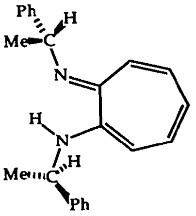
troponeimine ring with bond alterations consistent with the following tautomer:



The amino proton on N(1) is intramolecularly hydrogen bonded to the imino nitrogen atom N(2), the (N1)H···N(2) distance and N(1)—H(1N)···N(2) angle being 1·98 (4) Å and 116 (3)°, respectively (Fig. 1). These results may be contrasted with those reported previously for the structure determination of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene, in which C_2 symmetry was observed (Goldstein & Trueblood, 1967). Another important feature of H(CHIRAMT) is the positioning of hydrogen atoms H(21) and H(31) toward the tropone ring hydrogens on C(12) and C(16). This steric locking of the conformation may be of significance in orienting the phenyl and methyl groups in the transition state responsible for the chiral induction observed in the catalytic enantioselective conjugate addition reaction.

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Structures of (±)-*trans*-4-(2,3-Dimethoxyphenyl)- (I) and (+)-*trans*-4-(4-Methylphenyl)-2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]-[1]benzopyran-5-one (II)

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Abstract. Derivatives of 2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one. (I) Racemic *trans*-2-hydroxy-4-(2,3-dimethoxyphenyl), $C_{21}H_{20}O_6$, $M_r = 368·40$, monoclinic, $C2/c$, $a = 19·403\ (7)$, $b = 10·636\ (8)$, $c = 21·456\ (13)$ Å, $\beta = 123·94\ (5)°$, $V = 3673·8\ (85)$ Å^3, $Z = 8$, $D_x = 1·33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71078 Å, $\mu = 0·913$ cm^{-1}, $F(000) = 1552$, $T = 295$ K, final $R = 0·056$ for 2463 observations [$I \geq 2\sigma(I)$]. Molecules are hydrogen bonded between hydroxyls and coumarin carbonyls, O···O 2·812 (3) Å. The dihydropyran ring is in the *d,e*-diplanar conformation. (II) Resolved (2*R*,4*R*)-(+)-*trans*-2-hydroxy-4-(4-methylphenyl), $C_{20}H_{18}O_4$, $M_r = 322·36$, orthorhombic, $P2_12_12_1$, $a = 10·578\ (4)$, $b = 10·450\ (5)$, $c = 14·803\ (7)$ Å, $V = 1636·4\ (22)$ Å^3, $Z = 4$, $D_x = 1·31$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71078 Å, $\mu = 0·540$ cm^{-1}, $F(000) = 680$, $T = 294$ K, final $R = 0·044$ for 1580 observations [$I \geq 3\sigma(I)$]. Molecules are hydrogen bonded along a screw axis between hydroxyls and coumarin carbonyls, O···O 2·746 (3) Å. The dihydropyran ring is a nearly undistorted half-chair.

Introduction. Warfarin is a widely used anticoagulant agent. It and its derivatives crystallize as cyclic hemiketals containing a dihydropyran ring, which has been found to display a range of conformations. As part of a series of crystallographic studies on

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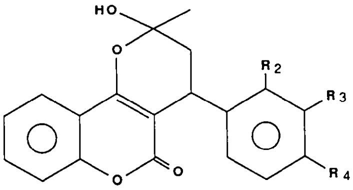
warfarin analogs aimed at exploring the shapes of the embedded dihydropyran, this contribution describes the structures of two substituted 4-aryl derivatives of 2-hydroxy-2-methyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one.



