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# Structure of Methyl 3-Benzyl-5-phenyl-3*H*-1,2,4-dioxazole-3-carboxylate

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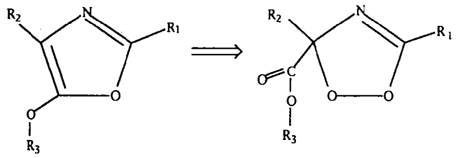
**Abstract.** $C_{17}H_{15}NO_4$, $M_r = 297.3$, monoclinic, $C2/c$, $a = 26.157$ (5), $b = 5.979$ (1), $c = 19.492$ (3) Å, $\beta = 97.79$ (1)°, $V = 3020$ (1) Å$^3$, $Z = 8$, $D_x = 1.31$ g cm$^{-3}$, $\lambda$(Cu $K\alpha$) = 1.5418 Å, $\mu = 7.36$ cm$^{-1}$, $F(000) = 1248$, room temperature, final $R = 0.058$ for 1545 independent reflections and 199 parameters. The five-membered heterocyclic ring shows an envelope conformation where one of the two peroxy O atoms occupies the apical position. The out-of-plane displacement is particularly small in relation to the valence state of the peroxy O atoms.

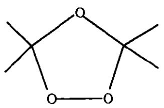
**Introduction.** Studies of oxidation with singlet molecular oxygen of 5-alkoxyoxazoles (I) have shown that, in favourable conditions, they are partly converted into 3-alkoxycarbonyl-1,2,4-dioxazoles (II) (Graziano, Iesce, Carotenuto & Scarpati, 1977*a*,*b*).



(I) (II)

The structure (II) was assigned on the basis of elemental and spectral data. To confirm the structure assignment, X-ray analysis of the title compound, where $R_1 = C_6H_5$, $R_2 = CH_2C_6H_5$ and $R_3 = CH_3$, has been carried out. This is the first X-ray characterization of this new heterocyclic system.

It is worth comparing the conformation of the dioxazole ring with that of trioxolane ring (III) as found in the structure of *trans*-5-[3,3-bis(methoxycarbonyl)-2-oxiranyl]-3-[2,2-bis(methoxycarbonyl)vinyl]-3,5-diphenyl-1,2,4-trioxolane (Giordano & Cermola, 1990).



(III)

Here the trioxolane ring exhibits a perfect envelope conformation with a pseudo-$C_s$ symmetry. One of the two adjacent peroxy O atoms is displaced by 0.657 (3) Å out of the plane formed by the other four intra-ring atoms. The relevant puckering of the ring has been ascribed to the need to stagger the electron lone pairs on the two adjacent O atoms, which appear to be in the $sp^3$-hybridized state.

**Experimental.** A prismatic crystal (0.2 × 0.3 × 0.5 mm), elongated along **b**, was used for data collection on an Enraf–Nonius CAD-4 automatic diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The unit-cell parameters and orientation matrix were obtained by a least-squares fitting of the setting angles of 25 reflections ($18 \leq \theta \leq 27°$). Out of 3146 independent reflections measured by the $\omega/\theta$ scan technique with $\theta \leq 75°$, 1545 having $I_o > 3\sigma(I_o)$ were used in the structure determination ($-32 \leq h \leq$

