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Structures of *cis*-4-(2'-Methoxyphenyl)- (1) and *trans*-4-(3'-Methoxy-4'-hydroxyphenyl)-2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one (2)

BY BRIAN S. CASTLEBERRY, GERARD RUGGIERO AND EDWARD J. VALENTE

Department of Chemistry, Mississippi College, Clinton, MS 39058, USA

AND DRAKE S. EGGLESTON

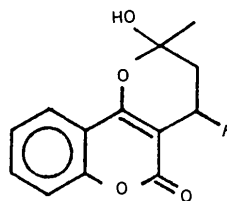
Department of Analytical, Physical and Structural Chemistry, Smith, Kline and French Laboratories, Philadelphia, PA 19101, USA

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Abstract. Derivatives of 2-methyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one. Racemic *cis*-2-hydroxy-4-(2'-methoxyphenyl) (1), C₂₀H₁₈O₅, *M_r* = 338.4, triclinic, *P* $\bar{1}$, *a* = 7.445 (3), *b* = 7.729 (3), *c* = 15.550 (4) Å, α = 96.66 (2), β = 97.04 (2), γ = 107.49 (3)°, *V* = 835.9 (5) Å³, *Z* = 2, *D_x* = 1.344 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 0.902 cm⁻¹, *F*(000) = 356, *T* = 293 K, final *R* = 0.0540 for 3724 observations. The *cis* hemiketal of 2'-methoxywarfarin contains a dihydropyran ring in a half-chair conformation. The axial 2-hydroxy group is hydrogen-bonded to a neighboring coumarin carbonyl oxygen, O...O 2.755 (1) Å. Racemic *trans*-2-hydroxy-4-(3'-methoxy-4'-hydroxyphenyl) (2), C₂₀H₁₈O₆, *M_r* = 354.4, monoclinic, *P*2₁/*n*, *a* = 10.581 (2), *b* = 9.954 (7), *c* = 16.360 (8) Å, β = 101.61 (3)°, *V* = 1687.7 (15) Å³, *Z* = 4, *D_x* = 1.395 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 0.966 cm⁻¹, *F*(000) = 744, *T* = 293 K, final *R* = 0.0415 for 2416 observations. The *trans* hemiketal of 3'-methoxy-4'-hydroxywarfarin contains a dihydropyran ring in a near half-chair conformation. Several intermolecular H bonds occur, O...O 2.865 (2), 3.104 (2) and 2.783 (2) Å, between hydroxyl groups and hydroxyl and carbonyl groups of neighboring molecules.

Introduction. As part of a study of the conformation of dihydropyran near its minimum-energy form, a series of

crystalline warfarin analogs have been prepared. The present study describes the structures of two substituted 4-aryl derivatives of 2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one.



(1) *R* = *o*-(OCH₃)C₆H₄-

(2) *R* = *m*-(OCH₃)-*p*-(OH)C₆H₃-

While these compounds exist in a dynamic solution equilibrium between two diastereomeric hemiketals and the intermediate keto form, they crystallize as cyclic hemiketals with axial hydroxyls. The resulting dihydropyran ring may adopt any accessible conformation.

Experimental. Warfarin derivatives are synthesized generally by Michael-type addition of unsaturated ketones to 4-hydroxycoumarin (Ikawa, Stahmann & Link, 1944), and recrystallized from aqueous acetone, m.p. (1) 464–465, (2) 451–454 K. *D_m*'s were not measured. Crystallographic specimens: (1) 0.2 × 0.35 × 0.35 mm; (2) 0.2 × 0.33 × 0.4 mm were chosen for data collection on a CAD-4 diffractometer. Intensities were collected to $2\theta = 57^\circ$ (*h* and *k*: -10 to