(I) $R_2 = R_3 = OCH_3$ $R_4 = H$
(II) $R_2 = R_3 = H$ $R_4 = CH_3$

Experimental. The reaction between *α*,*β*-unsaturated ketones and 4-hydroxycoumarin in a modified Michael addition (Bush & Trager, 1983) provides a simple route to warfarin derivatives. 2′,3′-Dimethoxywarfarin (I) was crystallized from acetone:water as colorless prisms, m.p. 467–468 K. 4′-Methylwarfarin (II) was resolved through its quinidine salts (West, Preis, Schroeder & Link, 1961), and the isomer from the more soluble diastereomeric salt was crystallized from acetone:water as colorless prisms, m.p. 477–478 K; $[\alpha]_D^{25} = +137\,(5)°$, 1·2 g 100 mL^{-1} (0·5 *M* NaOH). Crystallographic specimens: (I) 0·28 × 0·26 × 0·21 mm, (II) 0·6 × 0·35 × 0·35 mm were chosen for data collection on a CAD-4 diffractometer. Unit-cell dimensions were determined from the setting angles of 25 reflections with $30 \le 2\theta \le 35°$. Intensities were recorded to $2\theta = 56°$; *h*: 0–27, *k*: 0–14, *l*: −30 to 24 for (I) and *h*: 0 − 13, *k*: 0 − 13, *l*: 0 − 19 for (II) using variable-speed *θ*–2*θ* scans. Three standard intensities monitored every 3 h of exposure time showed variations of +2·4 (2·7)% and +2·2 (12·5)%, for (I) and (II) respectively, over the course of data collection; no correction for deterioration was made. The unique data [4498 (I), 2234 (II)] were corrected for coincidence and polarization. Symmetry-equivalent data for (I) were averaged [agreement on (I): 5·8%]. An extinction coefficient of the form proposed by Zachariasen (1963) was applied and refined for (II): $g = 3{\cdot}0\,(15) \times 10^{-7}$.

Structures were discovered with *MULTAN* (Germain, Main & Woolfson, 1971). Non-H-atom positions and their $U_{\rm iso}$'s were refined by full-matrix least squares (on *F*) minimizing $\sum w(|F_o|-|F_c|)^2$, then with their U_{ij}'s. Except for the hydroxyl H's, H-atom positions were calculated and placed 1·0 Å from their attached atom and assigned *B*'s approximately 1·3 times the $B_{\rm eq}$'s of the adjacent carbon; they were not refined. Scattering factors were from *International Tables for X-ray Crystallography* (1974) except for H (Stewart, Davidson & Simpson, 1965). Final agreement factors for (I): $R = 0{\cdot}056$, $wR = 0{\cdot}069$,

Table 1. *Positions and B_{eq}'s for* (I), *with e.s.d.'s in parentheses*

	x	*y*	*z*	$B_{\rm eq}$(Å^2)
O1	0·9142 (1)	0·4073 (2)	0·26744 (9)	3·91 (5)
O2	0·8286 (1)	0·5671 (2)	0·21069 (9)	4·03 (5)
O3	0·72066 (9)	0·1554 (2)	0·16001 (9)	3·26 (4)
O4	0·6316 (1)	0·2575 (2)	0·18332 (9)	3·79 (5)
O5	0·59583 (9)	0·6391 (2)	0·03857 (9)	3·88 (5)
O6	0·5953 (1)	0·7539 (2)	−0·0715 (1)	4·80 (5)
C2	0·8355 (1)	0·4540 (3)	0·2154 (1)	3·09 (6)
C3	0·7695 (1)	0·3652 (3)	0·1725 (1)	2·89 (6)
C4	0·7820 (1)	0·2424 (3)	0·1907 (1)	2·81 (6)
C5	0·8815 (2)	0·0673 (3)	0·2669 (1)	3·88 (7)
C6	0·9622 (2)	0·0305 (3)	0·3213 (2)	5·03 (9)
C7	1·0248 (2)	0·1197 (4)	0·3549 (2)	5·14 (9)
C8	1·0092 (2)	0·2449 (3)	0·3367 (2)	4·29 (8)
C9	0·9276 (1)	0·2810 (3)	0·2820 (1)	3·32 (6)
C10	0·8640 (1)	0·1943 (3)	0·2467 (1)	3·12 (6)
C11	0·6862 (1)	0·4174 (3)	0·1107 (1)	3·01 (6)
C12	0·6227 (1)	0·3102 (3)	0·0724 (1)	3·57 (7)
C13	0·6361 (1)	0·2067 (3)	0·1261 (1)	3·17 (6)
C14	0·5794 (2)	0·0950 (3)	0·0884 (2)	4·33 (8)
C15	0·6929 (1)	0·4857 (3)	0·0511 (1)	2·98 (6)
C16	0·6465 (1)	0·5935 (3)	0·0174 (1)	3·03 (6)
C17	0·6466 (1)	0·6516 (3)	−0·0409 (1)	3·42 (6)
C18	0·6953 (2)	0·6055 (3)	−0·0635 (1)	4·12 (7)
C19	0·7423 (1)	0·4970 (3)	−0·0294 (1)	4·26 (7)
C20	0·7408 (1)	0·4378 (3)	0·0265 (1)	3·76 (7)
C21	0·6284 (2)	0·7493 (3)	0·0839 (2)	5·14 (8)
C22	0·5897 (2)	0·8136 (4)	−0·1338 (2)	6·5 (1)
H3	0·639 (1)	0·199 (3)	0·213 (1)	2·5 (7)*

