

atomiques montre que toutes les liaisons Ga–Ga et T–Ga sont plus longues dans Cr_3Ga_4 que dans Fe_3Ga_4 .

Les liaisons T–T à l'intérieur des couches définies précédemment sont plus grandes dans Cr_3Ga_4 ; par contre, les distances Cr–Cr entre ces couches sont plus courtes que les distances Fe–Fe correspondantes.

Ces différences sont cependant mineures puisque nous avons vérifié que les deux phases sont totalement miscibles à l'état solide; elles sont donc isomorphes.

Acta Cryst. (1975). **B31**, 482

Structural Chemistry of the Benzotropone System.

I. The Crystal and Molecular Structure of 2,7-Pentamethylene-4,5-benzotropone

BY KOICHI IBATA, HIROTAKE SHIMANOUCI AND YOSHIO SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan

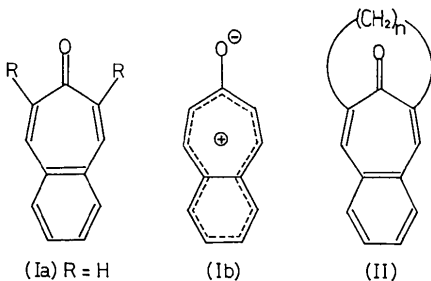
(Received 9 August 1974; accepted 27 September 1974)

Crystals of 2,7-pentamethylene-4,5-benzotropone, $\text{C}_{16}\text{H}_{16}\text{O}$, are monoclinic, space group $P2_1/n$, with unit-cell dimensions $a=9.803$ (2), $b=16.184$ (7), $c=7.802$ (2) Å, $\beta=90.39$ (2)° and $Z=4$. The structure was solved by the direct method and refined by the block-diagonal matrix least-squares method to a final R of 0.058. The seven-membered ring of the molecule adopts a marked boat form with bow angle of 51.3° and stern angle of 24.3°. The C=O bond length is 1.207 Å. The out-of-plane bending of the C=O bond is explained by the π -electronic effect.

Introduction

4,5-Benzotropone (*Ia*) exhibits a considerably high dipole moment, 4.70–4.88 D (Gäumann, Schmid & Heilbronner, 1956; Shimozawa, Kumakura, Hoshino & Ebine, 1971), notwithstanding the fact that the aromaticity decreases by annelation of the benzene ring (Cook & Forbes, 1968; Burnham & Cook, 1968). This suggests that there should be some contribution from the dipolar ionic form (*Ib*). X-ray analyses showed that the molecule of (*Ia*) is nearly planar (Hata, Shimanouchi & Sasada, 1969) and the planarity is maintained against steric hindrance in its derivatives (*Ic, d*) (Ibata, Shimanouchi & Sasada, 1973), whose spectra are similar.

On the other hand, the infrared and electronic spectra of 2,7-polymethylene-4,5-benzotropone (*II*) change markedly for the compounds with $n \leq 7$, where n is the number of methylene groups (Kloster-Jensen, Tarköy, Eschenmoser & Heilbronner, 1956). The dipole moment of (*II*) ($n=5$) is very low (Gäumann *et al.*, 1956), and the delocalization energy is about a half of that for (*Ic*) or (*II*) ($n=12$) (Schmid, Kloster-Jensen, Kováts & Heilbronner, 1956). From these facts it was deduced that the seven-membered ring is not planar because of the steric inhibition of benzotropylum resonance (*Ib*). The present structure determination of (*II*) ($n=5$) has been undertaken in order to give a structural chemical basis for this highly deformed 4,5-benzotropone.



(*Ia*) R = H
(*Ic*) R = CH_3
(*Id*) R = C_6H_5

(*Ib*)

(*II*)

Experimental

2,7-Pentamethylene-4,5-benzotropone [6,8-pentamethylene-7*H*-benzocyclohepten-7-one (*II*) ($n=5$)] was prepared from *o*-phthalaldehyde and cyclooctanone (Kloster-Jensen *et al.*, 1956). Colourless crystals were obtained from an ethanol solution. The unit-cell dimensions were determined from zero-layer Weissenberg photographs about the b and $[\bar{1}01]$ axes. Spacings of 63 reflexions in the range $\theta > 60^\circ$, calibrated with superimposed aluminum powder lines, were used for

Références

- BORNAND, J. D. & FESCHOTTE, P. (1972). *J. Less Common Met.* **29**, 84–91.
 GERMAIN, C., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–375.
 MEISSNER, H. & SCHUBERT, K. (1965). *Z. Metallkde*, **56**, 523–530.
 PHILIPPE, M. J., MALAMAN, B. & ROQUES, B. (1974). *C. R. Acad. Sci. Paris, Sér. C*, **278**, 1093.
 WACHTEL, E. & MAYER, J. (1967). *Z. Metallkde*, **58**, 761–767.

the least-squares refinement. The density of the crystal was measured by the flotation method in an aqueous solution of K_2HgI_4 . The crystal data are summarized in Table 1. The intensity data were collected on equi-inclination integrated Weissenberg photographs for the layers from 0 to 12 about the b axis and 0 to 9 about the $[\bar{1}01]$ axis, with Cu $K\alpha$ radiation. The cross sections of crystals used were 0.5×0.3 mm and 0.4×0.25 mm perpendicular to the b and $[\bar{1}01]$ rotation axes, respectively. The intensities were measured by a TV-densitometer (Izumi, 1971). Out of 2627 independent reflexions recorded (about 88.1% within the Cu $K\alpha$ sphere), 371 were too weak to be measured. Lorentz and polarization corrections were made as usual, but the absorption correction was omitted. The intensities of elongated and contracted reflexions on upper-layer photographs were corrected by a method proposed by Takenaka & Sasada (1973).

