XL 60 and PDP 11/34 computers. Atomic scattering factors those of *SHELX*. The final atomic parameters are listed in Table 1.*

Discussion. The structure of hypoxanthine exhibits two crystallographically independent molecules, shown in Fig. 1. Bond lengths and angles of the two molecules are summarized in Table 2.

Ultraviolet spectra indicate that neutral hypoxanthine is present in aqueous solutions predominantly as the 1*H*,9*H* tautomer (Lichtenberg, Bergmann & Neiman, 1972). The 1*H*,7*H* form has been predicted to be of similar intrinsic stability based on quantum chemical calculations (Pullman & Pullman, 1971). The solid-state structure presented here reveals the 1*H*,9*H* tautomer as the predominant form in both molecules. Considering the small residual peaks in the final difference Fourier map mentioned above, a minor contribution from other tautomeric forms of hypoxanthine cannot, however, be excluded with certainty. The relatively high temperature factors of H(9*A*) and H(9*B*) as well as those of H(1*B*) may hint at a

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44656 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters for hypoxanthine*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
N(1*A*)	0·4437 (2)	0·7164 (1)	0·4615 (1)	0·057
C(2*A*)	0·4588 (3)	0·8545 (2)	0·4578 (2)	0·069
N(3*A*)	0·3445 (2)	0·9934 (1)	0·4006 (1)	0·064
C(4*A*)	0·2054 (2)	0·9851 (1)	0·3462 (1)	0·048
C(5*A*)	0·1784 (2)	0·8524 (1)	0·3435 (1)	0·048
C(6*A*)	0·3075 (2)	0·7037 (1)	0·4040 (2)	0·052
O(6*A*)	0·3077 (1)	0·5742 (1)	0·4075 (1)	0·066
N(7*A*)	0·0218 (2)	0·8914 (1)	0·2779 (1)	0·061
C(8*A*)	−0·0434 (3)	1·0456 (1)	0·2433 (2)	0·064
N(9*A*)	0·0611 (2)	1·1072 (1)	0·2815 (1)	0·056
N(1*B*)	0·4405 (2)	0·3499 (1)	0·9662 (1)	0·058
C(2*B*)	0·4474 (3)	0·2065 (1)	0·9693 (2)	0·056
N(3*B*)	0·3334 (2)	0·1809 (1)	0·9144 (1)	0·056
C(4*B*)	0·2008 (2)	0·3148 (1)	0·8515 (2)	0·049
C(5*B*)	0·1823 (2)	0·4660 (1)	0·8406 (2)	0·048
C(6*B*)	0·3111 (2)	0·4910 (1)	0·8982 (2)	0·055
O(6*B*)	0·3201 (2)	0·6190 (1)	0·8937 (1)	0·079
N(7*B*)	0·0322 (2)	0·5710 (1)	0·7679 (1)	0·057
C(8*B*)	−0·0376 (2)	0·4850 (1)	0·7366 (2)	0·062
N(9*B*)	0·0604 (2)	0·3283 (1)	0·7848 (1)	0·062
H(1*A*)	0·531 (4)	0·636 (3)	0·497 (3)	0·088
H(2*A*)	0·562 (3)	0·849 (2)	0·499 (2)	0·034
H(8*A*)	−0·157 (3)	1·106 (2)	0·193 (2)	0·031
H(9*A*)	0·054 (4)	1·199 (3)	0·278 (3)	0·12
H(1*B*)	0·530 (3)	0·356 (2)	1·013 (2)	0·053
H(2*B*)	0·556 (3)	0·128 (2)	1·016 (2)	0·030
H(8*B*)	−0·150 (3)	0·525 (2)	0·681 (2)	0·039
H(9*B*)	0·052 (4)	0·243 (3)	0·765 (3)	0·11

partial distribution of different tautomers. Nevertheless, other findings are strongly in favor of the 1*H*,9*H* form:

(*a*) The C(8)–N(9)–C(4) bonding angle of the 1*H*,9*H* form is 107·3 (1), 107·1 (1) and 107·1 (3)°, respectively, in three recently determined structures of metal complexes involving neutral hypoxanthine (Dubler, Hänggi & Bensch, 1987; Dubler, Hänggi & Schmalle, 1987) and is expected to decrease by about 2–3° upon deprotonation at N(9) (Taylor & Kennard, 1982*a*). The values of 107·0 (1) and 106·6 (1)° found in hypoxanthine are in agreement with the 9*H* tautomer. The mean bonding angle at N(7), C(5)–N(7)–C(8), has been determined to be 104·2 (3)° in neutral guanine derivatives and is expected to increase to 108·0 (2)° upon protonation at N(7) (Taylor & Kennard, 1982*a*). Again, the values of 103·7 (1) and 104·8 (1)° found in hypoxanthine support the 9*H* tautomer. In addition, the C–O distances of 1·246 (2) and 1·247 (2) Å indicate the double-bond character of this bond and hence confirm the 1*H* lactam and not the lactim form.