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^2$) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| O(1) | 428 (1) | 5042 (4) | 3270 (1) | 606 (6) |
| O(2) | 814 (1) | 3919 (4) | 2913 (1) | 699 (6) |
| O(3) | 1494 (1) | −258 (6) | 3997 (1) | 739 (8) |
| O(4) | 1651 (1) | 3377 (6) | 3891 (2) | 894 (9) |
| N | 464 (1) | 1494 (5) | 3655 (2) | 521 (6) |
| C(1) | 241 (1) | 3394 (5) | 3641 (2) | 458 (7) |
| C(2) | 891 (1) | 1750 (6) | 3248 (2) | 508 (7) |
| C(3) | −190 (1) | 4042 (5) | 4002 (2) | 435 (7) |
| C(4) | −342 (1) | 2537 (6) | 4480 (2) | 485 (8) |
| C(5) | −747 (2) | 3125 (7) | 4840 (2) | 589 (9) |
| C(6) | −996 (2) | 5149 (7) | 4724 (2) | 617 (9) |
| C(7) | −845 (2) | 6586 (7) | 4243 (2) | 600 (9) |
| C(8) | −440 (2) | 6058 (6) | 3881 (2) | 525 (8) |
| C(9) | 884 (1) | −40 (6) | 2690 (2) | 529 (8) |
| C(10) | 1354 (1) | −28 (5) | 2310 (2) | 435 (7) |
| C(11) | 1442 (1) | 1740 (6) | 1883 (2) | 500 (8) |
| C(12) | 1866 (2) | 1682 (7) | 1522 (2) | 570 (9) |
| C(13) | 2194 (2) | −123 (7) | 1581 (2) | 571 (9) |
| C(14) | 2110 (2) | −1882 (7) | 2009 (2) | 591 (9) |
| C(15) | 1687 (2) | −1842 (6) | 2373 (2) | 548 (8) |
| C(16) | 1390 (1) | 1794 (7) | 3743 (2) | 576 (8) |
| C(17) | 1958 (2) | −571 (9) | 4464 (3) | 1082 (20) |

Table 2. *Bond lengths* (Å) *and selected valence and torsion angles* (°)

| | | | |
|---|---|---|---|
| O(1)—O(2) | 1.464 (2) | C(2)—C(9) | 1.524 (3) |
| O(1)—C(1) | 1.352 (2) | C(9)—C(10) | 1.520 (3) |
| O(2)—C(2) | 1.454 (2) | C(10)—C(11) | 1.384 (3) |
| N—C(1) | 1.276 (2) | C(11)—C(12) | 1.392 (3) |
| N—C(2) | 1.462 (2) | C(12)—C(13) | 1.373 (3) |
| C(1)—C(3) | 1.458 (3) | C(13)—C(14) | 1.378 (3) |
| C(3)—C(4) | 1.392 (2) | C(14)—C(15) | 1.394 (3) |
| C(4)—C(5) | 1.392 (3) | C(15)—C(10) | 1.385 (3) |
| C(5)—C(6) | 1.379 (3) | C(2)—C(16) | 1.516 (3) |
| C(6)—C(7) | 1.369 (3) | C(16)—O(3) | 1.337 (3) |
| C(7)—C(8) | 1.387 (3) | C(16)—O(4) | 1.179 (3) |
| C(8)—C(3) | 1.376 (3) | O(3)—C(17) | 1.427 (3) |
| C(1)—O(1)—O(2) | 104.1 (1) | N—C(2)—C(16) | 108.2 (2) |
| O(1)—O(2)—C(2) | 104.9 (1) | C(9)—C(2)—C(16) | 113.1 (2) |
| O(2)—C(2)—N | 105.6 (1) | N—C(2)—C(9) | 112.2 (2) |
| C(2)—N—C(1) | 106.0 (1) | C(2)—C(9)—C(10) | 114.3 (2) |
| N—C(1)—O(1) | 117.5 (2) | C(2)—C(16)—O(3) | 109.5 (2) |
| C(3)—C(1)—O(1) | 115.1 (2) | C(2)—C(16)—O(4) | 126.1 (3) |
| C(3)—C(1)—N | 127.4 (2) | O(3)—C(16)—O(4) | 124.4 (3) |
| O(2)—C(2)—C(9) | 108.5 (2) | C(16)—O(3)—C(17) | 118.0 (2) |
| O(2)—C(2)—C(16) | 109.0 (2) | | |
| C(1)—O(1)—O(2)—C(2) | −12.7 (3) | N—C(2)—C(9)—C(10) | −172.8 (3) |
| O(1)—O(2)—C(2)—N | 13.6 (3) | O(2)—C(2)—C(9)—C(10) | 70.9 (4) |
| O(2)—C(2)—N—C(1) | −9.6 (4) | C(2)—C(9)—C(10)—C(11) | −67.3 (4) |
| C(2)—N—C(1)—O(1) | 1.3 (4) | N—C(2)—C(16)—O(3) | 72.5 (3) |
| N—C(1)—O(1)—O(2) | 7.4 (4) | O(2)—C(2)—C(16)—O(4) | 7.2 (5) |
| N—C(1)—C(3)—C(4) | 8.0 (5) | C(2)—C(16)—O(3)—C(17) | 178.7 (3) |