Table 1. Crystal data

Formula	$C_{16}H_{16}O$
M.W.	224.3
Crystal system	Monoclinic
Space group	$P2_1/n$
Systematic absences	$0k0$ for k odd, $h0l$ for $h+l$ odd
a	9.803 ± 0.002 Å
b	16.184 ± 0.007
c	7.802 ± 0.002
β	$90.39 \pm 0.02^\circ$
Unit-cell volume	1237.7 ± 0.7 Å ³
Density (calculated)	1.203 g cm ⁻³
Density (observed)	1.200
Number of molecules per unit cell	4
$F(000)$	480
μ (Cu $K\alpha$)	5.76 cm ⁻¹

Structure determination and refinement

The structure was solved by the symbolic addition procedure. A starting set was chosen as follows:

 Table 2. Final atomic coordinates ($\times 10^4$), temperature factors ($\times 10^4$ for B_{ij} 's) and their standard deviations (in parentheses)

The anisotropic temperature factors are expressed in the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	2108 (1)	3280 (1)	4749 (2)	111 (1)	51 (1)	251 (3)	35 (1)	-44 (3)	-36 (2)
C(1)	3076 (2)	2820 (1)	4685 (2)	93 (2)	37 (1)	163 (3)	-1 (2)	-10 (3)	-2 (2)
C(2)	4180 (2)	2821 (1)	5985 (2)	95 (2)	41 (1)	134 (2)	-5 (2)	4 (3)	-13 (2)
C(3)	4532 (2)	2120 (1)	6799 (2)	94 (2)	45 (1)	144 (3)	-4 (2)	-12 (3)	-4 (2)
C(4)	4000 (2)	1289 (1)	6527 (2)	88 (2)	41 (1)	163 (3)	11 (2)	19 (3)	4 (2)
C(5)	3500 (2)	984 (1)	4949 (2)	98 (2)	40 (1)	187 (3)	8 (2)	5 (4)	-19 (2)
C(6)	3490 (2)	1467 (1)	3360 (2)	126 (2)	45 (1)	157 (3)	4 (2)	-17 (4)	-34 (2)
C(7)	3350 (2)	2291 (1)	3189 (2)	106 (2)	46 (1)	145 (3)	5 (2)	-31 (3)	-14 (2)
C(8)	4095 (2)	732 (1)	7920 (2)	113 (2)	47 (1)	205 (3)	19 (2)	31 (4)	33 (3)
C(9)	3668 (2)	-71 (1)	7803 (3)	135 (2)	46 (1)	280 (4)	22 (2)	76 (5)	49 (3)
C(10)	3169 (2)	-365 (1)	6254 (3)	150 (3)	40 (1)	329 (5)	0 (2)	69 (6)	3 (3)
C(11)	3111 (2)	152 (1)	4849 (3)	136 (2)	42 (1)	260 (4)	-5 (2)	12 (5)	-29 (3)
C(12)	4883 (2)	3637 (1)	6176 (2)	121 (2)	45 (1)	180 (3)	-24 (2)	-22 (4)	-12 (3)
C(13)	5734 (2)	3854 (1)	4593 (3)	124 (2)	54 (1)	230 (4)	-35 (2)	10 (5)	20 (3)
C(14)	4975 (2)	4001 (1)	2871 (3)	175 (3)	52 (1)	220 (4)	-33 (3)	32 (5)	37 (3)
C(15)	4867 (3)	3281 (2)	1597 (3)	205 (3)	68 (1)	188 (4)	-29 (3)	108 (6)	12 (3)
C(16)	3546 (2)	2765 (1)	1556 (2)	183 (3)	60 (1)	144 (3)	-8 (3)	-19 (5)	8 (3)

h	k	l	$ E $	Sign
7	7	2	3.21	+
5	2	-8	3.12	+
4	11	-3	3.08	+
3	3	7	3.29	$A (+)$
5	7	4	2.94	$B (-)$
0	1	6	2.77	$C (+)$
5	2	-1	2.60	$D (+)$
2	2	-7	3.06	$E (-)$

At the end of the procedure all the symbols were reasonably given the signs as shown in the parentheses. The E map calculated with 170 reflexions with determined signs revealed the positions of all the non-hydrogen atoms, although the peak for C(13) was lower than spurious peaks. The atomic coordinates and temperature factors, first isotropic and then anisotropic, were refined by the block-diagonal matrix least-squares method until R was reduced to 0.096. The hydrogen atoms obtained from a difference map at this stage were included in the subsequent refinement. In the later stages of refinement, the following weighting scheme was used:

$$w = 1 \quad \text{for } 0 < |F_o| \leq k_1$$

$$w = (k_1/F_o)^2 \quad \text{for } |F_o| > k_1$$

$$w = k_2 \quad \text{for } |F_o| = 0,$$

where $k_1 = 7.0$ and $k_2 = 0.3$. After R became 0.072, 22 reflexions were excluded from the refinement because these seemed to suffer from secondary extinction. With new parameters, $k_1 = 10.0$ and $k_2 = 0.2$, four further cycles of the refinement gave an R of 0.058 for the observed reflexions ($R = 0.072$ with zero reflexions included). The weighted R value, $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$, was 0.072.* The shifts in

* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30700 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(3)	5264 (21)	2137 (12)	7735 (27)	3.4 (4)
H(6)	3594 (20)	1100 (12)	2263 (25)	3.3 (4)
H(8)	4520 (21)	970 (13)	9020 (25)	3.5 (4)
H(9)	3678 (24)	-467 (14)	8828 (29)	5.0 (6)
H(10)	2864 (23)	-965 (14)	6136 (27)	4.5 (5)
H(11)	2835 (24)	-71 (13)	3707 (27)	4.3 (5)
H(121)	5488 (22)	3583 (13)	7161 (27)	4.0 (5)
H(122)	4176 (19)	4107 (12)	6396 (23)	2.7 (4)
H(131)	6442 (21)	3417 (13)	4361 (26)	3.7 (5)
H(132)	6270 (21)	4364 (13)	4854 (26)	3.9 (5)
H(141)	5508 (25)	4447 (14)	2280 (31)	5.2 (6)
H(142)	4063 (23)	4251 (14)	3007 (27)	4.2 (5)
H(151)	5527 (28)	2820 (15)	1851 (34)	5.9 (6)
H(152)	4987 (26)	3532 (15)	399 (31)	5.4 (6)
H(161)	3568 (24)	2360 (14)	581 (30)	4.6 (5)
H(162)	2725 (22)	3129 (13)	1385 (27)	3.8 (5)

atomic parameters at the final cycle were smaller than 0.1σ for C and O and smaller than 0.7σ for H atoms. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are given in Table 2.