(*b*) As a consequence of the differences in the purine ring geometry of different tautomeric forms of hypoxanthine, anisotropic thermal ellipsoids characteristic of a slightly disordered molecule would be expected, if statistical distribution of several tautomeric forms within the structure is assumed. As may be seen from Fig. 1, however, no obviously disordered molecules result from the structure analysis.

Comparing the purine ring dimensions of hypoxanthine with those of hypoxanthine hydrochloride monohydrate (Sletten & Jensen, 1969) and hypoxanthine nitrate monohydrate (Rosenstein *et al.*, 1982), where hypoxanthine is protonated at N(9) as well as at N(7), the main differences are observed within the imidazole moiety. As expected, the C(5)–N(7)–C(8) bonding angle, for example, is increased by about 3–4° upon protonation at N(7). On the other hand, the

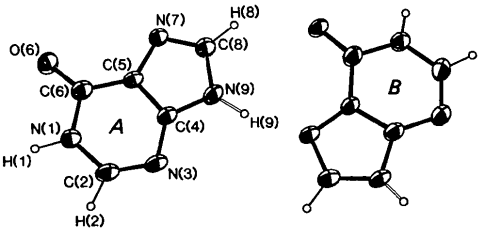

Fig. 1. *ORTEP* drawing (Johnson, 1971) of the two crystallographically independent hypoxanthine molecules *A* and *B* and the numbering system of the purine ring.

Table 2. *Interatomic bond distances* (Å) *and angles* (°)

	Molecule *A*	Molecule *B*
N(1)–C(2)	1·364 (2)	1·369 (2)
C(2)–N(3)	1·305 (2)	1·291 (2)
N(3)–C(4)	1·350 (2)	1·359 (2)
C(4)–C(5)	1·381 (2)	1·388 (2)
C(5)–C(6)	1·419 (2)	1·400 (2)
C(6)–N(1)	1·378 (2)	1·395 (2)
C(5)–N(7)	1·376 (2)	1·376 (2)
N(7)–C(8)	1·321 (2)	1·311 (2)
C(8)–N(9)	1·348 (2)	1·375 (2)
N(9)–C(4)	1·365 (2)	1·356 (2)
C(6)–O(6)	1·246 (2)	1·247 (2)
N(1)–H(1)	0·84 (3)	0·97 (2)
C(2)–H(2)	0·95 (2)	0·98 (2)
C(8)–H(8)	0·99 (2)	1·08 (2)
N(9)–H(9)	0·86 (3)	0·98 (2)
C(6)–N(1)–C(2)	125·0 (2)	124·0 (2)
N(1)–C(2)–N(3)	124·8 (2)	125·5 (2)
C(2)–N(3)–C(4)	112·0 (1)	112·1 (1)
N(3)–C(4)–C(5)	127·8 (2)	127·2 (2)
C(4)–C(5)–C(6)	118·9 (2)	119·4 (1)
C(5)–C(6)–N(1)	111·5 (1)	111·8 (1)
C(4)–C(5)–N(7)	110·8 (1)	110·2 (1)
C(5)–N(7)–C(8)	103·7 (1)	104·8 (1)
N(7)–C(8)–N(9)	113·3 (2)	112·5 (2)
C(8)–N(9)–C(4)	107·0 (1)	106·6 (1)
N(9)–C(4)–C(5)	105·2 (2)	105·9 (1)
N(3)–C(4)–N(9)	127·0 (1)	126·9 (1)
C(6)–C(5)–N(7)	130·2 (1)	130·5 (1)
N(1)–C(6)–O(6)	121·1 (2)	120·3 (2)
C(5)–C(6)–O(6)	127·4 (2)	127·9 (2)
C(2)–N(1)–H(1)	116 (2)	119 (1)
C(6)–N(1)–H(1)	119 (2)	117 (1)
N(1)–C(2)–H(2)	117 (1)	109 (1)
N(3)–C(2)–H(2)	118 (1)	126 (1)
N(7)–C(8)–H(8)	121 (1)	126 (1)
N(9)–C(8)–H(8)	126 (1)	121 (1)
C(4)–N(9)–H(9)	117 (2)	123 (2)
C(8)–N(9)–H(9)	136 (2)	130 (2)

average bond lengths and angles of the two independent molecules in hypoxanthine are not definitely different from those observed in the nucleoside inosine (representing a 9-substituted hypoxanthine) or in inosine dihydrate (Munns & Tollin, 1970; Thewalt, Bugg & Marsh, 1970).