* Starred atom was refined istropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 2. *Positions and B_{eq}'s for* (II), *with e.s.d.'s in parentheses*

	x	*y*	*z*	$B_{\rm eq}$(Å^2)
O1	0·1646 (2)	0·1321 (2)	0·6989 (2)	4·16 (4)
O2	0·2560 (2)	−0·0537 (2)	0·7153 (2)	4·86 (5)
O3	0·4948 (2)	0·3049 (2)	0·6221 (1)	3·54 (4)
O4	0·6462 (2)	0·2215 (2)	0·7187 (1)	4·20 (4)
C2	0·2703 (3)	0·0558 (3)	0·6911 (2)	3·57 (6)
C3	0·3846 (3)	0·1112 (3)	0·6556 (2)	3·12 (5)
C4	0·3900 (3)	0·2403 (3)	0·6451 (2)	2·96 (5)
C5	0·2771 (3)	0·4525 (3)	0·6411 (2)	4·07 (6)
C6	0·1660 (4)	0·5201 (3)	0·6515 (2)	4·75 (7)
C7	0·0565 (3)	0·4577 (4)	0·6748 (2)	4·81 (7)
C8	0·0555 (3)	0·3268 (3)	0·6913 (2)	4·45 (7)
C9	0·1681 (3)	0·2607 (3)	0·6811 (2)	3·52 (6)
C10	0·2790 (3)	0·3205 (3)	0·6557 (2)	3·10 (5)
C11	0·4991 (3)	0·0274 (3)	0·6412 (2)	3·29 (5)
C12	0·5970 (3)	0·1040 (3)	0·5897 (2)	3·77 (6)
C13	0·6158 (3)	0·2348 (3)	0·6290 (2)	3·46 (6)
C14	0·7072 (3)	0·3190 (3)	0·5777 (2)	4·69 (7)
C15	0·4763 (3)	−0·0965 (3)	0·5912 (2)	3·23 (5)
C16	0·3954 (3)	−0·1058 (3)	0·5176 (2)	4·71 (7)
C17	0·3885 (4)	−0·2173 (4)	0·4670 (2)	4·97 (8)
C18	0·4599 (3)	−0·3227 (3)	0·4872 (2)	3·96 (6)
C19	0·5399 (3)	−0·3129 (3)	0·5614 (2)	4·55 (7)
C20	0·5477 (3)	−0·2037 (3)	0·6113 (2)	4·02 (6)
C21	0·4535 (4)	−0·4422 (4)	0·4315 (3)	5·87 (9)
H4	0·670 (3)	0·292 (3)	0·739 (2)	3·1 (8)*

* Starred atom was refined istropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. *Principal bond distances* (Å) *and angles* (°) *for* (I)

