

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.140$   
 $S = 1.097$   
 3158 reflections  
 266 parameters  
 All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.3914P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

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## N-(2-Dimethoxymethyl-3-hydroxy-2-methyl-6-nitro-3,4-dihydro-2H-1-benzopyran-4-yl)-acetamide

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### Abstract

The benzopyran-based title compound, C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>7</sub>, is a potential potassium-channel opener with cardiovascular therapeutic activities. The 2-dimethoxymethyl and 3-hydroxyl groups are in axial positions while the 4-acetamide group is in a pseudo-equatorial position. The 4-acetamide group is nearly perpendicular to the benzopyran plane. There are two intermolecular hydrogen bonds; one between the hydroxyl O and acetamide O atoms [2.725 (5) Å], and the other between the acetamide N and methoxy O atoms [3.139 (5) Å].

### Comment

ATP-sensitive potassium-channel openers are promising in cardiovascular therapy as antihypertensives and coronary vasodilators and consist of several structural groups including benzopyran compounds such as cromakalim, (II) (Robertson & Steinberg, 1990). The title compound, (I), is one of a series of benzopyran-based

Table 1. Selected geometric parameters (Å, °)

C1—C12	1.735 (3)	C3—C13	1.537 (3)
O1—C2	1.345 (3)	C5—C17	1.506 (3)
N2—N1	1.266 (2)	C13—C15	1.532 (3)
N2—C1	1.405 (3)	C13—C14	1.535 (4)
N1—C7	1.417 (3)	C13—C16	1.536 (4)
C2—O1—H1	106.1 (19)	C14—C13—C16	110.1 (2)
N1—N2—C1	115.8 (2)	C15—C13—C3	111.8 (2)
N2—N1—C7	115.1 (2)	C14—C13—C3	110.2 (2)
C15—C13—C14	106.7 (2)	C16—C13—C3	109.7 (2)
C15—C13—C16	108.3 (2)		
C1—N2—N1—C7	177.3 (2)	N2—N1—C7—C12	−179.0 (2)
N1—N2—C1—C6	−179.4 (2)	N2—N1—C7—C8	−0.1 (3)
N1—N2—C1—C2	−1.0 (3)		

Data were corrected for Lorentz-polarization factors. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined by full-matrix least squares using *SHELXL93* (Sheldrick, 1993). Non-H atoms were refined anisotropically. The H atoms were located from difference-Fourier maps and refined isotropically. C—H distances were in the range 0.88 (6)–1.03 (3) Å, and  $U_{\text{iso}}$  values for H atoms were in the range 0.044 (6)–0.18 (2) Å<sup>2</sup>.

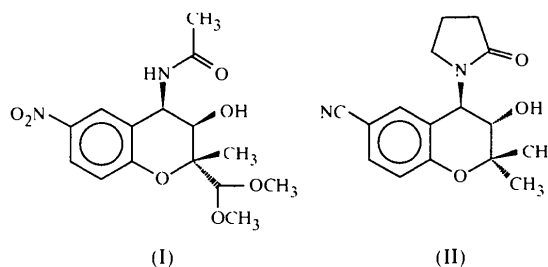
Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

The authors wish to acknowledge for the use of the *CAD-4* diffractometer (purchased under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey) of the Physics Engineering Department, Hacettepe University, Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1105). Services for accessing these data are described at the back of the journal.

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 İşik, Ş., Aygün, M., Kocaokutgen, H., Tahir, M. N., Büyükgüngör, O. & Erdönmez, A. (1998). *Acta Cryst.* **C54**, 859–860.  
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compounds prepared in a search for potential drugs (Kwak *et al.*, 1995). An ORTEPII drawing (Johnson, 1976) of the molecule with the atomic numbering scheme is presented in Fig. 1. The present study establishes that the 2-dimethoxymethyl and 3-hydroxyl groups are *trans*-related, and that the 3-hydroxyl and 4-acetamide groups are *cis*-related. The substituents at the 2 and 3 positions are in axial positions, while the 4-acetamide group is in a pseudo-equatorial position. In cromakalim, the 3-hydroxyl and 4-oxopyrrolidine groups are *trans*-related and the 3-hydroxyl group is in a pseudo-equatorial position. Fig. 2 shows a stereoscopic view of molecules (I) and (II) superimposed. The acetamide moiety is nearly perpendicular to the benzopyran plane, with a dihedral angle of  $86.58(14)^\circ$ . Atom O17 is situated in the same direction as the oxo group in the oxopyrrolidine ring of cromakalim.

