

Fig. 2. Molecular packing viewed down the *b* axis.

The glycosyl torsion angle C(2)—N(1)—C(1')—O(4') is $-74.2(2)^\circ$. The sugar pucker is in a twisted form, C(4')-endo—C(3')-exo, with pseudorotation angle $P = 220.9^\circ$ as defined by Altona & Sundaralingam (1972). A similar conformation is also observed in 8,2'-*O*-cycloadenosine ($P = 217.5^\circ$) and in 8,2'-*S*-cyclo-5'-AMP ($P = 232.7^\circ$).

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Structure of 1-(*p*-Ethoxyphenyl)-1,3-dihydro-3-phenyl-2*H*-benzimidazole-2-thione, C₂₁H₁₈N₂OS

BY A. CRIADO, A. CONDE AND R. MÁRQUEZ

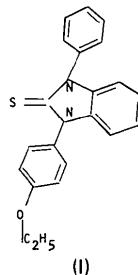
Departamento de Óptica y Sección de Física del Centro Coordinado de CSIC, Universidad de Sevilla, Spain

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Abstract. $M_r = 346.4$, orthorhombic, $P2_12_12_1$, $a = 7.600(1)$, $b = 11.132(2)$, $c = 20.767(3)$ Å, $V = 1756.9(5)$ Å³, $Z = 4$, $D_x = 1.31$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 1.67$ mm⁻¹, $F(000) = 728$, $T = 300$ K. Final $R = 0.049$ for 1531 observed independent reflections. The benzimidazole bicycle is quasi-planar, the dihedral angle between the two fused rings being $1.6(2)^\circ$. The unsubstituted phenyl ring is planar while the phenyl ring with the ethoxy substituent deviates significantly from the expected planar conformation.

Introduction. The crystal structure of the title compound has been determined as part of a systematic structural analysis of imidazole C-nucleosides synthesized in the Organic Chemistry Department of this University. Recently, we have reported (Criado, Conde & Márquez, 1983) the structure of the first disubstituted (at both N atoms) imidazole C-nucleoside.

The title compound (I) has been obtained (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1983*a*) from the *p*-toluenesulfonate of 4-(β -D-erythrofuranosyl)-1-(*p*-ethoxyphenyl)-1,3-dihydro-3-phenyl-2*H*-imidazole-2-thione (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1983*b*) using a reaction similar to that of Tipson & Cohen (1965). This synthesis is the first case of nucleoside aromatization.



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Experimental. Needle-shaped colorless crystals, $0.05 \times 0.06 \times 0.14$ mm, kindly supplied by Professor Fernández-Bolaños of the Organic Chemistry Department of this University; preliminary studies showed orthorhombic symmetry, systematic absences consistent with $P2_12_12_1$. Philips PW 1100 four-circle computer-controlled diffractometer, graphite-monochromated radiation. Unit-cell parameters from least-squares refinement of θ values of 33 reflections. 1729 reflections with $\theta < 65^\circ$ ($h < 9$, $k < 14$, $l < 25$) measured, ω - 2θ scan mode, 1531 with $I > 2\sigma(I)$ considered observed. Two reference reflections monitored periodically, intensity changes less than 2%. Lorentz and polarization corrections, none for absorption or extinction effects. Weighted tangent-formula refinement (*MULTAN78*, Main, Hull, Lesinger, Germain, Declercq & Woolfson, 1978) of 180 reflections with $E > 1.5$. Full-matrix least-squares refinement of 281 parameters based on F_o over all observed reflections (*CRYLSQ* of XRAY70, Stewart, Kundell & Baldwin, 1970). Fourier difference synthesis up to $\sin\theta/\lambda = 0.7 \text{ \AA}^{-1}$ gave all H-atom positions; a least-squares refinement in a mixed mode including H atoms, each one with an isotropic temperature factor equal to that of the attached skeleton atom, gave $R = R_w = 0.049$. Last-cycle parameter shifts less than 0.3σ , average 0.1σ . Final difference Fourier map excursions $-0.25 \leq \Delta\rho \leq 0.35 \text{ e \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Weighting scheme in the form $1/\sigma^2(I)$ based on counting statistics.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) are given in Table 1.* Bond lengths and angles for the non-H atoms are given in Fig. 1. The C—H distances range from 0.95 to 1.19 Å, with a mean value of 1.08 (6) Å.