Thermal motion

The thermal ellipsoids of the atoms are shown in Fig. 1. It seems that the molecule as a whole undergoes a rigid-body libration. The results of the analysis of thermal motion are summarized in Tables 3 and 4. U tensors are referred to the three principal axes of the moment of inertia of the molecule. The translation and libration tensors, **T** and ω , of the rigid molecule were obtained from the observed U_{ij} 's by least-squares calculations. Except for U_{33} 's of peripheral atoms C(8), C(9), C(14) and C(15), agreement between observed and calculated U_{ij} 's is good. The corrected bond lengths for libration are shown in Fig. 3. Since the corrections are small (0.002 – 0.005 Å), the discussion is based on the uncorrected bond lengths.

Table 3. *R.m.s. amplitudes and directions of principal components of molecular translation and libration tensors*

R.m.s. amplitude	Direction cosines of principal tensor axes along inertial axes 1, 2 and 3 defined in Table 4		
	1	2	3
0.200 Å	0.0845	0.6607	0.7458
0.204	0.0635	-0.7503	0.6581
0.237	0.9944	-0.0082	-0.1053
2.57°	0.1679	0.9857	-0.0137
3.23	-0.0633	-0.0031	-0.9980
4.25	0.9838	-0.1684	-0.0618

The computations were carried out on a HITAC 8700 at Tokyo Institute of Technology and on a HITAC 8800 at the University of Tokyo. The programs in the *Universal Crystallographic Computation Program System* (1967) were used with some modifi-

Table 4. *Components of molecular inertial axes 1, 2 and 3 along the rectangular coordinate axes a, b and c**

	<i>l</i>	<i>m</i>	<i>n</i>
1	0.1468	0.9026	-0.4047
2	-0.3318	-0.3405	-0.8797
3	0.9318	-0.2635	-0.2495

The inertial axis 3 is almost parallel to the plane normal of the benzene ring. The axes 1 and 2 are almost parallel, respectively, to $C(2)\cdots C(7)$ and to the vector joining the mid-points of $C(9)$ – $C(10)$ and $C(4)$ – $C(5)$.

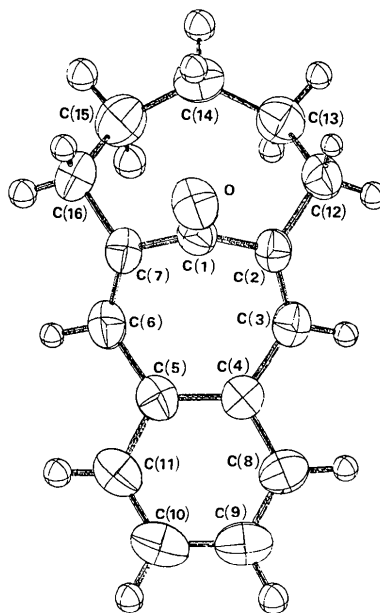
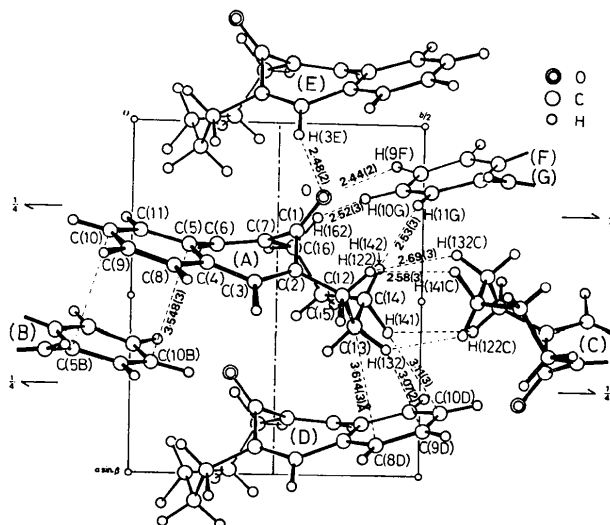


Fig. 1. Thermal ellipsoids at the 50% probability level for C and O and 20% for H, viewed along the plane normal of the benzene ring.

Fig. 2. Arrangement of molecules in the crystal viewed along the *c* axis. Several short intermolecular distances (Å) are shown. Symmetry codes: (A) x, y, z , (B) $1-x, \bar{y}, 1-z$, (C) $1-x, 1-y, 1-z$, (D) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$, (E) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$, (F) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$, and (G) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

cations. The programs *TDRW* for data reduction, *TLSU* for the determination of the unit-cell dimensions, and *DEAM* for plotting the thermal ellipsoids, written by Takenaka, were also used.

Results and discussion

Crystal structure

The arrangement of molecules in the crystal viewed along the *c* axis is shown in Fig. 2. Main intermolecular contacts are π - π contacts between benzene rings (*A* and *B*), contacts between methylene bridges (*A* and *C*), and contacts between the aliphatic part of *A* and the aromatic part of *D*. The distances between O and H(3*E*) and between O and H(9*F*) are 2.48 and 2.44 Å, respectively, which are slightly shorter than the sum of the van der Waals radii. The direction of O...H deviates from the assumed direction of the lobe of the lone-pair electron on O by 17° for O...H(3*E*) and by 26° for O...H(9*F*). The other contacts are all longer than the sum of the van der Waals radii. From such a packing feature, it may be assumed that the conformation of the molecule is not affected seriously by intermolecular forces.

Molecular geometry

The bond lengths and angles are shown in Fig. 3. It appears that the molecule has an approximate mirror plane through O, C(1), C(14), H(141) and H(142). Therefore, the average values of the chemically equivalent bond lengths and angles, shown in Fig. 4(a), will be used in the following discussion.

