

[1,434 (3) Å] et pour la liaison nitrile C(14)–N(15) [1,150 (3) Å]. Les homologues des deux dernières mesurent respectivement 1,43 et 1,15 Å dans le cyano-9 anthracène (Wyckoff, 1971), 1,44 et 1,14 Å dans le tétracyano-7,7,8,8 quinodiméthane (Wyckoff, 1969). L'angle C(1)–C(14)–N(15) est égal à 178,1 (2)°.

Si l'on admet pour rayons de van der Waals des atomes de carbone et d'azote, les valeurs suivantes (Bondi, 1964): $r(\text{C aliphatique}) = 1,70$, $r(\text{C aromatique}) = 1,77$, $r(\text{N pyrazinylique}) = 1,55$ et $r(\text{N nitrilique}) = 1,60$ Å, on constate que les trois distances interatomiques intermoléculaires les plus courtes diffèrent de moins de 0,200 Å de la somme des rayons des atomes concernés. Il s'agit de C(13)–C(13ⁱ) [3,475 (3) Å] [(i): 1–x, –y, –z], de C(10)–C(13ⁱⁱ) [3,641 (3) Å] [(ii): 1+x, y, z] et de C(7)–N(15ⁱⁱⁱ) [3,482 (3) Å] [(iii): –1+x, y, z].

La Fig. 2 montre que la structure peut être considérée comme formée de couches de molécules dont les positions moyennes sont les plans (100). Sa cohésion est due aux interactions de van der Waals.

Références

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 FRENZ, B. A. (1982). *Structure Determination Package*. College Station, Texas, et Enraf–Nonius, Delft.
International Tables for X-ray Crystallography (1974). Tome IV, p. 72. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)
 ITO, T. & SUGAWARA, Y. (1983). *BEST-PLANE PROGRAM*, 3^e version (BP7C). Institute of Physical and Chemical Research, Wako-Shi, Japon.
 JOHNSON, C. K. (1965). *ORTEP*. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KITANO, Y., ASHIDA, T., OHTA, A., WATANABE, T. & AKITA, Y. (1983). *Acta Cryst.* **C39**, 136–139.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. de York, Angleterre, et de Louvain, Belgique.
 VIOSSAT, B., RODIER, N., LEHUÉDÉ, J. & VIERFOND, J.-M. (1986). *Acta Cryst.* **C42**, 227–230.
 WYCKOFF, R. W. G. (1969). *Crystal Structures*. Vol. 6, partie 1, 2^e édition, pp. 138–140. New York: Wiley–Interscience.
 WYCKOFF, R. W. G. (1971). *Crystal Structures*. Vol. 6, partie 2, 2^e édition, pp. 473–476. New York: Wiley–Interscience.

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Structures of an Ozonide, a Spirocyclic Acetal and a Hydroperoxide Derived from Cyclopenteno-1,2,4-trioxanes

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Abstract. Ozonide (II): 3,4a β ,5,7,8,8a-hexahydro-3,3-dimethyl-7 β ,8a β -diphenyl-5 α ,7 α -epidioxypyranol[3,4-*e*]-[1,2,4]trioxine, C₂₀H₂₀O₆, m.p. 406–408 K, $M_r = 356.4$, triclinic, $P\bar{1}$, $a = 5.634$ (1), $b = 10.079$ (3), $c = 16.785$ (3) Å, $\alpha = 104.48$ (4), $\beta = 93.48$ (3), $\gamma = 103.93$ (1)°, $V = 888.3$ (4) Å³, $Z = 2$, $D_x = 1.33$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.092$ mm⁻¹, $F(000) = 376$, room temperature, $R = 0.069$ for 1022 observed reflections [$|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 4.0$]. Spirocyclic acetal (III): 3,4a β ,5,7,8,8a-hexahydro-3,3-dimethyl-7 α -phenyl-7,8a-(epoxy-*o*-benzeno)pyranol[3,4-*e*]-[1,2,4]trioxin-5 α -ol, C₂₀H₂₀O₆, m.p. 408–416 K, $M_r = 356.4$, monoclinic, $C2/c$, $a = 30.962$ (4), $b = 6.126$ (1), $c = 18.862$ (3) Å, $\beta = 104.52$ (1)°, $V = 3463.3$ (9) Å³, $Z = 8$, $D_x =$