O1—C2	1·385 (3)	C5—C10	1·401 (3)
O1—C9	1·371 (3)	C6—C7	1·384 (4)
O2—C2	1·208 (3)	C7—C8	1·374 (4)
O3—C4	1·353 (3)	C8—C9	1·399 (3)
O3—C13	1·478 (3)	C9—C10	1·380 (3)
O4—C13	1·389 (3)	C11—C12	1·537 (3)
O4—H3	0·84 (3)	C11—C15	1·538 (3)
O5—C16	1·381 (3)	C12—C13	1·506 (3)
O5—C21	1·426 (3)	C13—C14	1·510 (3)
O6—C17	1·369 (3)	C15—C16	1·386 (3)
O6—C22	1·428 (3)	C15—C20	1·395 (3)
C2—C3	1·438 (3)	C16—C17	1·396 (3)
C3—C4	1·346 (3)	C17—C18	1·372 (4)
C3—C11	1·513 (3)	C18—C19	1·398 (4)
C4—C10	1·450 (3)	C19—C20	1·371 (3)
C5—C6	1·389 (4)		

C2—O1—C9	121·3 (2)	C5—C10—C9	119·1 (2)
C4—O3—C13	114·8 (2)	C3—C11—C12	109·9 (2)
C13—O4—H3	108 (2)	C3—C11—C15	111·0 (2)
C16—O5—C21	112·8 (2)	C12—C11—C15	108·7 (2)
C17—O6—C22	117·2 (2)	C11—C12—C13	112·9 (2)
O1—C2—O2	116·4 (2)	O3—C13—O4	108·0 (2)
O1—C2—C3	117·9 (2)	O3—C13—C12	108·5 (2)
O2—C2—C3	125·7 (2)	O3—C13—C14	104·5 (2)
C2—C3—C4	120·0 (2)	O4—C13—C12	108·8 (2)
C2—C3—C11	117·0 (2)	O4—C13—C14	113·1 (2)
C4—C3—C11	122·9 (2)	C12—C13—C14	113·7 (2)
O3—C4—C3	123·7 (2)	C11—C15—C16	119·5 (2)
O3—C4—C10	115·0 (2)	C11—C15—C20	121·7 (2)
C3—C4—C10	121·3 (2)	C16—C15—C20	118·7 (2)
C6—C5—C10	119·8 (2)	O5—C16—C15	119·6 (2)
C5—C6—C7	119·7 (3)	O5—C16—C17	119·7 (2)
C6—C7—C8	121·8 (2)	C15—C16—C17	120·6 (2)
C7—C8—C9	118·1 (3)	O8—C17—C16	114·7 (2)
O1—C9—C8	116·2 (2)	O6—C17—C18	125·0 (2)
O1—C9—C10	122·1 (2)	C16—C17—C18	120·2 (2)
C8—C9—C10	121·6 (2)	C17—C18—C19	119·2 (2)
C4—C10—C5	124·1 (2)	C18—C19—C20	120·6 (2)
C4—C10—C9	116·8 (2)	C15—C20—C19	120·5 (2)

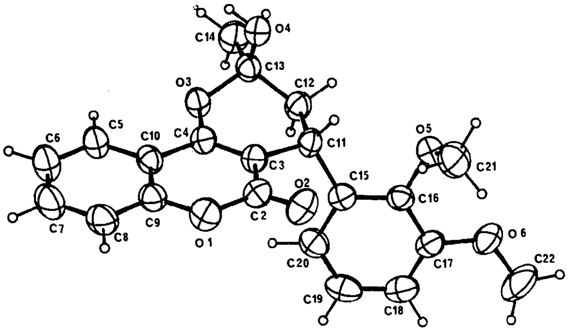


Fig. 1. A drawing of (I) with 50% probability ellipsoids for the non-H atoms.

