

forms only one intramolecular I...O secondary bond [2.939 (8) Å]. But this is precisely coplanar with its primary bonds and has a length significantly shorter than any other I...O distance in OFAPI or OFATI. In the unbridged compound FAIB the I atom forms two intra- [3.00 (1), 3.16 (1) Å] and one intermolecular [3.06 (1) Å] secondary I...O bonds, *i.e.* three in all instead of two. One of the former is approximately coplanar with its primary bonds but the other two lie well out of the plane of the covalent bonds. Their lengths are unequal with differences less than those in the case of OFAPI but still greater than those in the case of the present compound OFATI.

It is worthwhile to note that in all three compounds one of the acetoxy groups is twisted in an identical way so that the deviations of respective O atoms from the mean planes of the corresponding T-groups are almost the same [2.19 (1) in OFATI, 2.19 (1) in FAIB, 2.22 Å in OFAPI]. In no case are there obvious steric constraints to which this twist may be attributed.

Fig. 2 shows the molecular packing of OFATI in the unit cell. The centrosymmetrical dimers repeat along the *c* axis to form columns. A short intermolecular contact [O(5)...H(6') = 2.6 (2) Å, O(5)...C(6') = 3.31 (2) Å, angle O(5)...H(6')—C(6') = 133.8 (5)°, with the symmetry code (i) 1 - *x*, 1 - *y*, 1 - *z*] suggests that they may be interconnected by a possible weak O...H—C hydrogen bond.

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Structure of 5,7-Dibromo-3-phenyl-1,2-benzisoxazole 2-Oxide

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Abstract. C₁₃H₇Br₂NO₂, *M_r* = 369.02, monoclinic, *P*2₁/*n*, *a* = 13.362 (3), *b* = 23.544 (4), *c* = 3.8893 (8) Å, β = 96.10 (2)°, *V* = 1216.59 Å³, *Z* = 4, *D_x* = 2.014 Mg m⁻³, λ (Mo *K*α) = 0.71069 Å, μ = 7.05 mm⁻¹, *F*(000) = 712, *T* = 298 K, *R* = 0.062 for 970 independent non-zero reflections. In the isoxazole 2-oxide ring the acyclic N—O bond distance compares well with that of a nitro group while the cyclic one is longer. Both compare very well with the corresponding bond distances in furoxans. These features may be used to interpret some aspects of the mass spectra of benzisoxazole *N*-oxides.

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Introduction. Recently, Tsiamis & Tsoungas (1985) reported the electron-impact mass spectra of a series of 1,2-benzisoxazole *N*-oxides. They are representative of a new class of heterocyclic *N*-oxides, the molecular structure of which has already been confirmed by X-ray analysis of 5-chloro-3-methyl-1,2-benzisoxazole 2-oxide (CMBO hereafter) (Chiari & Viterbo, 1982). In order to have further evidence for those structural features of these compounds which are correlated with their mass spectra, we have elected to carry out the X-ray crystal structure determination of the title compound, suitable crystals of which were generously supplied by Professor C. Tsiamis.

Experimental. Transparent crystals, 0.54 × 0.48 × 0.37 mm, computer-controlled Philips PW 1100 four-