1.37 Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.094$ mm⁻¹, $F(000) = 1504$, room temperature, $R = 0.066$ for 1163 observed reflections [$|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 8.0$]. Hydroperoxide (V): *cis*-3,4a,5,7a-tetrahydro-6,7a-diphenylcyclopenta[1,2-*e*]-[1,2,4]trioxin-5 β -yl hydroperoxide, C₁₈H₁₆O₅, m.p. 401–403 K, $M_r = 312.3$, monoclinic, $P2_1/c$, $a = 8.9185$ (12), $b = 22.595$ (3), $c = 8.0069$ (12) Å, $\beta = 111.01$ (2)°, $V = 1506.2$ (4) Å³, $Z = 4$, $D_x = 1.38$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.094$ mm⁻¹, $F(000) = 656$, room temperature, $R = 0.038$ for 1047 observed reflections [$|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 7.0$]. All three molecules possess 1,2,4-trioxane rings which adopt chair conformations and are *cis* fused to the adjacent ring. Hydrogen bonds occur in the molecular packing of

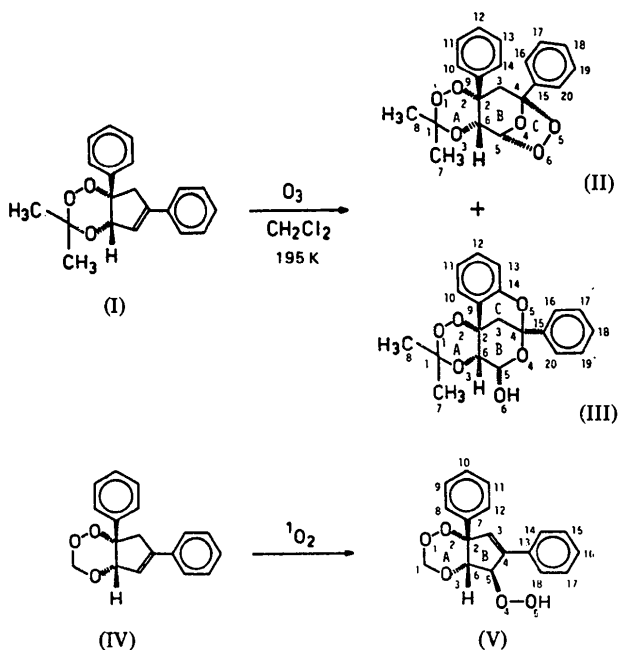
compound (V). No especially short interatomic contacts were observed for (II) and (III).

Introduction. Structural studies on 1,2,4-trioxanes are poorly represented in the literature (Wilson, Gardner, Elder, Squire & Florian, 1974; Yamamoto, Aoyama, Omote, Akutagawa, Takenaka & Sasada, 1977; Yamamoto, Nakai, Kashima, Omote & Akutagawa, 1983; Jefford, Jaggi, Boukouvalas, Kohmoto & Bernardinelli, 1984*a,b*; Jefford, Boukouvalas, Kohmoto & Bernardinelli, 1985; Allen, Bellard & Kennard, 1986). However, in recent years, Jefford and co-workers have developed a new methodology enabling the synthesis of a wide variety of 1,2,4-trioxane derivatives (Jefford, Ferro *et al.*, 1986). Considerable attention attaches to this class of saturated oxygen heterocycles, since the only known naturally occurring member, artemisin or Qinghaosu (Qinghaosu Antimalarial Coordinating Research Group, 1979), is a potent antimalarial agent, constituting a significant, new therapeutic lead. Consequently, studies on the structure of trioxanes become of paramount importance, especially as they will have a bearing on biological activity.

The three compounds presented here were obtained from a mechanistic study of the ozonolysis of cyclopenteno-1,2,4-trioxanes (Jefford, Boukouvalas, Jaggi, Kohmoto & Bernardinelli, 1986). The action of ozone on *cis*-3,4a,7,7a-tetrahydro-3,3-dimethyl-6,7a-diphenylcyclopenta[1,2-*e*][1,2,4]trioxine (I) gave the secondary ozonide (II) and the spirocyclic acetal (III). This last compound is the first example of the intramolecular oxidation of a phenyl substituent by a contiguous carbonyl oxide.

In an associated study aimed at seeking information on the steric congestion of molecules such as (I), the photo-oxygenation of the bis-dimethylated analogue of (I), namely (IV) was undertaken. A single hydroperoxide (V) was obtained indicating that oxygenation

occurred exclusively on the *exo* face of the double bond in (IV).