Benzimidazole ring. Bond distances and angles in the imidazole ring are in good agreement with the reported values for imidazole-2-thione compounds (Conde, López-Castro & Márquez, 1978; Criado *et al.*, 1983) showing no appreciable distortion due to the bicycle formation. Only the C(2)—C(3) bond distance is somewhat long in comparison with the mean value [1.345 (5) Å] of the forementioned compounds. The ring keeps its planar feature and the atomic deviations from the least-squares plane through the five atoms are within the standard deviations ($\chi^2 = 0.72$). The benzene ring, on the contrary, shows an appreciable distortion from planarity ($\chi^2 = 27.39$), with atoms whose distance

to the least-squares plane is greater than three standard deviations. The average C—C bond length in the ring is 1.389 (7) Å and C—C—C angle is $120.0 (5)^\circ$. The whole bicycle is quasi-planar, the dihedral angle between the imidazole and benzene least-squares planes being $1.6 (2)^\circ$.

Table 1. *Positional parameters* ($\times 10^5$) and *equivalent isotropic thermal parameters* ($\times 10^4$) for the non-H atoms with *e.s.d.*'s in parentheses

	x	y	z	$U_{eq}(\text{Å}^2)$
S	52527 (18)	10175 (13)	-23129 (6)	450 (4)
O(1)	-4101 (48)	-27848 (31)	-11181 (18)	501 (12)
N(1)	52808 (54)	3744 (34)	-10470 (19)	365 (12)
N(2)	73068 (55)	16914 (35)	-13045 (19)	365 (13)
C(1)	59232 (63)	10275 (44)	-15567 (22)	371 (14)
C(2)	62185 (64)	6115 (41)	-4873 (22)	351 (15)
C(3)	75071 (67)	14402 (41)	-6487 (23)	362 (15)
C(4)	86847 (76)	18824 (47)	-2034 (25)	475 (18)
C(5)	85689 (85)	14255 (53)	4187 (27)	549 (20)
C(6)	72880 (88)	5597 (52)	5804 (26)	542 (20)
C(7)	61161 (75)	1292 (45)	1287 (24)	430 (16)
C(8)	37658 (65)	-4036 (42)	-10742 (23)	372 (15)
C(9)	37768 (70)	-14158 (46)	-14696 (25)	432 (16)
C(10)	23521 (75)	-21796 (45)	-14697 (26)	447 (17)
C(11)	9032 (68)	-19503 (44)	-10830 (24)	394 (15)
C(12)	8414 (67)	-9217 (47)	-6999 (23)	411 (15)
C(13)	23083 (72)	-1425 (45)	-7045 (25)	404 (16)
C(14)	-20360 (76)	-25485 (55)	-7782 (31)	568 (21)
C(15)	-32549 (77)	-35714 (56)	-9505 (32)	577 (21)
C(16)	84187 (65)	24958 (46)	-16586 (23)	377 (15)
C(17)	101124 (72)	21513 (47)	-18020 (26)	465 (18)
C(18)	112177 (73)	29465 (54)	-21276 (28)	542 (20)
C(19)	105956 (72)	40733 (53)	-23039 (28)	536 (19)
C(20)	88844 (83)	43990 (52)	-21639 (32)	608 (22)
C(21)	77897 (77)	36129 (48)	-18433 (30)	531 (20)

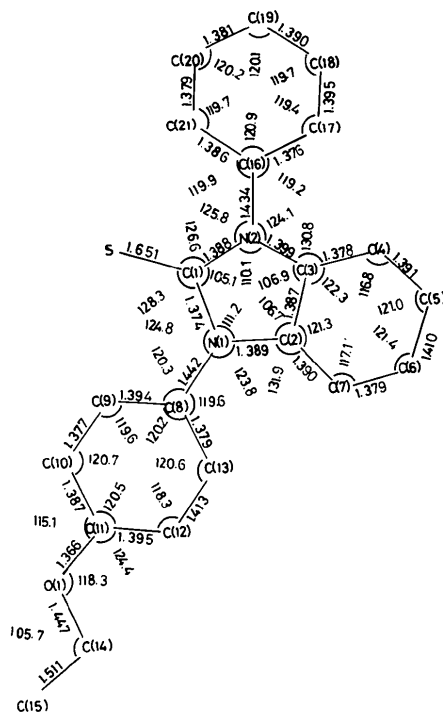


Fig. 1. Bond lengths (Å) and angles ($^\circ$) in the molecule. Standard deviations are below 0.009 Å and 0.6° .