circle single-crystal diffractometer, three-dimensional data, graphite-monochromated Mo $K\alpha$, ω -scan mode; cell parameters and standard deviations by least-squares analysis of measured θ angles of the 58 strongest reflections, $P2_1/n$ from systematic absences, three standard reflections per 90 min (111, 221, 240) without significant intensity variation, 1193 (of 2657 possible) measured reflections [with $I_{\text{top}} - 2(I_{\text{top}})^{1/2} > I_{\text{bck}}$, where $I_{\text{top}} = \text{counts s}^{-1}$ at the top of reflection, $I_{\text{bck}} = \text{mean counts s}^{-1}$ of background at each side of reflection], $\theta = 3\text{--}27^\circ$, max. $\sin\theta/\lambda = 0.6388 \text{ \AA}^{-1}$, max. $hkl \pm 16, 26, 8$; 1033 unique reflections, $R_{\text{int}} = 0.054$, 63 unobserved with $F_o < 4\sigma(F_o)$ [$\sigma(F_o)$ from counting statistics], no absorption correction; Br atoms located by Patterson synthesis, remaining non-H atoms by difference Fourier synthesis; blocked full-matrix least squares using F with *SHELX76* (Sheldrick, 1976) and *SHELXTL* (Sheldrick, 1981); atomic scattering factors from *International Tables for X-ray Crystallography* (1974); H atoms included at calculated positions very close to those from difference Fourier map, with isotropic temperature factors as those of C atoms to which they are bonded, were refined; H(9) riding on C(9) during last cycles; the weighting scheme chosen was $w = 1/[\sigma^2(F_o) + gF_o^2]$ where g was fixed at 0.00215, a value which gave the least variation of the mean value of $w(F_o - F_c)^2$ with the magnitude of F_o [$\sigma(F_o)$ from counting statistics]; $R = 0.062$, $wR = 0.073$, $S = 1.113$, $(\Delta/\sigma)_{\text{max}} = 0.199$, $(\Delta/\sigma)_{\text{mean}} = 0.029$, $\Delta\rho = -1.50$ to 1.22 e \AA^{-3} in the region of Br atoms.

Discussion. Final positional parameters and equivalent isotropic temperature coefficients are given in Table 1.* An *ORTEPII* (Johnson, 1976) view of the molecule is shown in Fig. 1. The benzisoxazole fragment is almost planar, the dihedral angle between its two ring planes being only $0.9 (4)^\circ$. The planar phenyl ring is turned so that it forms a dihedral angle of $42.3 (4)^\circ$ with the plane of the isoxazole ring. The bond lengths and angles in the isoxazole ring compare very well with the corresponding ones in CMBO. Consequently, the same structural similarities and differences found between CMBO and a considerable number of furoxans (Chiari & Viterbo, 1982, and literature cited therein) hold also between the latter group and the present compound. In fact, both bond distances $\text{N--O}(1) = 1.46 (2)$ and $\text{N--O}(2) = 1.22 (2) \text{ \AA}$ are very close to the corresponding N–O distances in the furoxans mentioned above, since they fall just in the middle of the range of values

found for them (1.425–1.50 and 1.204–1.242 \AA respectively). This provides additional support for the attribution of the resemblance of the mass and ^{13}C NMR spectra of benzisoxazole and furoxans to this particular structural similarity (Chiari & Viterbo, 1982). Conversely, as in CMBO, the bond angles $\text{C}(1)\text{--N--O}(1) = 111 (1)$ and $\text{C}(1)\text{--N--O}(2) = 134 (1)^\circ$ differ from the corresponding angles in the same furoxan compounds, since the latter are distributed around and close to the mean values 107.5 and 107.4° respectively.

The two N–O bonds in the isoxazole ring are quite different in length. The cyclic N–O(2) distance, comparable with that of a nitro group, is significantly shorter than the cyclic N–O(1) distance. The latter is also longer than the N–O bond lengths, 1.42 or 1.40 \AA , in compounds with a similar isoxazole ring (Bozopoulos, Kokkou & Rentzeperis, 1980, and literature cited therein; Sax, Pletcher, Scholtz, Gerkin &

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} *
Br(1)	5761 (1)	4164 (1)	−2938 (5)	42
Br(2)	1967 (1)	4648 (1)	1642 (5)	46
O(1)	1957 (7)	3290 (4)	1851 (22)	37
O(2)	1517 (8)	2370 (4)	2546 (24)	55
N	2167 (8)	2685 (5)	1662 (26)	37
C(1)	3063 (9)	2599 (6)	556 (27)	33
C(2)	3479 (9)	3141 (6)	−7 (27)	27
C(3)	2786 (10)	3552 (6)	822 (27)	29
C(4)	2935 (9)	4114 (6)	508 (27)	34
C(5)	3832 (10)	4304 (6)	−656 (27)	31
C(6)	4543 (10)	3910 (6)	−1438 (26)	34
C(7)	4396 (10)	3318 (6)	−1194 (27)	32
C(8)	3461 (10)	2037 (6)	221 (26)	31
C(9)	2848 (11)	1604 (6)	−1285 (27)	38
C(10)	3256 (12)	1061 (7)	−1678 (29)	51
C(11)	4247 (12)	940 (7)	−551 (29)	56
C(12)	4864 (11)	1374 (8)	881 (29)	54
C(13)	4473 (9)	1915 (6)	1290 (27)	32