Experimental. Experimental data and structure refinement are summarized in Table 1.* Philips PW 1100 diffractometer, graphite-monochromated Mo *K*α: ω/2θ

* Lists of structure factors, atomic positional and anisotropic displacement parameters for all atoms and other information in the printed form of the Standard Crystallographic File Structure of Brown (1985) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP. 43581 (107 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Summary of crystal data, intensity measurement and structure refinement

	(II)	(III)	(V)
Crystal size (mm)	0.10 × 0.27 × 0.32	0.10 × 0.25 × 0.30	0.23 × 0.23 × 0.30
Unit-cell determination*			
No. of reflections	27	34	27
θ range	18 ≤ 2θ ≤ 38°	19 ≤ 2θ ≤ 34°	26 ≤ 2θ ≤ 39°
(sinθ/λ) _{max} (Å ⁻¹)	0.49	0.49	0.53
<i>h, k, l</i> range	-5, 5; -9, 9; 0, 16	-28, 28; 0, 5; 0, 18	-8, 8; 0, 23; 0, 8
No. of standard reflections [variation]	2 [<i>l</i> ≤ 1.6σ(<i>l</i>)]	2 [<i>l</i> ≤ 1.7σ(<i>l</i>)]	3 [<i>l</i> ≤ 1.7σ(<i>l</i>)]
No. of measured reflections	1658	1860	2058
No. of unique reflections	1658	1603	1850
Criterion for observed reflections	<i>F</i> ≥ 3σ(<i>F</i>) and <i>F</i> ≥ 4	<i>F</i> ≥ 4σ(<i>F</i>) and <i>F</i> ≥ 8	<i>F</i> ≥ 3σ(<i>F</i>) and <i>F</i> ≥ 7
No. of observed reflections	1022	1163	1059
Refinement (on <i>F</i>)	Two blocks	Full matrix	Full matrix
No. of parameters	236	235	208
Weighting scheme	$w(F) = 1$ for <i>F</i> ≤ 32 $w(F) = (32/ F)^2$ for <i>F</i> > 32	$w(F) = (F /48)^2$ for <i>F</i> ≤ 48 $w(F) = (48/ F)^2$ for <i>F</i> > 48	$w(F) = \exp[18(\sin\theta/\lambda)^2]$
H atoms	Calculated	Calculated†	Calculated†
Max. and average Δ/σ	0.258, 0.041	0.006, 0.002	0.001, 0.000
Max. and min. Δρ (e Å ⁻³)	0.30, -0.53	0.34, -0.37	0.39, -0.47
<i>S</i>	12.3	3.1	1.9
<i>R</i> , <i>wR</i> (%)	6.9, 7.6	6.6, 5.3	3.8, 5.3

* Unit cell determined by least-squares fit.

† The H atom of the hydroxyl group was located from a difference electron density map.

scans, Lorentz-polarization correction; no absorption correction; structures solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); no secondary-extinction correction; all calculations performed with a local version of *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEPII* (Johnson, 1976).

Discussion. The positional parameters are shown in Table 2, and the bond distances and relevant bond angles in Table 3. For non-aromatic rings, the endocyclic torsional angles, ring-puckering parameters

Table 2. Fractional coordinates and, for non-H atoms, equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