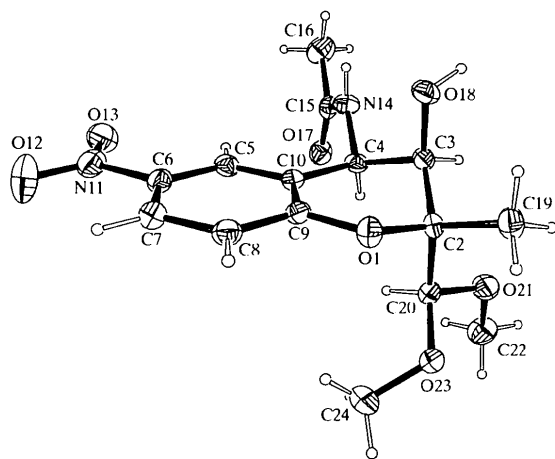


Fig. 1. ORTEPII (Johnson, 1976) view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The molecular dimensions agree well with those of related compounds. The atoms in the benzopyran ring system, except for C2 and C3, form a plane with a maximum deviation of  $0.014(4) \text{ \AA}$  for C10. Atoms C2 and C3 deviate from the plane by  $-0.239(6)$  and  $0.487(6) \text{ \AA}$ , respectively. The pyran ring assumes a half-chair conformation, with the ring torsion angles being  $40.5(5)$ ,  $-59.1(5)$  and  $47.5(5)^\circ$  for the O1—C2, C2—C3 and C3—C4 bonds, respectively. The acetamide moiety is planar with a maximum deviation of  $0.004(4) \text{ \AA}$  for C15. The nitro group is coplanar with the benzopyran ring system, with a dihedral angle of  $1.8(3)^\circ$ . The molecules are linked together by two intermolecular hydrogen bonds, one between the hydroxyl O18 and acetamide O17 atoms [ $O18 \cdots O17(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$   $2.725(5)$ ,  $H \cdots O$   $1.94(7) \text{ \AA}$  and  $O-H \cdots O$   $1.63(7)^\circ$ ], and the other between the acetamide N14 and methoxy O23 atoms [ $N14 \cdots O23(\frac{1}{2}-x, 2-y, -\frac{1}{2}+z)$

$3.139(5)$ ,  $H \cdots O$   $2.33(5) \text{ \AA}$  and  $N-H \cdots O$   $157(5)^\circ$ ]. Besides these hydrogen-bonding interactions, there are only van der Waals interactions between the molecules.

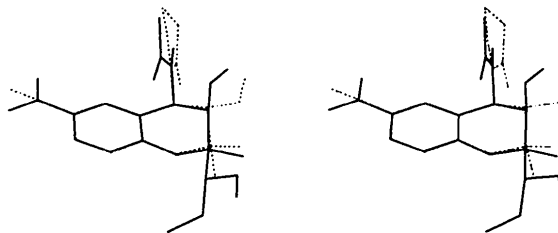


Fig. 2. Stereoscopic view of the superimposed structures of (I) (solid line) and (II) (dotted line).

## Experimental

Synthesis of (I) has been performed at the Korea Research Institute of Chemical Technology.

### Crystal data

$C_{15}H_{20}N_2O_7$   
 $M_r = 340.33$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 10.579(3) \text{ \AA}$   
 $b = 10.124(3) \text{ \AA}$   
 $c = 15.147(3) \text{ \AA}$   
 $V = 1622.2(7) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.393 \text{ Mg m}^{-3}$   
 $D_m = 1.39(2) \text{ Mg m}^{-3}$   
 $D_m$  measured by flotation  
 in cyclohexane/ethylene  
 bromide

Mo  $K\alpha$  radiation  
 $\lambda = 0.7107 \text{ \AA}$   
 Cell parameters from 29  
 reflections  
 $\theta = 7.72-16.92^\circ$   
 $\mu = 0.111 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
 Block  
 $0.40 \times 0.40 \times 0.30 \text{ mm}$   
 Colorless

### Data collection

Rigaku AFC-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none  
 1709 measured reflections  
 1642 independent reflections  
 1093 reflections with  
 $I > 2\sigma(I)$

$R_{int} = 0.011$   
 $\theta_{max} = 25.0^\circ$   
 $h = -12 \rightarrow 0$   
 $k = 0 \rightarrow 12$   
 $l = 0 \rightarrow 18$   
 3 standard reflections  
 every 100 reflections  
 intensity decay: 2%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.109$   
 $S = 1.080$   
 1638 reflections  
 245 parameters  
 H atoms treated by a  
 mixture of constrained and  
 independent refinement