The purine ring is approximately planar in both molecules of hypoxanthine with maximum deviations of 0·013 Å for N(1) in molecule *A* and of 0·016 Å for N(1) and C(6) in molecule *B* from the least-squares plane through the nine ring atoms. The deviations of the extraannular O atoms from the purine planes are 0·041 Å in molecule *A* and 0·060 Å in molecule *B*. The two crystallographically independent molecules are nearly parallel with a dihedral angle of 177·2° between the purine planes.

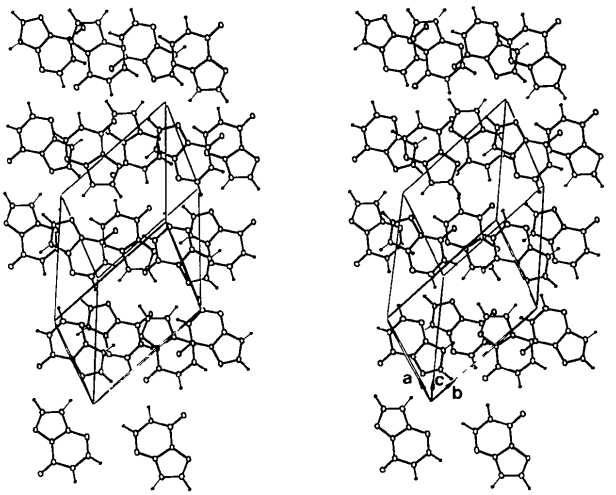

Fig. 3. *ORTEP* stereo plot of the packing diagram of hypoxanthine.

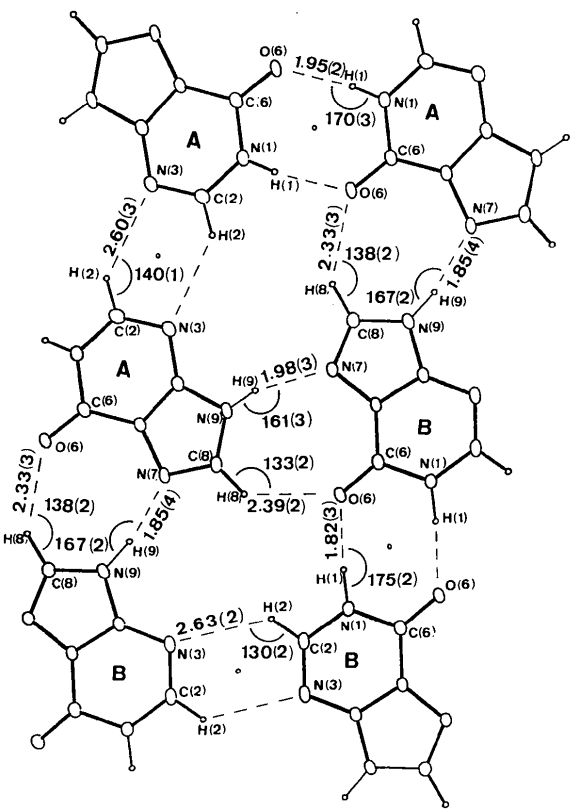

Fig. 2. Hydrogen-bonding scheme of hypoxanthine. (Distances in Å, angles in °.)

Fig. 2 gives a representation of the hydrogen-bonding scheme and corresponding bond lengths and angles in hypoxanthine; donor–acceptor distances are listed in Table 3. Each molecule is involved in four hydrogen bonds, two of the type N–H···O and two of the type N–H···N. The strongest hydrogen-bonded interactions include N(1*A*)–H(1*A*)···O(6*A*) and N(1*B*)–H(1*B*)···O(6*B*) with N···O donor–acceptor distances of 2·779 (2) and 2·786 (3) Å respectively. In addition, there are different weak intermolecular contacts (Taylor & Kennard, 1982*b*) of the form C–H···O and C–H···N. Molecules *A* and *B* form different pairs of symmetry-related dimers *via* N(1*A*)–H(1*A*)···O(6*A*) and N(1*B*)–H(1*B*)···O(6*B*) hydrogen bonds [see Fig. 2 for distances and angles around H(1*A*) and H(1*B*)]. Crystallographically independent molecules are linked *via* N(9*A*)–H(9*A*)···N(7*B*) and N(9*B*)–H(9*B*)···N(7*A*) bonds, thus forming sheets approximately parallel to the (10$\bar{2}$) plane.