Table 1. Positions ($\times 10^4$, $z \times 10^5$) and B_{eq} for (1) with e.s.d.'s in parentheses
$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
O(1)	3903 (2)	8400 (1)	8820 (6)	5.09 (2)
O(2)	4304 (2)	9740 (1)	22455 (7)	5.92 (3)
O(3)	1613 (1)	3281 (1)	15110 (5)	4.00 (2)
O(4)	3597 (1)	2992 (1)	27111 (6)	4.17 (2)
O(5)	2886 (1)	7116 (1)	47165 (6)	4.70 (2)
C(2)	3758 (2)	8295 (2)	17473 (8)	4.13 (3)
C(3)	2997 (2)	6515 (1)	19958 (7)	3.32 (2)
C(4)	2386 (2)	5005 (1)	13651 (7)	3.23 (2)
C(5)	1913 (2)	3637 (2)	-2291 (8)	4.05 (3)
C(6)	2128 (2)	3899 (2)	-10742 (9)	4.64 (3)
C(7)	2934 (2)	5651 (2)	-12595 (9)	4.65 (3)
C(8)	3526 (2)	7141 (2)	-6092 (9)	4.71 (3)
C(9)	3297 (2)	6877 (2)	2447 (8)	3.85 (3)
C(10)	2508 (2)	5137 (2)	4537 (7)	3.28 (2)
C(11)	2775 (2)	6438 (2)	29418 (8)	3.37 (2)
C(12)	1401 (2)	4530 (2)	29942 (8)	3.99 (3)
C(13)	1756 (2)	2986 (2)	24309 (8)	3.98 (3)
C(14)	262 (3)	1133 (2)	23940 (1)	5.91 (4)
C(16)	4650 (2)	6961 (1)	35791 (8)	3.22 (2)
C(17)	4627 (2)	7304 (2)	44824 (8)	3.67 (3)
C(18)	6309 (2)	7802 (2)	50821 (9)	4.82 (3)
C(19)	8010 (2)	7975 (2)	47900 (1)	5.22 (4)
C(20)	8071 (2)	7648 (2)	39100 (1)	4.74 (3)
C(21)	6389 (2)	7150 (2)	33124 (8)	3.86 (3)
C(22)	2783 (3)	7304 (2)	56339 (9)	5.84 (4)

Table 2. Positions ($\times 10^4$) and B_{eq} for (2) with e.s.d.'s in parentheses
$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
O(1)	2197 (1)	148 (1)	5112 (1)	3.34 (3)
O(2)	2906 (1)	2037 (1)	4688 (1)	3.61 (3)
O(3)	610 (1)	2084 (1)	6880 (1)	3.17 (3)
O(4)	-237 (1)	4050 (2)	6230 (1)	3.47 (3)
O(5)	7410 (1)	5514 (2)	6149 (1)	3.67 (3)
O(6)	7104 (1)	2991 (2)	6473 (1)	4.31 (4)
C(2)	2402 (2)	1514 (2)	5211 (1)	2.77 (4)
C(3)	2005 (2)	2177 (2)	5893 (1)	2.47 (4)
C(4)	1215 (2)	1515 (2)	6319 (1)	2.55 (4)
C(5)	190 (2)	-651 (2)	6628 (1)	3.34 (4)
C(6)	-0 (2)	-2007 (2)	6455 (2)	4.06 (5)
C(7)	531 (2)	-2612 (2)	5847 (2)	4.30 (5)
C(8)	1274 (2)	-1889 (2)	5404 (2)	3.75 (5)
C(9)	1479 (2)	-536 (2)	5585 (1)	2.94 (4)
C(10)	944 (2)	100 (2)	6185 (1)	2.72 (4)
C(11)	2308 (2)	3646 (2)	6043 (1)	2.50 (4)
C(12)	1952 (2)	4037 (2)	6872 (1)	3.00 (4)
C(13)	616 (2)	3562 (2)	6923 (1)	2.86 (4)
C(14)	239 (2)	3881 (3)	7739 (2)	4.38 (5)
C(15)	3696 (2)	4085 (2)	6959 (1)	2.48 (4)
C(16)	4758 (2)	3246 (2)	6273 (1)	2.67 (4)
C(17)	5992 (2)	3740 (2)	6305 (1)	2.80 (4)
C(18)	6169 (2)	5084 (2)	6132 (1)	2.67 (4)
C(19)	5124 (2)	5921 (2)	5935 (1)	2.99 (4)
C(20)	3895 (2)	5415 (2)	5892 (1)	2.91 (4)
C(21)	7002 (2)	1597 (3)	6618 (2)	5.35 (6)