Seven-membered ring

The seven-membered ring adopts a boat form as shown in Fig. 4(b). The bow plane (plane I in Table 5) and the stern plane (plane III) make dihedral angles of $\delta_1 = 51.3^\circ$ and $\delta_2 = 24.3^\circ$ with the bottom plane (plane II), respectively. These angles are the largest among those in related compounds as shown in Table 6, and are close to the corresponding angles in the cycloheptatriene moiety of thujic acid (Davis & Tulinsky, 1966). The boat shape of the seven-membered ring indicates that the tension of the short methylene bridge overcomes the tendency of the seven-membered ring to be planar. In consequence, the angles C(1)C(2)-C(3), C(2)C(1)C(7) and C(1)C(7)C(6) are reduced, to almost strain-free values, by about 9° with respect to the corresponding values in 4,5-benzotropone (*Ia*)

Table 5. *Least-squares planes and interplanar angles*

(a) Coefficients for weighted least-squares planes, $lX + mY + nZ + d = 0$, and the deviations of atoms from these planes. E.s.d.'s ($\times 10^4$ except for *d*, $\times 10^3$ for *d*)† are shown in parentheses. *X*, *Y* and *Z* are orthogonal coordinates in Å along *a*, *b* and *c**. Weights used are reciprocals of e.s.d.'s squared.

Plane	<i>l</i>	<i>m</i>	<i>n</i>	<i>d</i>
I	-0.4359 (21)	-0.7716 (14)	0.4634 (9)	3.132 (6)
II	-0.9270 (3)	-0.0647 (13)	0.3694 (7)	2.344 (4)
III	-0.9192 (4)	0.3287 (13)	0.2171 (9)	1.775 (5)
IV	-0.9286 (3)	0.2596 (8)	0.2652 (8)	1.726 (5)
V	-0.9312 (4)	0.2435 (14)	0.2714 (10)	1.732 (5)
VI	-0.9251 (4)	0.2801 (17)	0.2566 (12)	1.758 (6)
VII	-0.6728 (14)	0.1971 (26)	0.7131 (8)	-1.494 (18)
VIII	0.9823 (3)	0.1150 (17)	0.1478 (28)	-4.003 (5)

† Calculated by the methods proposed by Waser (1973) and Waser, Marsh og Cordes (1973).

Table 5 (cont.)

	Plane I	Plane II	Plane III	Plane IV	Plane V	Plane VI	Plane VII	Plane VIII
O	-0.137	1.478	-	-	-	-	0.821	-0.840
C(1)	0.000*	0.627	-	-	-	-	0.000*	0.000*
C(2)	0.000*	0.004*	0.552	0.374	-	-	0.000*	-
C(3)	1.022	-0.004*	0.003*	-0.069	-0.097	-	0.000*	-
C(4)	-	0.487	-0.007*	0.009*	0.003*	0.053	-0.067	-
C(5)	-	0.511	0.007*	0.002*	-0.003*	0.045	-	0.095
C(6)	1.031	0.004*	-0.004*	-0.123	-0.148	-	-	0.000*
C(7)	0.000*	-0.005*	0.531	0.315	-	-	-	0.000*
C(8)	-	-	-0.146	-0.017*	-0.002*	0.000*	-	-
C(9)	-	-	-0.209	0.010*	0.046	-0.001*	-	-
C(10)	-	-	-0.186	0.012*	0.050	0.001*	-	-
C(11)	-	-	-0.103	-0.015*	0.002*	0.000*	-	-
C(12)	-	-	-	-	-	-	-0.096	-
C(16)	-	-	-	-	-	-	-	0.097

(b) Interplanar angles (°). E.s.d.'s ($\times 10$)† are shown in parentheses.

Plane	II	III	IV	V	VI	VII	VIII
I	51.3 (2)	75.7 (2)	70.9 (2)	69.9 (2)	72.2 (2)	61.9 (2)	63.4 (2)
II	-	24.3 (1)	19.6 (1)	18.6 (1)	20.9 (1)	29.0 (1)	30.3 (2)
III	-	-	4.9 (1)	5.8 (1)	3.6 (1)	33.1 (1)	33.6 (1)
IV	-	-	-	1.0 (1)	1.3 (1)	30.1 (1)	32.5 (1)
V	-	-	-	-	2.3 (2)	29.8 (1)	32.2 (1)
VI	-	-	-	-	-	30.6 (1)	33.0 (1)
VII	-	-	-	-	-	-	57.8 (2)

* Atoms defining the plane.

† Calculated by the methods proposed by Waser (1973) and Waser, Marsh & Cordes (1973).

Table 6. Comparison of planarity of seven-membered rings

Compound	Boat angles (°)*			Reference†
	δ_1	δ_2	δ_3	
2,7-Pentamethylene-4,5-benzotropone (II) ($n=5$)	51.3	24.3	6.5 (2)‡	<i>a</i>
2,7-Dimethyl-4,5-benzotropone (Ic)	11.5	4.7	2.5	<i>b</i>
2,7-Diphenyl-4,5-benzotropone (Id), mol. 1	7.0	2.8	1.0	<i>b</i>
mol. 2	3.7	1.7	2.0	<i>b</i>
4,5-Benzotropone (Ia)	6.1	2.9	0.3	<i>c</i>
Dibenzo[<i>b,f</i>]tropone	37	20	6	<i>d</i>
5-Chloro-2,3-benzotropone	12	3	3	<i>e</i>
5,7-Dibromo-2,3-benzotropone	6	1	1	<i>e</i>
Tricarbonyltropone chromium	28.5	4.4	10	<i>f</i>
1,6-Dimethyl-8,8-dicyanoheptafulvene	45.3	20.1	4.0	<i>g</i>
1-Isopropyl-8,8-dicyanoheptafulvene	37.3	19.5	5.6	<i>h</i>
Heptafulvalene	24.7	15.7	6.7	<i>i</i>
1,2,3,4-Tetrachlorobenzo[<i>g</i>]sesquifulvalene	14	6	10	<i>j</i>
Tropolone	2.4	1.2	0.8	<i>k</i>
Thujic acid	47.9	24.4	—	<i>l</i>

* See Fig. 4(b).

† (*a*) Present work. (*b*) Iyata *et al.* (1973). (*c*) Iyata *et al.* (1974). (*d*) Shimanouchi *et al.* (1974). (*e*) Iyata *et al.* (1972). (*f*) Barrow & Mills (1971). (*g*) Shimanouchi, Sasada, Kabuto & Kitahara (1974*a*). (*h*) Shimanouchi, Sasada, Kabuto & Kitahara (1974*b*). (*i*) Thomas & Coppens (1972). (*j*) Nishi, Sasada, Ashida & Kakudo (1966). (*k*) Shimanouchi & Sasada (1973). (*l*) Davis & Tulinsky (1966).