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38889 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The dihedral angles formed by the imidazole ring and the two bound phenyl rings are 73.7 (2)° for the N(2)-attached ring and 61.4 (2)° for the N(1)-attached ring, both values being similar to those encountered in the analogous compounds studied previously, ranging from 60 to 80°. The torsional angles describing the bonding are C(1)–N(1)–C(8)–C(9) = 63.5 (6) and C(1)–N(2)–C(16)–C(21) = 75.2 (7)°, respectively.

Phenyl rings. The N(2)-attached phenyl ring is planar, with atomic deviations from the mean plane within the standard deviations ($\chi^2 = 4.52$). The average C–C bond length is 1.385 (8) Å and the mean C–C–C angle is 120.0 (5)°. The N(1)-attached phenyl ring, on the contrary, deviates significantly from the expected planar conformation ($\chi^2 = 29.07$), with an average C–C bond length of 1.390 (7) Å and C–C–C angle of 120.0 (5)°.

The ethoxy group exhibits asymmetry in the C(10)–C(11)–O(1) = 115.1 (5) and C(12)–C(11)–O(1) = 124.4 (5)° angles, a common feature of the phenoxy group (Domiano, Nardelli, Balsamo, Macchia & Macchia, 1979).

Fig. 2 shows a view of the unit cell along the *b* axis. No evidence for hydrogen bonds exists and no intermolecular contacts appreciably shorter than the sum of the van der Waals radii have been detected.

The authors thank Professor Fernández-Bolaños for supplying the crystals and the staff of the Instituto 'Rocasolano' of CSIC (Madrid) for collecting the diffractometer data. The present work forms part of a wider research project supported by the Government through the 'Comisión Asesora de Investigación Científica y Técnica'.

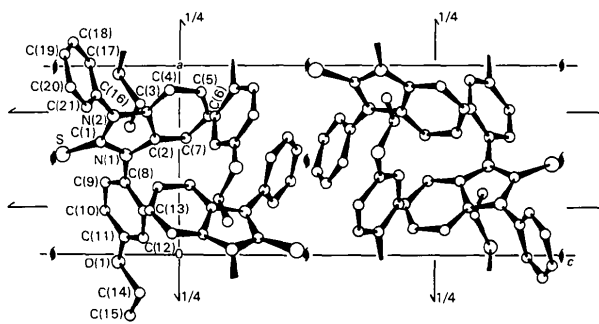


Fig. 2. Unit cell viewed along the *b* axis.

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2-(1,3-Dithiol-2-ylidene)-4-cyclopentene-1,3-dione, C₈H₄O₂S₂, and 2-(1,3-Benzodithiol-2-ylidene)cyclohexanone, C₁₃H₁₂OS₂

BY WILLIAM H. WATSON, JEAN GALLOY AND DAVID A. GROSSIE

FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, USA

AND JUZO NAKAYAMA

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

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Abstract. C₈H₄O₂S₂ (2), *M_r* = 196.25, orthorhombic, *Pnma*, *a* = 18.080 (2), *b* = 11.102 (1), *c* = 3.8904 (4) Å, *V* = 780.9 (1) Å³, *Z* = 4, *D_x* = 1.67 Mg m⁻³, *Cu Kα*, λ = 1.54178 Å, μ = 5.549 mm⁻¹, *F*(000) = 400, room temperature, *R* = 0.046 based on 597 unique reflections. C₁₃H₁₂OS₂ (3), *M_r*

= 248.24, monoclinic, *P2₁/c*, *a* = 6.459 (1), *b* = 14.263 (3), *c* = 13.514 (4) Å, β = 112.16 (2)°, *V* = 1153.0 (6) Å³, *Z* = 4, *D_x* = 1.43 Mg m⁻³, *Cu Kα*, μ = 3.90 mm⁻¹, *F*(000) = 520, room temperature, *R* = 0.074 based on 1429 unique reflections. Compound (2) is planar except for a slight 2° fold along the S...S line.

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