10; l : 0 to 20) for (1) and to 56° (h : 0-13; k : 0-12; l : -20 to 20) for (2); no deterioration was noted. The unique data (4212 and 4054 reflections, respectively) were corrected for coincidence and polarization but not for absorption. Data set for (1) required an extinction coefficient, $g = 4.86 (1) \times 10^{-7}$. Structures were discovered with *MULTAN* (Germain, Main & Woolfson,

1971). Non-H-atom positions were refined with their U_{iso} 's by full-matrix least squares, then with their U_{ij} 's. H atoms were refined from calculated positions with their U_{iso} 's. Scattering factors were from *International Tables for X-ray Crystallography* (1974) except for H (Stewart, Davidson & Simpson, 1965). Final agreement factors for (1): $R = 0.046$, $wR = 0.067$, $GOF = 1.76$, and for (2): $R = 0.042$, $wR = 0.052$, $GOF = 1.33$ for the 3044 and 2416 intensities greater than three times their estimated standard deviations, respectively. Least-squares weights were taken as $4F_o^2/\sigma^2(I)$ where $\sigma^2(I) = \sigma^2(I)_c + p(I)_c^2$, $p = 0.05$; and the structure-factor differences were minimized additionally for (1) and (2): 299 and 307 variables refined; scale factors 0.0595 (1) and 0.272 (1); final maximum Δ/σ 0.04 for each structure; maximum $|\Delta\rho|$ excursions less than 0.23 and 0.18 e Å⁻³.

Discussion. Final atom positions and equivalent isotropic thermal parameters for non-H atoms are given in Tables 1 and 2.*

Both crystal structures show intermolecular hydrogen bonding. In (1), the hydroxy group is H-bonded to a coumarin carbonyl O in a neighboring molecule, O...O 2.755 (1) Å. In (2), the 2-hydroxy forms a bifurcated H bond: donor to a 4'-hydroxy oxygen, O...O 2.865 (2) Å, and donor to a 3'-methoxy oxygen, O...O 3.104 Å. The angles at the H atom are 140 (2) and 148 (3)°, respectively. The 4-hydroxy group is also H-bonded to a coumarin carbonyl oxygen, O...O 2.783 (2) Å.

An operative anomeric effect is indicated by the axial disposition of the 2-hydroxy group in each structure. Hemiketal hydroxy H atoms are *gauche* synclinal to the dihydropyran oxygen and directed *exo* to the ring

* 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 44795 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

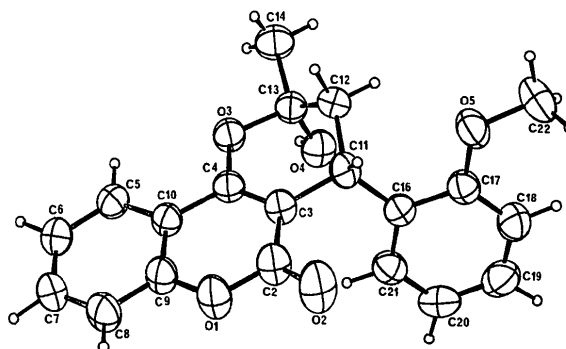


Fig. 1. An ORTEP plot (Johnson, 1976) of (1) showing 50% probability vibrational ellipsoids for non-H atoms.