‡ E.s.d. ($\times 10$) of δ_3 was calculated by the method proposed by Waser *et al.* (1973).

(Iyata, Hata, Shimanouchi & Sasada, 1974). At the same time, the presumed stabilization results from the strengthened interaction between $p\pi$ -electrons on C(2) and C(7). The overlap integral between them is calculated to be 0.065 (Mulliken, Rieke, Orloff & Orloff, 1949), which is comparable to that in thujic acid (0.072) (Davis & Tulinsky, 1966), where an appreciable interaction is expected.

Definite bond alternation is observed in the seven-membered ring. The C(1)–C(2) bond length (1.476 Å) is regarded as a typical C(sp^2)–C(sp^2) single-bond length (Stoicheff, 1962; Dewar & Schmeising, 1960). The C=O length (1.207 Å) and CCC angle (114.1°) are in good agreement with those in aliphatic ketones, such as 1.210 Å and 116.2° in cyclohexane-1,4-dione (Mossel & Romers, 1964). The present length is also close to the value 1.205 Å proposed by Hahn (1957). These features indicate that there is no appreciable contribution from the dipolar ionic form (Ib). This is compatible with a high C=O stretching frequency (1685 cm^{-1} in $CHCl_3$) (Kloster-Jensen *et al.*, 1956), diminution of the ultraviolet absorption in the longer wavelength region (Kloster-Jensen *et al.*, 1956), low dipole moment (3.09 D) (Gäumann *et al.*, 1956), and small delocalization energy (48.7 kcal mol $^{-1}$) which is about a half that for (Ic) (82.7 kcal mol $^{-1}$) and (II) ($n=12$) (84.6 kcal mol $^{-1}$) (Schmid *et al.*, 1956).

On the other hand, the length of the formal single bond C(3)–C(4) (1.462 Å) is significantly shorter than that of C(1)–C(2). This may be due to some π -electron delocalization between C(2)=C(3) and the benzene ring through the C(3)–C(4) bond. In fact, the torsion angles

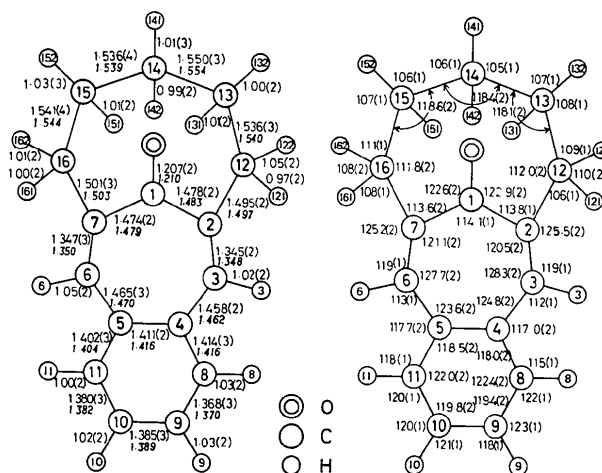


Fig. 3. Bond lengths (Å) and angles (°). The corresponding e.s.d.'s, given in parentheses, refer to the last decimal positions. Bond lengths corrected for libration are shown in italics. Bond angles which are not shown in the figure are: C(2)C(12)H(122) = 111 (1), C(13)C(12)H(121) = 109 (1), C(12)C(13)H(131) = 111 (1), C(14)C(13)H(131) = 106 (1), H(131)C(13)H(132) = 105 (2), C(13)C(14)H(142) = 114 (1), C(15)C(14)H(142) = 109 (1), H(141)C(14)H(142) = 103 (2), C(14)C(15)H(151) = 113 (2), C(16)C(15)H(151) = 98 (2), H(151)C(15)H(152) = 113 (2), C(7)C(16)H(162) = 108 (1), and C(15)C(16)H(161) = 110 (1)°.

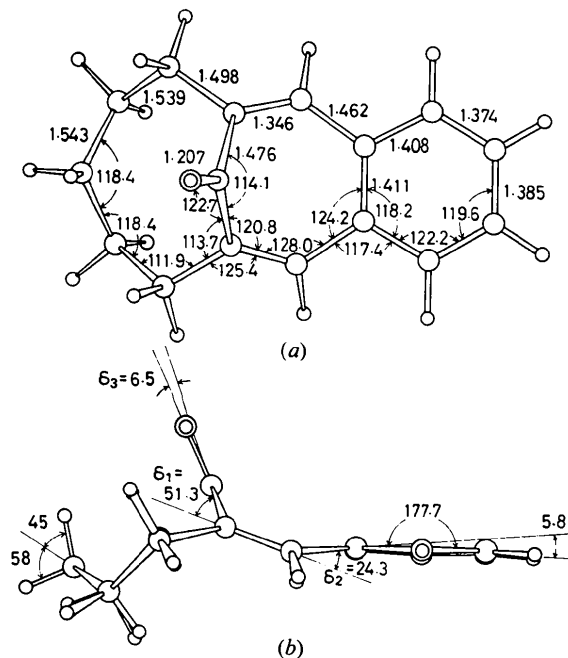
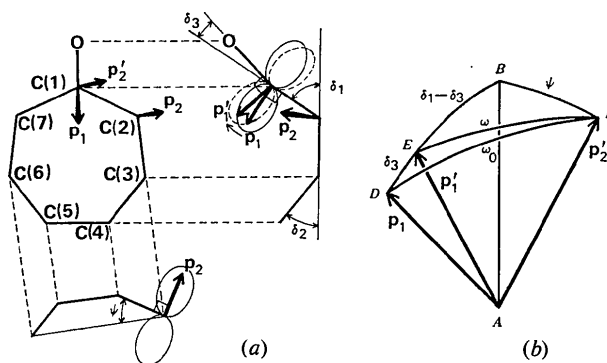
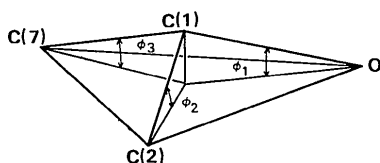


Fig. 4. (a) The average values of bond lengths (Å) and angles (°). (b) Side view along the line C(7)···C(2).