Table 4. *Principal bond distances* (Å) *and angles* (°) *for* (II)

O1—C2	1·379 (3)	C7—C8	1·390 (4)
O1—C9	1·370 (3)	C8—C9	1·385 (4)
O2—C2	1·209 (3)	C9—C10	1·381 (3)
O3—C4	1·342 (3)	C11—C12	1·515 (3)
O3—C13	1·479 (3)	C11—C15	1·512 (3)
O4—C13	1·373 (3)	C12—C13	1·499 (3)
O4—H4	0·83 (3)	C13—C14	1·512 (4)
C2—C3	1·439 (3)	C15—C16	1·389 (4)
C3—C4	1·360 (3)	C15—C20	1·383 (3)
C3—C11	1·510 (3)	C16—C17	1·386 (4)
C4—C10	1·450 (3)	C17—C18	1·370 (4)
C5—C6	1·380 (4)	C18—C19	1·389 (9)
C5—C10	1·397 (4)	C18—C21	1·498 (4)
C6—C7	1·373 (4)	C19—C20	1·362 (4)

C2—O1—C9	122·0 (2)	C5—C10—C9	118·5 (2)
C4—O3—C13	116·6 (2)	C3—C11—C12	108·2 (2)
C13—O4—H4	109 (2)	C3—C11—C15	116·0 (2)
O1—C2—O2	114·9 (2)	C12—C11—C15	108·4 (2)
O1—C2—C3	118·6 (2)	C11—C12—C13	112·1 (2)
O2—C2—C3	126·5 (2)	O3—C13—O4	108·6 (2)
C2—C3—C4	118·4 (2)	O3—C13—C12	108·0 (2)
C2—C3—C11	119·5 (2)	O3—C13—C14	103·3 (2)
C4—C3—C11	121·7 (2)	O4—C13—C12	108·3 (2)
O3—C4—C3	124·3 (2)	O4—C13—C14	113·3 (2)
O3—C4—C10	113·9 (2)	C12—C13—C14	114·9 (2)
C3—C4—C10	121·8 (2)	C11—C15—C16	122·9 (2)
C6—C5—C10	120·0 (3)	C11—C15—C20	120·1 (2)
C5—C6—C7	120·2 (3)	C16—C15—C20	116·6 (2)
C6—C7—C8	121·2 (3)	C15—C16—C17	121·0 (3)
C7—C8—C9	117·7 (3)	C16—C17—C18	121·9 (3)
O1—C9—C8	116·4 (2)	C17—C18—C19	116·7 (3)
O1—C9—C10	121·2 (2)	C17—C18—C21	121·7 (3)
C8—C9—C10	122·3 (2)	C19—C18—C21	121·6 (3)
C4—C10—C5	124·4 (2)	C18—C19—C20	121·8 (2)
C4—C10—C9	117·1 (2)	C15—C20—C19	121·9 (2)

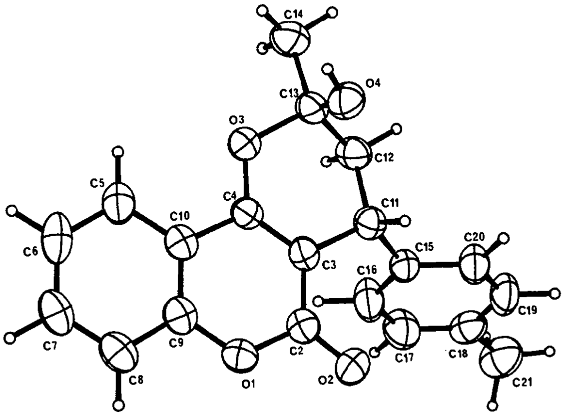


Fig. 2. A drawing of (II) with 50% probability ellipsoids for the non-H atoms.

GOF = 1·54, and for (II): $R = 0·044$, $wR = 0·060$, GOF = 1·68 for 2463 [$I \geq 2\sigma(I)$] and 1580 [$I \geq 3\sigma(I)$] intensities, respectively. The weights were taken as $1/(\sigma_F)^2 = 4F^2/\sigma(F^2)$ where $\sigma(F^2) = [\sigma(I)^2 + (0·05F^2)^2]^{1/2}$, in the refinement of the 248 (I) and 222 (II) variables; scale factors 0·754 (I) and 0·147 (II); final maximum $\Delta/\sigma < 0·02$ for each structure; maximum $|\Delta\rho|$ excursions less than 0·243 e Å^{-3}. Final atom positions and equivalent isotropic vibrational factors for the non-H atoms are given in Tables 1 and 2.* All programs used were from the locally modified Enraf–Nonius (1979) *SDP*. Principal bond distances and angles are given in Tables 3 and 4.