U_{eq} is the average of the eigenvalues of U .				
Compound (II)	x	y	z	U_{eq}
O(1)	0.8267 (10)	0.7916 (6)	0.4013 (3)	52 (3)
O(2)	0.7498 (9)	0.6887 (5)	0.3198 (3)	47.2 (25)
O(3)	1.1498 (10)	0.6868 (6)	0.4178 (3)	58 (3)
O(4)	1.1221 (11)	0.4388 (6)	0.2156 (4)	72 (3)
O(5)	0.7209 (12)	0.3827 (6)	0.2350 (4)	71 (3)
O(6)	0.8803 (15)	0.3972 (7)	0.3118 (4)	85 (4)
C(1)	0.9388 (17)	0.7225 (10)	0.4524 (6)	61 (4)
C(2)	0.9734 (13)	0.6965 (8)	0.2809 (5)	40 (3)
C(3)	0.8850 (15)	0.5971 (9)	0.1927 (5)	49 (4)
C(4)	0.8858 (17)	0.4449 (10)	0.1824 (6)	61 (4)
C(5)	1.1109 (19)	0.4810 (11)	0.3019 (6)	67 (5)
C(6)	1.1473 (14)	0.6412 (9)	0.3309 (5)	48 (4)
C(7)	1.0432 (20)	0.8376 (11)	0.5316 (6)	83 (5)
C(8)	0.7520 (19)	0.5987 (11)	0.4670 (6)	82 (5)
C(9)	1.0746 (15)	0.8472 (8)	0.2755 (5)	45 (4)
C(10)	1.3159 (17)	0.9283 (10)	0.3045 (6)	59 (4)
C(11)	1.3972 (17)	1.0641 (11)	0.2941 (6)	72 (5)
C(12)	1.2425 (21)	1.1217 (10)	0.2543 (6)	65 (5)
C(13)	1.0012 (21)	1.0436 (11)	0.2281 (6)	74 (5)
C(14)	0.9191 (15)	0.9087 (10)	0.2379 (6)	60 (4)
C(15)	0.8113 (20)	0.3486 (10)	0.0955 (6)	71 (5)
C(16)	0.628 (4)	0.3518 (21)	0.0469 (12)	267 (14)
C(17)	0.562 (4)	0.2598 (24)	-0.0333 (12)	277 (15)
C(18)	0.666 (3)	0.1661 (13)	-0.0638 (8)	97 (6)
C(19)	0.848 (4)	0.1638 (17)	-0.0158 (10)	170 (11)
C(20)	0.928 (3)	0.2545 (17)	0.0637 (8)	150 (9)
Compound (III)	x	y	z	U_{eq}
O(1)	0.40688 (14)	-0.2174 (7)	0.33016 (23)	55.6 (18)
O(2)	0.36971 (12)	-0.0613 (7)	0.30953 (20)	47.8 (18)
O(3)	0.45161 (13)	0.0000 (7)	0.27639 (21)	48.1 (18)
O(4)	0.40697 (13)	0.0356 (7)	0.11446 (21)	44.1 (17)
O(5)	0.32925 (14)	0.0970 (7)	0.08783 (21)	52.4 (18)
O(6)	0.46179 (14)	0.2722 (7)	0.16771 (23)	61.7 (19)
C(1)	0.44809 (21)	-0.0980 (12)	0.3442 (4)	56 (3)
C(2)	0.37091 (19)	0.0197 (10)	0.2380 (3)	39 (3)
C(3)	0.36390 (19)	-0.1642 (10)	0.1821 (3)	40 (3)
C(4)	0.36467 (21)	-0.0650 (11)	0.1101 (3)	47 (3)
C(5)	0.41829 (20)	0.2095 (11)	0.1674 (3)	48 (3)
C(6)	0.41445 (19)	0.1356 (10)	0.2431 (3)	40 (3)
C(7)	0.48284 (23)	-0.2735 (13)	0.3603 (4)	81 (4)
C(8)	0.45153 (22)	0.0685 (13)	0.4051 (4)	71 (3)
C(9)	0.33257 (18)	0.1756 (10)	0.2162 (3)	39 (3)
C(10)	0.31644 (20)	0.3010 (11)	0.2659 (3)	45 (3)
C(11)	0.28058 (22)	0.4405 (11)	0.2409 (4)	52 (3)
C(12)	0.26060 (19)	0.4595 (12)	0.1666 (4)	55 (3)
C(13)	0.27746 (20)	0.3418 (11)	0.1163 (3)	48 (3)
C(14)	0.31307 (20)	0.2037 (11)	0.1417 (3)	44 (3)
C(15)	0.35763 (22)	-0.2314 (11)	0.0481 (3)	45 (3)
C(16)	0.39178 (23)	-0.3602 (12)	0.0387 (4)	60 (3)
C(17)	0.3845 (3)	-0.5273 (13)	-0.0134 (4)	69 (4)
C(18)	0.3424 (3)	-0.5624 (12)	-0.0570 (4)	63 (3)
C(19)	0.3083 (3)	-0.4333 (13)	-0.0484 (4)	66 (3)
C(20)	0.31510 (21)	-0.2677 (12)	0.0042 (4)	56 (3)
H(O6)	0.4714	0.1018	0.1882	

Table 2 (cont.)