Table 7. Torsion angles and their standard deviations

	Angles	E.s.d.'s*	Averages
OC(1)C(2)C(3)	125.9°	0.2°	125.1°
OC(1)C(7)C(6)	-124.4	0.2	
OC(1)C(2)C(12)	-58.2	0.2	58.9
OC(1)C(7)C(16)	59.7	0.2	
C(7)C(1)C(2)C(3)	-61.9	0.2	62.6
C(2)C(1)C(7)C(6)	63.4	0.2	
C(7)C(1)C(2)C(12)	114.1	0.2	113.4
C(2)C(1)C(7)C(16)	-112.6	0.2	
C(1)C(2)C(3)C(4)	3.3	0.3	4.0
C(1)C(7)C(6)C(5)	-4.7	0.3	
C(2)C(3)C(4)C(5)	30.0	0.3	30.7
C(7)C(6)C(5)C(4)	-31.4	0.3	
C(3)C(4)C(5)C(6)	1.8	0.3	-
C(3)C(2)C(12)C(13)	106.7	0.2	
C(6)C(7)C(16)C(15)	-108.0	0.2	107.4
C(1)C(2)C(12)C(13)	-69.1	0.2	
C(1)C(7)C(16)C(15)	67.7	0.2	68.4
C(2)C(12)C(13)C(14)	65.0	0.2	
C(7)C(16)C(15)C(14)	-66.0	0.3	65.5
C(12)C(13)C(14)C(15)	-96.5	0.2	
C(16)C(15)C(14)C(13)	97.9	0.3	97.2
C(2)C(3)C(4)C(8)	-155.2	0.2	
C(7)C(6)C(5)C(11)	154.8	0.2	155.0
C(3)C(4)C(5)C(11)	175.4	0.2	
C(6)C(5)C(4)C(8)	-173.0	0.2	174.2
C(8)C(4)C(5)C(11)	0.7	0.3	
C(3)C(4)C(8)C(9)	-178.0	0.2	177.0
C(6)C(5)C(11)C(10)	175.9	0.2	
C(5)C(4)C(8)C(9)	-2.8	0.3	2.3
C(4)C(5)C(11)C(10)	1.9	0.3	
C(4)C(8)C(9)C(10)	2.4	0.3	2.4
C(5)C(11)C(10)C(9)	-2.3	0.4	
C(8)C(9)C(10)C(11)	0.2	0.3	-

* Calculated by the method proposed by Waser, Marsh & Cordes (1973).

Fig. 5. Relative orientation of the $p\pi$ orbitals on C(1) and C(2).Fig. 6. Definition of ϕ_j 's.

of C(2)C(3)C(4)C(5) (30.7°) and C(2)C(3)C(4)C(8) (25.0°) are considerably smaller than that of OC(1)-C(2)C(3) (54.9°), the C(2)=C(3) bond (1.346 \AA) is slightly longer than the C=C length in ethylene (1.337 \AA) (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965), and the torsion angle C(1)C(2)C(3)C(4) is 4.0° . The torsion angles in the molecule are listed in Table 7.

Out-of-plane bending of the C=O bond and the related phenomena

It is noteworthy that the C=O bond makes an angle of 6.5° (δ_3) with plane I [Fig. 4(b)]. A similar feature is found in all benzotropones and other unsaturated seven-membered ring compounds so far analysed, as shown in Table 6.* Let us consider the overlap of π -electrons between C(1) and C(2). In Fig. 5(a), \mathbf{p}_1 and \mathbf{p}_2 are the unit vectors representing the $p\pi$ orbitals on C(1) and C(2), respectively. The vector \mathbf{p}_1 is perpendicular to plane I (bow plane) and \mathbf{p}_2 to plane VII [C(1), C(2) and C(3)]. The vector \mathbf{p}_2' through C(1) is parallel to \mathbf{p}_2 . The relation between them can be adequately illustrated by a spherical triangle in Fig. 5(b). AB is parallel to the normal of the bottom plane. Since the planes ABD and ADF are perpendicular to the bow plane and the former bisects the angle C(2)-C(1)C(7), the angle D is $\frac{1}{2}\{\pi - \angle C(2)C(1)C(7)\}$. If the C=O bond is coplanar with the bow plane, the overlap integral S_{12}^0 is $S_{\pi\pi} \cos \omega_0$, where $S_{\pi\pi}$ is the overlap integral between parallel $2p$ orbitals. If the C=O bond bends by δ_3 , the $p\pi$ lobe is displaced to \mathbf{p}_1' , and the overlap integral S_{12} is $S_{\pi\pi} \cos \omega$, where

$$\cos \omega = \cos \delta_3 \cos \omega_0 + \sin \delta_3 \sin \omega_0 \cos D. \quad (1)$$

In the present molecule, $D = 33.0^\circ$ and $\omega_0 = 62.6^\circ$. Since $\cos \delta_3 \approx 1$ and the second term in equation (1) is positive, $\cos \omega > \cos \omega_0$. Hence, the overlap of π -electrons is partially recovered by the C=O bending. An approximate estimation of the energy associated with the bending was made by the use of a potential energy function, $E = -2E_t + E_b$. The first term is due to the torsion of the two C(sp^2)-C(sp^2) bonds, C(1)-C(2) and C(1)-C(7), (Allinger & Sprague, 1973), as

$$E_t = 54 \cdot 2 p_{12}^2 \cos^2 \omega + 0 \cdot 5(1 + \cos \omega), \quad (2)$$

where the bond order p_{12} is calculated by a linear bond order-bond length relationship, $r_{12} = 1.525 - 0.191 p_{12}$ (Allinger & Graham, 1973). The second comes from the out-of-plane bending of exocyclic bonds (Allinger, Tribble & Miller, 1972), as

$$E_b = \sum_{j=1}^3 k(\varphi_j^2 + f\varphi_j^3), \quad (3)$$

where k and f are the out-of-plane bending constant and the cubic bending constant, respectively, and the

* Bürgi, Dunitz & Shefter (1974) reported that the C=O bending is observed in the $O \cdots C=O$ contact shorter than 3 \AA . In the present case, however, there is no such contact in the crystal.