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

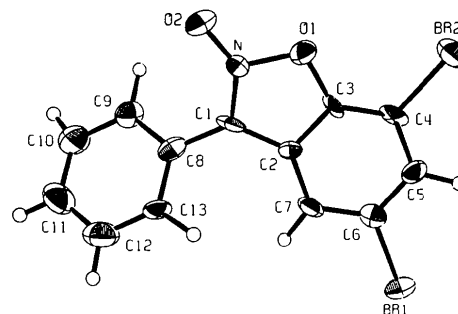


Fig. 1. *ORTEPII* drawing (Johnson, 1976) of the molecule. Thermal ellipsoids are drawn at 50% probability level while isotropic hydrogen thermal parameters are represented as spheres of arbitrary size.

* Lists of structure amplitudes, bond distances and angles, anisotropic thermal parameters of the non-H atoms, coordinates and isotropic temperature factors for H atoms and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43200 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

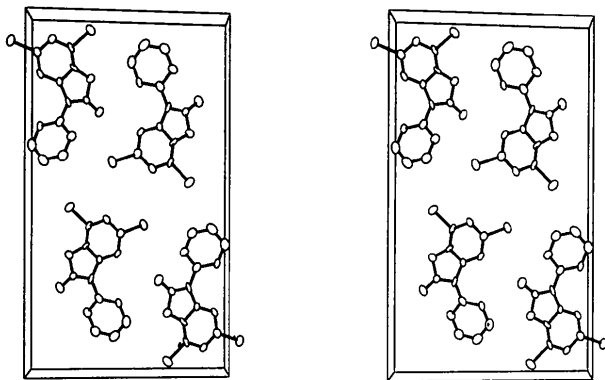


Fig. 2. Stereo plot of the unit cell.

Pinkus, 1971). This difference in length between the two N—O bonds, and the implied difference in their strength, justifies the easy cleavage of the heterocyclic N—O bond observed experimentally (Boulton & Tsoungas, 1980) and supports the electron-impact-induced isomerization proposed by Tsiamis & Tsoungas (1985) to describe the fragmentation process of 1,2-benzisoxazole *N*-oxides occurring during the production of their mass spectra.

Fig. 2 shows the molecular packing in the unit cell. An intermolecular contact [H(7)···O(2)ⁱ = 2.38 (5), C(7)···O(2) = 3.35 (2) Å, angle C(7)—H(7)···O(2)ⁱ =

163.3 (22)°, where (i) = $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$] suggests the existence of a possible O···H interaction.

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Structure of 5,4'-Dihydroxy-3,6,7,8-tetramethoxyflavone, Calycopterin*

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Abstract. C₁₉H₁₈O₈, *M_r* = 374.3, monoclinic, *P*2₁/*c*, *a* = 17.156 (6), *b* = 6.781 (5), *c* = 15.541 (4) Å, β = 105.46 (2)°, *V* = 1742 (2) Å³, *Z* = 4, *D_m* = 1.40 (2), *D_x* = 1.427 (2) Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 0.121 mm⁻¹, *F*(000) = 784, *T* = 298 K,

R = 0.066 for 1345 unique reflections. The γ-pyrone ring is planar and makes an angle of 3.1 (5)° with the benzene ring. The phenyl ring is planar and makes an angle of 161.4 (6)° with the pyrone ring. All the methoxy planes are nearly perpendicular to the plane of the γ-benzopyrone ring.

* 5-Hydroxy-2-(4-hydroxyphenyl)-3,6,7,8-tetramethoxy-4*H*-1-benzopyran-4-one.

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