Compound (V)	x	y	z	U_{eq}
O(1)	0.59504 (22)	0.01505 (8)	0.2640 (3)	43.2 (7)
O(2)	0.54891 (22)	0.05954 (9)	0.37388 (24)	38.5 (6)
O(3)	0.32748 (21)	-0.00103 (9)	0.0922 (3)	39.9 (6)
O(4)	0.03733 (22)	0.02443 (8)	0.2219 (3)	40.5 (7)
O(5)	-0.05166 (23)	0.07159 (9)	0.1013 (3)	50.0 (8)
C(1)	0.4700 (4)	-0.02605 (12)	0.2144 (4)	44.0 (11)
C(2)	0.4204 (3)	0.09419 (12)	0.2508 (4)	33.5 (9)
C(3)	0.3533 (3)	0.12960 (12)	0.3680 (4)	39.2 (10)
C(4)	0.2269 (3)	0.10302 (12)	0.3871 (4)	34.5 (9)
C(5)	0.1983 (3)	0.04347 (11)	0.2949 (4)	33.8 (9)
C(6)	0.2793 (3)	0.05192 (11)	0.1565 (3)	33.5 (9)
C(7)	0.4796 (3)	0.13250 (11)	0.1319 (4)	34.5 (9)
C(8)	0.6426 (3)	0.13825 (13)	0.1628 (4)	44.8 (10)
C(9)	0.6937 (4)	0.17459 (15)	0.0549 (6)	59.0 (14)
C(10)	0.5868 (4)	0.20621 (15)	-0.0818 (5)	59.1 (14)
C(11)	0.4235 (4)	0.20166 (14)	-0.1133 (5)	55.1 (12)
C(12)	0.3712 (3)	0.16483 (13)	-0.0067 (4)	44.8 (10)
C(13)	0.1254 (3)	0.12686 (13)	0.4815 (4)	36.5 (9)
C(14)	0.0918 (4)	0.18713 (13)	0.4710 (4)	45.3 (10)
C(15)	-0.0044 (4)	0.21079 (15)	0.5567 (5)	57.2 (13)
C(16)	-0.0676 (4)	0.17484 (18)	0.6527 (5)	59.6 (13)
C(17)	0.0345 (4)	0.11462 (16)	0.6650 (5)	54.1 (13)
C(18)	0.0600 (4)	0.09065 (13)	0.5798 (4)	45.0 (11)
H(O5)	-0.1452	0.0532	0.0474	

(Cremer & Pople, 1975) and minimum values of asymmetry parameters (Nardelli, 1983) are reported in Table 4. Fig. 1 shows stereoviews of the three 1,2,4-trioxane derivatives.

The atomic displacements associated with compound (II) are large, especially for the phenyl ring [C(15) to C(20)]; this accounts for the high values of the goodness of fit and the large estimated standard deviations relative to the geometrical parameters of this molecule.

1,2,4-Trioxane rings. The molecular structure of (I) has already been determined (Allen, Bellard & Kennard, 1986) and reveals that the 1,2,4-trioxane ring adopts a twist-boat conformation while compounds (II), (III) and (V) are all characterized by chair conformations. The chair conformation in (III) is essentially ideal (average of endocyclic torsional angles $\langle \tau \rangle = 59.4^\circ$) in spite of the multiple fusion of the rings, whereas in (II) the chair is flattened with a minimum value of $\tau = 26.7^\circ$ for C(6)-O(3). The maximum absolute value of τ in these three 1,2,4-trioxane rings is always associated with the O(1)-O(2) bond (see Table 4, ring A). Moreover, the best values of the asymmetry parameters show that all three compounds possess C_2 symmetry passing through this bond.

Allen and co-workers have suggested that the twist-boat conformation of the trioxane ring observed in (I) results from the geometrical constraints imposed by the *cis*-fused cyclopentene ring. It appears that this may not be the case since in the similar compound (V), the trioxane ring enjoys the chair conformation. The mere fact of *cis* fusion to a cyclopentene ring is not a sufficient reason for preferred boat conformations since in most molecules containing this moiety the heterocycle prefers the chair conformation. However, other factors such as the nature of the C(1) substituent or the strain found in bridged bicyclic molecules are

probably responsible for the adoption of boat conformations in certain 1,2,4-trioxanes.

The O—O bond lengths of the 1,2,4-trioxane rings [1.463 (7), 1.472 (6) and 1.488 (3) Å for (II) (III) and (V) respectively] are in good agreement with the mean value of 1.470 (2) Å observed for cyclic fragments $Csp^3-O-O-Csp^3$ (Allen *et al.*, 1979).

Other rings. The non-aromatic rings may adopt different conformations. Ring *B* of compound (II) exists

essentially in a half-chair conformation with C_s symmetry passing through the C(2) and O(4) atoms. In (III) ring *B* exists as a chair displaying a minimum value of the asymmetry parameter associated with a C_2 relation. The six-membered *C* ring of (III) is characterized by an envelope conformation with the C(3) atom displaced from the mean plane passing through atoms C(2), C(4), O(5), C(14) and C(9) [maximum deviation = 0.037 Å for O(5)]. In compounds (II) and (V), both the 1,2,4-trioxolane and cyclopentene rings exist in envelope conformations.