φ_j 's are defined as shown in Fig. 6. In the present case, $k=0.80$ mdynÅrad⁻² and $f=0.40$ rad⁻¹. The E vs. δ_3 curve obtained has a minimum at $\delta_3=4.3^\circ$, which is comparable with the observed value of 6.5° . For dibenzo[*b,f*]tropone a minimum is at $\delta_3=2.3^\circ$ as compared with the observed value of 5.7° .

It should be added that the same reasoning is applicable to the bending of the bonds C(4)–C(8) and C(5)–C(11) with respect to the stern plane [Fig. 4(b)].

The benzene ring is slightly but significantly distorted to a boat shape as shown in Fig. 4(b), the bow and stern being C(8) and C(11), respectively. The out-of-plane bending of the bonds C(4)–C(8) and C(5)–C(11) necessarily gives rise to their twist, but because of the resistance of the bonds to twisting, the remaining strain is transmitted to C(8)–C(9) and C(10)–C(11), resulting in a shallow boat form.

In-plane deformation in the benzene ring

There is a slight but significant fluctuation in bond lengths and angles in the benzene ring. The bonds C(4)–C(5), C(4)–C(8) and C(5)–C(11) are longer than C(8)–C(9), C(9)–C(10) and C(10)–C(11), while the angles C(5)C(4)C(8) and C(4)C(5)C(11) are smaller than C(4)C(8)C(9) and C(5)C(11)C(10). The average differences between longer and shorter bond lengths and between larger and smaller angles are 0.032 Å and 4.0°, respectively. The same feature is observed in other related compounds; the differences are 0.034 Å and 3.6° in (Ia) (Ibata *et al.*, 1974), 0.027 Å and 3.9° in (Ic), 0.023 Å and 3.6° in (Id) (Ibata *et al.*, 1973), 0.027 Å and 3° in 5-chloro-2,3-benzotropone (Ibata, Hata, Shimanouchi & Sasada, 1972), 0.025 Å and 2.5° in dibenzo[*b,f*]tropone (Shimanouchi, Hata & Sasada, 1974), 0.037 Å and 3.8° in 2-methoxy-4-hydroxy-5-oxobenz[*f*]azepine (Denne & Mackay, 1972), and 0.032 Å and 4.3° in 5*H*-10,11-dioxodihydrodibenz[*b,f*]azepine (Denne & Mackay, 1970). The bond angle compression of C(5)C(4)C(8) and C(4)C(5)C(11) due to the fusion with the seven-membered ring would be propagated to make all the lengths and angles as equal as possible. This might induce the observed fluctuation.

Eight-membered ring

The methylene bridge together with the atoms C(2), C(1) and C(7) forms an eight-membered ring. The ring adopts a stretched crown, chair-chair (Anet, 1971) conformation [Fig. 4(b)], although Kloster-Jensen *et al.* (1956) assumed the boat-chair form for it. The angles C(12)C(13)C(14) (118.4°) and C(13)C(14)C(15) (118.4°) are larger than those in normal paraffins (average value, 112.5°) (Bonham, Bartell & Kohl, 1959) and those in cyclooctane derivatives (116.8° and 116.0°) (Bürgi & Dunitz, 1968; Dobler, Dunitz & Mugnoli, 1966). The bond length of C(2)–C(12) (1.498 Å) is slightly shorter than the C(sp²)–C(sp³) bond length (1.515 Å) (Dewar & Schmeising, 1960). The bonds C(2)–C(12) and C(7)–C(16) are bent below

planes VII and VIII, respectively, by 3.7°. While the torsion angle C(2)C(12)C(13)C(14) (65.5°) is close to 60°, a fairly large angle, 97.2°, is observed for C(12)–C(13)C(14)C(15), which results in a short contact between H(132) and H(141) (2.14 Å). The hydrogen atoms H(141) and H(142) deviate unsymmetrically from the plane C(13)C(14)C(15) [Fig. 4(b)], indicating the repulsion between H(142) and C(1). In fact, the H(142)···C(1) distance (2.84 Å) is slightly shorter than the sum of the van der Waals radii. Although the out-of-plane deformation of the seven-membered ring system relieves much of the strain imposed by the short methylene bridge, the remaining strain would give rise to several of the features mentioned above.

A comment on the estimation of the standard deviations of dihedral angles

Although the deviations of atoms from planes II and III are small, these planes are non-planar on the basis of the χ^2 test. Since it is reasonable to assume that these structural units are planar, the observed non-planarity seems to be due to the underestimation of the standard deviations in positional parameters and/or the distortion by the crystalline field effect. In such circumstances, it is inadequate to use the standard deviations of the pertinent dihedral angles in Table 5 in order to discuss the significance of the foldings and the out-of-plane bendings mentioned above. The χ^2 value was brought to a non-significant level by the multiplication of the e.s.d.'s in positional parameters by a factor $k=(\chi^2/\chi_{0.05}^2)^{1/2}$, because the correction for the crystalline field effect has not been evaluated. The multiplication factors were calculated to be 1.6 and 2.1 for planes II and III, respectively. The maximum value was taken and the modified standard deviations of the dihedral angles, which probably correspond to the upper limit, are listed below:

Plane or bond	Plane	Dihedral angles or bending angles	Modified e.s.d.'s
C=O	I	6.49° (δ_3)	0.46°
I	II	51.31 (δ_1)	0.38
II	III	24.35 (δ_2)	0.29
III	V	5.83	0.29
V	VI	2.29	0.36
C(2)–C(12)	VII	3.68	0.48
C(7)–C(16)	VIII	3.72	0.55

Even if the modified e.s.d.'s are used, the folding between the planes and the bending of the bonds are significant.

The authors wish to thank Dr A. Takenaka for the use of the modified version of the program *DEAM*.

References

- ALLINGER, N. L. & GRAHAM, J. C. (1973). *J. Amer. Chem. Soc.* **95**, 2523–2526.