$\Delta\rho_{max} = 0.195 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.169 \text{ e \AA}^{-3}$   
 Extinction correction:  
 SHELXL93  
 Extinction coefficient:  
 0.028(2)  
 Scattering factors from  
 International Tables for  
 Crystallography (Vol. C)

$$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.504P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.023$

Absolute structure: assumed from synthetically related compounds with known configuration

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## $\alpha$ -Naphthyl Phenyl Pinacols

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### Abstract

Treatment of  $\alpha$ -naphthyl phenyl ketone with Zn/acetic acid gives racemic  $\alpha$ -naphthyl phenyl pinacol [1,2-di(1-naphthyl)-1,2-diphenylethane-1,2-diol], C<sub>34</sub>H<sub>26</sub>O<sub>2</sub>, but reaction with Mg/MgI<sub>2</sub> gives a product which proves to be not a pinacol, but a tricyclic compound (with four chiral centers, formed by addition at the 2-position of one of the naphthalene groups), racemic 5-(1-naphthyl)-3,5-diphenyl-4-oxatricyclo[7.4.0.0<sup>2,6</sup>]trideca-7,9,11,13-tetraen-3-ol, C<sub>34</sub>H<sub>26</sub>O<sub>2</sub>. The aromatic ring in this tricyclic compound is planar, but the other six-membered ring, and the five-membered furano ring, are non-planar. Bond lengths and angles in both molecules correspond to the molecular formulations. In both structures, the OH groups are involved in only weak intermolecular interactions.

### Comment

Glycols, which may be synthesized by the dissolving-metal reduction of ketones, undergo dehydration and skeletal rearrangement when treated with mineral acids, a process known as the pinacol rearrangement. A study of the rearrangement of benzpinacols was initiated, in order to obtain details of the geometrical parameters in solid-state reactions (*cf.* Jones *et al.*, 1989; Toda & Shigemasa, 1989; Chen *et al.*, 1991). For various reasons this study was discontinued, but some interesting results did emerge, which shed light on some long-outstanding ambiguities.

Reduction of  $\alpha$ -naphthyl phenyl ketone (1-benzoyl-naphthalene), (1), with Zn/acetic acid is reported to produce a material with m.p. 431 K, while reduction with Mg/MgI<sub>2</sub> gives a different material, with m.p. 493 K (Bachmann & Shankland, 1929; Bergmann & Schuchardt, 1931). Although not specifically stated, the implication is that these materials are racemic, (2), and *meso* forms, respectively, of di- $\alpha$ -naphthyl diphenyl pinacol. These syntheses have been repeated, giving crystalline materials with m.p. 421 and 479 K (see supplementary material). X-ray analysis of the lower-melting

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C9	1.366 (5)	C5—C6	1.386 (6)
O1—C2	1.454 (5)	C6—C7	1.374 (6)
C2—C3	1.529 (6)	C7—C8	1.379 (6)
C3—O18	1.431 (6)	C8—C9	1.396 (6)
C3—C4	1.531 (6)	C9—C10	1.393 (6)
C4—N14	1.460 (6)	C15—O17	1.224 (5)
C4—C10	1.522 (6)	C15—C16	1.503 (7)
C5—C10	1.381 (6)		
C9—O1—C2	118.7 (3)	C7—C8—C9	120.5 (4)
O1—C2—C3	109.7 (4)	O1—C9—C10	123.8 (4)
O18—C3—C2	108.9 (4)	O1—C9—C8	115.2 (4)
O18—C3—C4	108.5 (4)	C10—C9—C8	121.0 (4)
C2—C3—C4	111.0 (4)	C5—C10—C9	117.8 (4)
N14—C4—C10	110.9 (4)	C5—C10—C4	122.3 (4)
N14—C4—C3	110.7 (4)	C9—C10—C4	119.8 (4)
C10—C4—C3	110.4 (4)	C15—N14—C4	122.8 (5)
C10—C5—C6	120.6 (4)	O17—C15—N14	121.9 (5)
C7—C6—C5	121.8 (4)	O17—C15—C16	123.1 (5)
C6—C7—C8	118.2 (5)	N14—C15—C16	115.0 (5)

The position and isotropic displacement parameters of three aromatic and 12 methyl H atoms were constrained using the AFIX43 and AFIX137 options in SHELXL93 (Sheldrick, 1993), respectively. Other H atoms were refined without constraints.

Data collection: local program (Yoon *et al.*, 1994). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1040). Services for accessing these data are described at the back of the journal.

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