In compounds (II) and (III) there are no intermolecular distances significantly shorter than those found for normal values. The H atom of the hydroxyl group of (III) is involved in an intramolecular hydrogen bond with O(3) and O(4) [$H(O6)\cdots O(3) = 2.011$ Å; $H(O6)\cdots O(4) = 2.165$ Å]. In the hydroperoxide (V) an intermolecular hydrogen bond occurs between O(5) and O(3)($-x, -y, -z$) [2.874 (3) Å].

Table 3. *Interatomic distances (Å) with e.s.d.'s in parentheses and bond angles (°) (average e.s.d. 0.5°)*

	(II)	(III)	(V)
O(1)—O(2)	1.463 (7)	1.472 (6)	1.488 (3)
O(1)—C(1)	1.437 (13)	1.436 (8)	1.395 (3)
O(2)—C(2)	1.448 (9)	1.447 (7)	1.445 (3)
O(3)—C(1)	1.438 (12)	1.443 (9)	1.414 (3)
O(3)—C(6)	1.414 (10)	1.430 (7)	1.428 (4)
O(4)—O(5)	—	—	1.466 (3)
O(4)—C(4)	1.434 (12)	1.431 (8)	—
O(4)—C(5)	1.414 (12)	1.441 (8)	1.410 (3)
O(5)—O(6)	1.481 (10)	—	—
O(5)—C(4)	1.460 (12)	1.460 (8)	—
O(5)—C(14)	—	1.403 (8)	—
O(6)—C(5)	1.413 (13)	1.399 (8)	—
C(1)—C(7)	1.504 (12)	1.497 (10)	—
C(1)—C(8)	1.509 (14)	1.519 (10)	—
C(2)—C(3)	1.540 (10)	1.520 (8)	1.510 (5)
C(2)—C(6)	1.540 (13)	1.505 (9)	1.544 (3)
C(2)—C(7)	—	—	1.515 (4)
C(2)—C(9)	1.516 (12)	1.498 (8)	—
C(3)—C(4)	1.501 (14)	1.495 (9)	1.334 (4)
C(4)—C(5)	—	—	1.512 (4)
C(4)—C(13)	—	—	1.473 (5)
C(4)—C(15)	1.505 (12)	1.526 (9)	—
C(5)—C(6)	1.524 (13)	1.532 (9)	1.536 (5)
C(7)—C(8)	—	—	1.391 (4)
C(7)—C(12)	—	—	1.390 (4)
C(8)—C(9)	—	—	1.381 (6)
C(9)—C(10)	1.393 (11)	1.398 (8)	1.367 (5)
C(9)—C(14)	1.393 (14)	1.393 (8)	—
C(10)—C(11)	1.393 (15)	1.387 (9)	1.389 (5)
C(11)—C(12)	1.382 (17)	1.389 (9)	1.387 (5)
C(12)—C(13)	1.378 (15)	1.393 (10)	—
C(13)—C(14)	1.381 (15)	1.377 (9)	1.390 (4)
C(13)—C(18)	—	—	1.399 (5)
C(14)—C(15)	—	—	1.384 (6)
C(15)—C(16)	1.29 (2)	1.366 (10)	1.371 (6)
C(15)—C(20)	1.31 (2)	1.386 (8)	—
C(16)—C(17)	1.40 (2)	1.399 (11)	1.388 (5)
C(17)—C(18)	1.25 (3)	1.373 (11)	1.372 (6)
C(18)—C(19)	1.27 (3)	1.361 (12)	—
C(19)—C(20)	1.39 (2)	1.397 (10)	—
O(2)—O(1)—C(1)	106.0	108.5	104.8
O(1)—O(2)—C(2)	104.6	105.6	106.4
C(1)—O(3)—C(6)	120.6	113.6	113.4
O(5)—O(4)—C(5)	—	106.4	—
C(4)—O(4)—C(5)	101.6	114.7	—
O(6)—O(5)—C(4)	105.4	—	—
O(5)—O(6)—C(5)	103.5	—	—
C(4)—O(5)—C(14)	—	119.1	—
O(1)—C(1)—O(3)	109.6	108.0	111.0
O(2)—C(2)—C(3)	103.8	111.0	104.9
O(2)—C(2)—C(6)	107.3	109.5	107.8
C(3)—C(2)—C(6)	111.9	111.4	101.3
C(2)—C(3)—C(4)	115.4	107.2	111.9
O(4)—C(4)—O(5)	102.6	109.5	—
O(4)—C(4)—C(3)	109.6	110.2	—
O(5)—C(4)—C(3)	110.4	110.8	—
C(3)—C(4)—C(5)	—	—	110.2
O(4)—C(5)—O(6)	104.1	105.8	—
O(4)—C(5)—C(4)	—	—	116.3
O(4)—C(5)—C(6)	109.8	111.4	114.3
O(6)—C(5)—C(6)	115.6	112.1	—
C(4)—C(5)—C(6)	—	—	101.6
O(3)—C(6)—C(2)	114.2	111.3	113.4
O(3)—C(6)—C(5)	110.8	109.8	115.9
C(2)—C(6)—C(5)	114.0	110.9	103.6