- ALLINGER, N. L. & SPRAGUE, J. T. (1973). *J. Amer. Chem. Soc.* **95**, 3893–3907.
- ALLINGER, N. L., TRIBBLE, M. T. & MILLER, M. A. (1972). *Tetrahedron*, **28**, 1173–1190.
- ANET, F. A. L. (1971). In *Conformational Analysis, Scope and Present Limitations*, edited by G. CHIURDOGLU, pp. 15–29. New York & London: Academic Press.
- BARROW, M. J. & MILLS, O. S. (1971). *Chem. Commun.* p. 119.
- BARTELL, L. S., ROTH, E. A., HOLLOWELL, C. D., KUCHITSU, K. & YOUNG, J. E. JR (1965). *J. Chem. Phys.* **42**, 2683–2686.
- BONHAM, R. A., BARTELL, L. S. & KOHL, D. A. (1959). *J. Amer. Chem. Soc.* **81**, 4765–4769.
- BÜRGI, H. B. & DUNITZ, J. D. (1968). *Helv. Chim. Acta*, **51**, 1514–1526.
- BÜRGI, H. B., DUNITZ, J. D. & SHEFTER, E. (1974). *Acta Cryst.* **B30**, 1517–1527.
- BURNHAM, D. R. & COOK, M. J. (1968). *Tetrahedron Lett.* p. 3771.
- COOK, M. J. & FORBES, E. J. (1968). *Tetrahedron*, **24**, 4501–4508.
- DAVIS, R. E. & TULINSKY, A. (1966). *J. Amer. Chem. Soc.* **88**, 4583–4588.
- DENNE, W. A. & MACKAY, M. F. (1970). *Tetrahedron*, **26**, 4435–4442.
- DENNE, W. A. & MACKAY, M. F. (1972). *Tetrahedron*, **28**, 1795–1802.
- DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96–120.
- DOBLER, M., DUNITZ, J. D. & MUGNOLI, A. (1966). *Helv. Chim. Acta*, **49**, 2492–2502.
- GÄUMANN, T., SCHMID, R. W. & HEILBRONNER, E. (1956). *Helv. Chim. Acta*, **39**, 1985–1993.
- HAHN, T. (1957). *Z. Kristallogr.* **109**, 438–466.
- HATA, T., SHIMANOUCI, H. & SASADA, Y. (1969). *Tetrahedron Lett.* p. 753.
- IBATA, K., HATA, T., SHIMANOUCI, H. & SASADA, Y. (1972). *Chem. Commun.* p. 339.
- IBATA, K., HATA, T., SHIMANOUCI, H. & SASADA, Y. (1974). To be published.
- IBATA, K., SHIMANOUCI, H. & SASADA, Y. (1973). *Chem. Lett.* p. 269.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
- IZUMI, T. (1971). *Jap. J. Appl. Phys.* **10**, 1724–1728.
- KLOSTER-JENSEN, E., TARKÖY, N., ESCHENMOSE, A. & HEILBRONNER, E. (1956). *Helv. Chim. Acta*, **39**, 786–805.
- MOSSSEL, A. & ROMERS, C. (1964). *Acta Cryst.* **17**, 1217–1223.
- MULLIKEN, R. S., RIEKE, C. A., ORLOFF, D. & ORLOFF, H. (1949). *J. Chem. Phys.* **17**, 1248–1267.
- NISHI, Y., SASADA, Y., ASHIDA, T. & KAKUDO, M. (1966). *Bull. Chem. Soc. Japan*, **39**, 818–826.
- SCHMID, R. W., KLOSTER-JENSEN, E., KOVÁTS, E. & HEILBRONNER, E. (1956). *Helv. Chim. Acta*, **39**, 806–812.
- SHIMANOUCI, H., HATA, T. & SASADA, Y. (1974). To be published.
- SHIMANOUCI, H. & SASADA, Y. (1973). *Acta Cryst.* **B29**, 81–90.
- SHIMANOUCI, H., SASADA, Y., KABUTO, C. & KITAHARA, Y. (1974a). *Acta Cryst.* **B30**, 1267–1273.
- SHIMANOUCI, H., SASADA, Y., KABUTO, C. & KITAHARA, Y. (1974b). *Acta Cryst.* **B30**, 1273–1277.
- SHIMOZAWA, T., KUMAKURA, S., HOSHINO, M. & EBINE, S. (1971). *Bull. Chem. Soc. Japan*, **44**, 565–566.
- STOICHEFF, B. P. (1962). *Tetrahedron*, **17**, 135–145.
- TAKENAKA, A. & SASADA, Y. (1973). Annual Meeting of the Crystallographic Society of Japan at Osaka, Abstract, p. 27.
- THOMAS, R. & COPPENS, P. (1972). *Acta Cryst.* **B28**, 1800–1806.
- Universal Crystallographic Computation Program System* (1967). Edited by T. SAKURAI. Crystallographic Society of Japan.
- WASER, J. (1973). *Acta Cryst.* **A29**, 621–631.
- WASER, J., MARSH, R. E. & CORDES, A. W. (1973). *Acta Cryst.* **B29**, 2703–2708.

Acta Cryst. (1975). **B31**, 489

Structural Chemistry of N(7)-Substituted Purines: The Crystal and Molecular Structure of 7-Methylxanthine Hydrochloride Monohydrate

BY THOMAS J. KISTENMACHER AND THEOPHILUS SORRELL

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, U.S.A.

(Received 25 July 1974; accepted 27 September 1974)

7-Methylxanthine hydrochloride monohydrate, $C_6N_4O_2H_6 \cdot HCl \cdot H_2O$, crystallizes in the monoclinic system, systematic absences $0k0$, $k=2n+1$ and $h0l$, $l=2n+1$ consistent with the space group $P2_1/c$, with crystal data: $a=7.047$ (1), $b=8.630$ (3), $c=15.000$ (7) Å, $\beta=91.09$ (3)°, $V=912.1$ Å³, $D_m=1.59$ (1), D_c (four formula units per unit cell) = 1.61 g cm⁻³, $\mu(\text{Mo } K\alpha)=4.1$ cm⁻¹. Intensities for 2111 independent reflections were collected by counter methods. Full-matrix least-squares refinement has led to final unweighted and weighted R values of 0.065 and 0.046, respectively. The crystal structure contains an extensive array of hydrogen bonds and some stacking of the pyrimidine rings of the substituted xanthine moieties.

Introduction

The crystal structure of 7-methylxanthine hydrochloride monohydrate was undertaken in order to establish

that methylation of the xanthine ligand in the complex [bis(dimethylglyoximato)(xanthinato)(tri-*n*-butylphosphine)cobalt(III)] had taken place exclusively at the N(7) position. The analysis also forms an integral