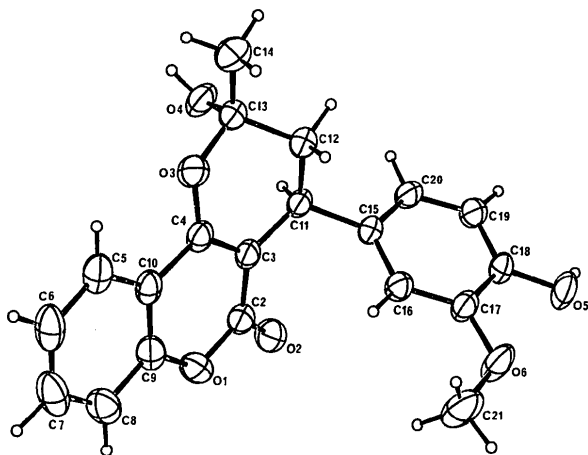


Fig. 2. An ORTEP plot (Johnson, 1976) of (2) showing 50% probability vibrational ellipsoids for non-H atoms.

(exoanomeric effect). Conformations of the dihydropyran ring in the structures are quite similar. Essentially half-chairs, (2) is slightly distorted towards the *ef*-

dipolar conformation. Ring asymmetry parameters ΔC_2 are (1) 0.0096 (6) and (2) 0.0292 (9) (Duax, Weeks & Rohrer, 1976). Figs. 1 and 2 show plots of the structures.

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Structure de l'Hexanitro-2,2',4,4',6,6' Stilbène, HNS, et Comparaison avec le Trinitro-2,4,6 Toluène, TNT

PAR FRANÇOIS GÉRARD ET ANTOINE HARDY

Laboratoire de Cristalchimie Minérale, Université de Poitiers, 40 avenue du Recteur Pineau, F-86022 Poitiers CEDEX, France

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Abstract. $C_{14}H_6N_6O_{12}$, $M_r = 450.232$, monoclinic, $P2_1/c$, $a = 22.326$ (7), $b = 5.5706$ (9), $c = 14.667$ (2) Å, $\beta = 110.04$ (1)°, $V = 1714$ (1) Å³, $Z = 4$, $D_m = 1.74$ (1), $D_x = 1.745$ (1) g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54051$ Å, $\mu = 13.30$ cm⁻¹, $F(000) = 912$, room temperature, $R = 0.051$ for 2345 independent reflections. Two different molecules have a symmetry centre either in 2(*d*) or in 2(*c*). Their benzene planes are parallel and 1.298 and 1.428 Å apart respectively. The NO₂ groups are twisted in the range 5.51 to 48.64° with respect to the carbon rings. The molecules are tilted with regard to the axes and make a herringbone pattern. Molecular stacking gives the shortest intermolecular distances along **b**. A structural comparison between HNS and TNT is made.

Introduction. Les propriétés germinatives exceptionnelles de l'hexanitro-2,2',4,4',6,6' stilbène-*trans* (HNS)

vis à vis du trinitro-2,4,6 toluène (TNT) sont brevetées et largement utilisées (Back, Söderberg & Hakanson, 1970). Ce phénomène a été étudié par l'équipe de Thorpe (Parry & Thorpe, 1979) qui met en évidence le rôle d'un complexe HNS [(TNT)₂]. La comparaison structurale étant à la base d'une explication de ce pouvoir germinatif, nous avons entrepris la détermination de la structure de l'HNS (Gérard, Hardy, Delachaux & Sauvestre, 1985; Hardy, 1986), celle du TNT orthorhombique a déjà été déterminée par Carper, Davis & Extine (1982) et celle du TNT monoclinique par nous-même (Gérard & Hardy, 1988).

Partie expérimentale. A partir de l'HNS fourni par la SNPE, nous avons préparé les monocristaux par dilution par l'eau d'une solution de l'HNS dans l'acide nitrique fumant. Ils se présentent sous la forme de barres allongées selon **b** de dimension 0,3 × 0,2 ×