Table 4. *Endocyclic torsional angles (°), ring-puckering parameters and minimum values of asymmetry parameters*

Ring-puckering parameters (Q , φ_2 , θ_2) according to Cremer & Pople (1975); asymmetry parameters (ΔC_s , ΔC_2) according to Nardelli (1983).

	(II)	(III)	(V)
Ring A			
O(1)—O(2)	-79.4 (7)	69.7 (5)	-73.5 (2)
O(2)—C(2)	66.0 (6)	-61.8 (5)	60.9 (3)
C(2)—C(6)	-40.7 (7)	53.4 (6)	-46.9 (3)
C(6)—O(3)	26.7 (1.0)	-49.9 (6)	42.5 (3)
O(3)—C(1)	-36.9 (9)	55.9 (6)	-55.1 (3)
C(1)—O(1)	61.2 (7)	-65.4 (6)	69.0 (3)
Q	0.604 (7)	0.601 (5)	0.603 (3)
φ_2	-82. (2)	87. (3)	-97. (1)
θ_2	147.8 (7)	12.2 (5)	161.1 (2)
ΔC_s	O(2) = 0.091 (4)	O(1) = 0.040 (3)	O(1) = 0.051 (1)
ΔC_2	O(1)—O(2) = 0.026 (3)	O(1)—O(2) = 0.008 (2)	O(1)—O(2) = 0.020 (1)
Ring B			
C(2)—C(3)	25. (1)	-58.9 (6)	17.1 (3)
C(3)—C(4)	-51. (1)	61.2 (5)	3.9 (3)
C(4)—O(4)	75. (1)	-60.7 (6)	—
C(4)—C(5)	—	—	-23.4 (2)
O(4)—C(5)	-76. (1)	52.9 (6)	—
C(5)—C(6)	53. (1)	-48.0 (7)	32.6 (2)
C(6)—C(2)	-25. (1)	52.8 (6)	-30.4 (2)
Q	0.601 (8)	0.562 (6)	0.336 (3)
φ_2	1. (2)	72. (4)	138.3 (5)
θ_2	145. (1)	8.8 (6)	—
ΔC_s	C(2) = 0.006 (5)	C(3) = 0.018 (3)	C(6) = 0.027 (1)
ΔC_2	C(2)—C(3) = 0.097 (4)	C(3)—C(4) = 0.011 (3)	C(3) - 0.040 (1)
Ring C			
O(5)—O(6)	7.4 (8)	C(2)—C(3)	63.1 (6)
O(6)—C(5)	-33.9 (9)	C(3)—C(4)	-60.2 (6)
C(5)—O(4)	48.2 (9)	C(4)—O(5)	26.1 (7)
O(4)—C(4)	-42.0 (8)	O(5)—C(14)	6.3 (9)
C(4)—O(5)	21.2 (7)	C(14)—C(9)	-2.2 (9)
Q	0.431 (8)	C(9)—C(2)	-32.7 (8)
φ_2	135. (1)	—	0.555 (6)
θ_2	—	—	-126. (1)
ΔC_s	O(4) = 0.057 (5)	—	122.9 (6)
ΔC_2	O(5) = 0.042 (3)	—	C(3) = 0.033 (3)
			C(2)—C(3) = 0.110 (3)