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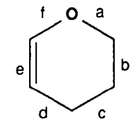
* Lists of H-atom positions, anisotropic vibrational amplitudes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52058 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The crystal structure of racemic 2′,3′-dimethoxywarfarin (I) contains hydrogen-bonded columnar chains of molecules related by a twofold screw operation along the *b* axis, therefore linking molecules of like configuration. An hydroxyl group on one molecule donates a hydrogen bond to a coumarin carbonyl of a neighbor, O···O = 2·812 (3), H···O = 1·97 (3) Å, O—H···O angle 173 (2)°. The hydroxy group is disposed axially and the 4-aryl substituent pseudoequatorially (*trans*) on a dihydropyran ring, which adopts a *d*,*e*-planar conformation with ring displacement asymmetry parameter ΔC_2 = 0·0669 (12) (Nardelli, 1983). The 2′-methoxy methyl group rotates out of the phenyl plane (76°) while the 3′-methoxy methyl lies nearly in the phenyl plane (4°). The dihedral angle between the phenyl and coumarin planes is 78°. An *ORTEP* drawing (Johnson, 1976) of the molecule is given in Fig. 1.

The crystal structure of (+)-4′-methylwarfarin (II) is pseudoisomorphous with that of (*S*)-(−)-warfarin (Valente, Trager & Jensen, 1975). Hydrogen bonding occurs between screw related molecules along the *b* axis with donor hydroxyls and acceptor carbonyls, the O···O and H···O separations are 2·746 (3) and 1·95 (3) Å, respectively, with an O—H···O angle of 174 (3)°. As in (I), the hydroxyl group is disposed axially, the 4′-methylphenyl group is pseudoequatorial and its plane is inclined at 70° with respect to the coumarin plane. The embedded dihydropyran ring is a nearly undistorted half-chair; ring displacement asymmetry parameter ΔC_2 = 0·0156 (17). A drawing of the structure is given in Fig. 2; intraring torsion angles for (I) and (II) are given in Table 5.

Table 5. *Torsion angles* (°) *in the dihydropyran rings*

E.s.d.'s are at most about 0·4°; common configuration.



	a	*b*	*c*	*d*	*e*	*f*
(I)	−51·9	58·9	−34·2	2·0	5·4	20·9
(II)	−44·2	62·1	−47·5	16·4	0·4	14·2

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Structure of Tris(pentafluorophenyl)phosphine

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Abstract. $C_{18}F_{15}P$, M_r = 532·1, monoclinic, $P2_1/c$, a = 7·194 (2), b = 17·930 (4), c = 13·834 (2) Å, β = 94·29 (2)°, V = 1779 Å^3, Z = 4, D_m = 2·00, D_x = 1·99 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 3·3 cm^{-1}, $F(000)$ = 1032, $T \simeq$ 296 K, final R = 0·055 for 2352 unique observed reflections. The three planar C_6F_5 groups are twisted about the C—P bonds to give extensive deviations from molecular C_3 symmetry similar to those in the crystal structure of triphenylphosphine. The P—C bond lengths and C—P—C bond angles are 1·834 (4), 1·832 (4), 1·824 (4) Å and 104·4 (2), 106·0 (2), 99·6 (1)°, respectively. There are two short C···F non-bonded distances in the structure (2·99, 2·79 Å).

Introduction. Although the structural characteristics of free triphenylphosphine as well as $(C_6H_5)_3P$ fragments have been extensively studied (Daly, 1964; Brock & Ibers, 1973; Bye, Schweizer & Dunitz, 1982), there have been very few reported structural