The molecular packing in the unit cell is shown in Fig. 3. Hypoxanthine molecules are infinitely stacked approximately perpendicular to the (10$\bar{2}$) plane. The mean stacking distance, calculated as the mean distance of individual atoms of a molecule from the least-squares plane through the stacking molecule, is 3·25 Å. There is only minor direct overlap of stacking molecules. Stacking patterns of type I (Bugg, 1972) with imidazole rings of adjacent bases pointing in the same direction as well as those of type II with the imidazole moieties pointing in opposite directions are observed.

Table 3. *Hydrogen-bonded contacts* (Å) *in hypoxanthine*

N(1*A*)···O(6*A*)	2·779 (2)	C(8*A*)···O(6*B*)	3·146 (2)
N(1*B*)···O(6*B*)	2·786 (3)	C(8*B*)···O(6*A*)	3·167 (4)
N(9*A*)···N(7*B*)	2·802 (2)	C(2*B*)···N(3*B*)	3·348 (2)
N(9*B*)···N(7*A*)	2·807 (3)	C(2*A*)···N(3*A*)	3·383 (4)

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Acta Cryst. (1988). C**44**, 736–737

Methyl *rel*-(2*R*,3*S*,5*R*,6*S*)-7-Oxabicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylate

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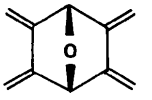
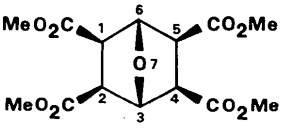
(*Received* 22 *October* 1987; *accepted* 4 *January* 1988)

Abstract. $C_{14}H_{18}O_9$, $M_r = 330{\cdot}3$, orthorhombic, *F*2*dd*, $a = 5{\cdot}065$ (1), $b = 13{\cdot}632$ (3), $c = 43{\cdot}636$ (9) Å, $V = 3013$ Å^3, $Z = 8$ (the molecule possesses a twofold axis), $D_x = 1{\cdot}45$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}10$ mm^{-1}, $F(000) = 1392$, room temperature, $R = 0{\cdot}048$ for 572 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The all-*exo* configuration of the ester group proposed on the basis of NMR spectroscopic studies for the title compound is confirmed.

Introduction. In the course of the synthesis (Kohnke, Slawin, Stoddart & Williams, 1987) of a new class of rigid macropolycyclic molecules with belt-like shapes that relies upon the Diels–Alder reaction, the bisdiene (1) (Vogel & Florey, 1974) was identified as one of the key starting materials. It can be prepared (Mahaim, Carrupt, Hagenbuch, Florey & Vogel, 1980) in four steps from the *exo*-furan–maleic anhydride adduct which is subjected, in the first instance, to catalytic carbonylation (James & Stille, 1976) in methanolic solution to afford a tetraester. On basis of the ^{1}H and ^{13}C NMR spectroscopic data, this compound has been assigned (Mahaim *et al.*, 1980) the all-*exo* configuration (2). During our own preparation of a sample of the bisdiene (1), good-quality single crystals were obtained (Kohnke *et al.*, 1987). Here we report the results of an X-ray crystallographic investigation carried out on the tetraester (2).



(1)



(2)

Experimental. Single crystals (found: C 51·1, H 5·5%. $C_{14}H_{18}O_9$ requires C 50·9, H 5·5%) of (2), suitable for X-ray crystallography, were grown at room temperature from $CHCl_3$ and had m.p. 430–431 K. Crystal size 0·20 × 0·30 × 0·40 mm. Refined unit-cell parameters obtained from setting angles of 19 reflections with $8 \le \theta \le 33°$. Nicolet *R*3*m* diffractometer. 574 independent reflections ($\theta \le 58°$) measured, Cu $K\alpha$ radiation (graphite monochromator), ω scan. 572 [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range *h* 0/5, *k* 0/14, *l* 0/46; two check reflections measured every 50 reflections, net count constant; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods; non-hydrogen atoms refined anisotropically; positions of H atoms calculated (C—H = 0·96 Å); H atoms assigned isotropic thermal parameters, $U(H) = 1{\cdot}2\,U_{eq}(C)$, and allowed to ride on parent C atoms; methyl groups refined as rigid bodies. An empirical extinction correction was applied [$g = 0{\cdot}007$ (1)]. Refinement using *F*

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0108-2701/88/040736-02$03.00