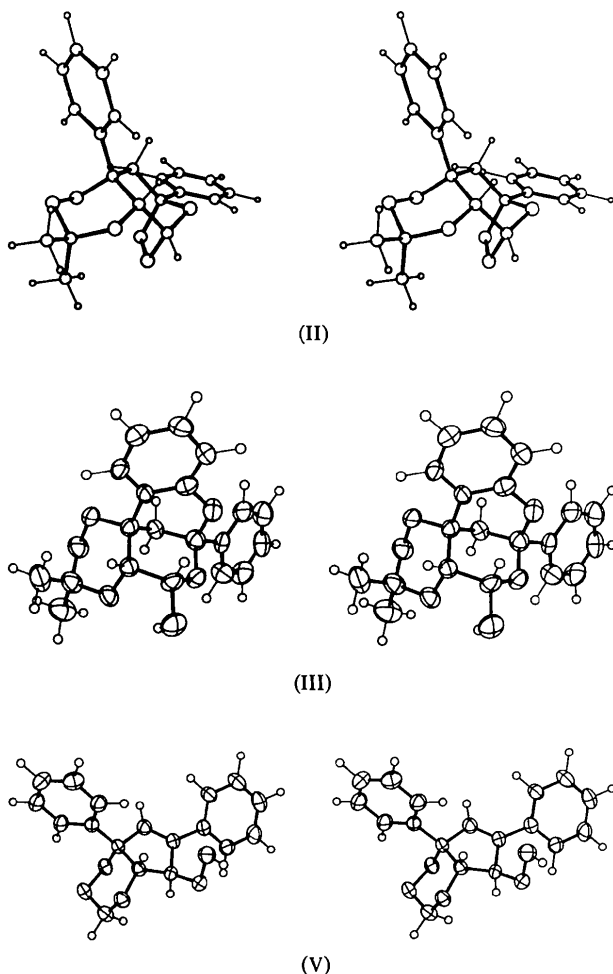


Fig. 1. Stereoviews of 1,2,4-trioxane derivatives: (II) ozonide, (III) spirocyclic acetal and (V) hydroperoxide.

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References

- ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* B35, 2331–2339.
- ALLEN, F. H., BELLARD, S. A. & KENNARD, O. (1986). *Acta Cryst.* C42, 829–832.
- BROWN, I. D. (1985). *Acta Cryst.* A41, 339.
- CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* 97, 1354–1358.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JEFFORD, C. W., BOUKOUVALAS, J., JAGGI, D., KOHMOTO, S. & BERNARDINELLI, G. (1986). *Helv. Chim. Acta*, 69, 941–948.
- JEFFORD, C. W., BOUKOUVALAS, J., KOHMOTO, S. & BERNARDINELLI, G. (1985). *Tetrahedron*, 41, 2081–2088.
- JEFFORD, C. W., FERRO, S., MOULIN, M.-C., VELARDE, J., JAGGI, D., KOHMOTO, S., RICHARDSON, G. D., GODOY, J., ROSSIER, J.-C., BERNARDINELLI, G. & BOUKOUVALAS, J. (1986). *New Trends Nat. Prod. Chem.* 26, 163–183. Elsevier. In the press.
- JEFFORD, C. W., JAGGI, D., BOUKOUVALAS, J., KOHMOTO, S. & BERNARDINELLI, G. (1984a). *Helv. Chim. Acta*, 67, 1104–1111.
- JEFFORD, C. W., JAGGI, D., BOUKOUVALAS, J., KOHMOTO, S. & BERNARDINELLI, G. (1984b). *Helv. Chim. Acta*, 67, 2254–2260.
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
- NARDELLI, M. (1983). *Acta Cryst.* C39, 1141–1142.
- QINGHAOSU ANTIMALARIAL COORDINATING RESEARCH GROUP (1979). *Chin. Med. J.* 92, 811–819.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WILSON, R. M., GARDNER, E. J., ELDER, R. C., SQUIRE, R. H. & FLORIAN, L. R. (1974). *J. Am. Chem. Soc.* 96, 2955–2963.
- YAMAMOTO, H., AOYAMA, H., OMOTE, Y., AKUTAGAWA, M., TAKENAKA, A. & SASADA, Y. (1977). *J. Chem. Soc. Chem. Commun.* pp. 63–64.
- YAMAMOTO, H., NAKAI, I., KASHIMA, C., OMOTE, Y. & AKUTAGAWA, M. (1983). *Chem. Lett.* pp. 1841–1844.

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Structure of Erythrosine B Ethanolate

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Abstract. $C_{20}H_{14}O_5 \cdot C_2H_6O$, $M_r = 881.95$, monoclinic, $P2_1/n$, $a = 12.509$ (3), $b = 12.940$ (2), $c = 16.129$ (3) Å, $\beta = 111.6$ (1)°, $V = 2427.4$ (2) Å³, $Z = 4$, $D_x = 2.41$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu =$

51.14 cm⁻¹, $F(000) = 1624$, $T = 295$ K, $R = 0.071$ for 6065 unique reflections. Erythrosine B, also known as FD and C Red No. 3, crystallizes as a free acid–ethanol solvate. The relative orientation of the benzoic acid and