32, $-7 \le k \le 0$, $0 \le l \le 24$). The intensities of three monitor reflections, measured every 160 reflections, showed decay (maximum 10%); a linear correction was applied, in addition to the corrections for Lorentz–polarization effects, while absorption was neglected. The structure was solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares minimized $\sum w(\Delta F)^2$, where $w = 1/\sigma^2(F)$. The H atoms, generated at the expected positions taking into account the $\Delta F$ synthesis for the methyl group, were included in the final refinement with isotropic thermal factors 1.2 times larger than the $B_{eq}$ values of the carrier atoms. 199 refined parameters included an overall scale factor, and positional and anisotropic thermal parameters for the non-H atoms. Final $R = 0.058$, $wR = 0.096$, $S = 3.70$. Final $(\Delta/\sigma)_{max} = 0.01$; final difference electron density within ± 0.28 e Å$^{-3}$.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed by the Enraf–Nonius (1979) system of programs (*SDP*) on a VAX 750 computer at the Centro di Metodologie Chimico-fisiche dell'Università di Napoli.

Final atomic parameters of the non-H atoms are listed in Table 1.*

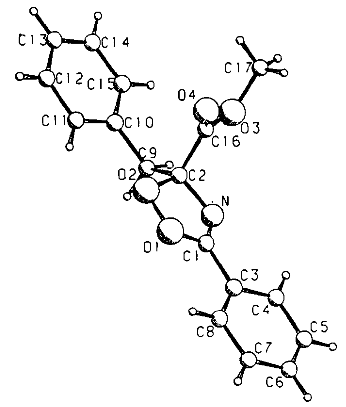

Fig. 1. Perspective view of the molecule with the atom-labelling scheme.

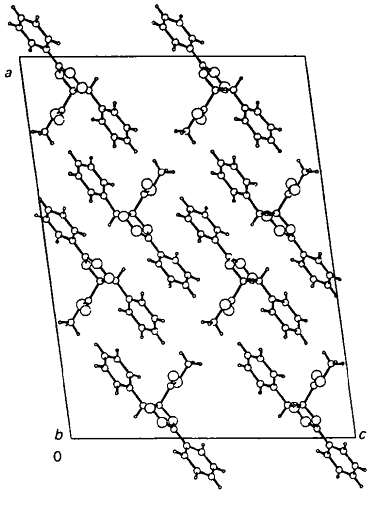

Fig. 2. Crystal packing projected down **b**.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55354 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0306]

**Discussion.** A view of the molecule with the atom-labelling scheme is shown in Fig. 1. Bond lengths and selected valence and torsion angles are presented in Table 2. The results of the X-ray analysis confirm the assignment of Graziano, Iesce, Carotenuto & Scarpati (1977*a*). The only structural features worthy of discussion concern the dioxazole ring. The ring displays an envelope conformation with the peroxy O(2) atom displaced by 0.211 (3) Å out of the plane of the other intra-ring atoms, each of which deviates by no more than 0.007 (4) Å. The puckering of the ring can also be expressed by the dihedral angle formed by the plane defined by O(1), C(1), N and C(2) and the plane defined by O(1), O(2) and C(2). The value of this angle is 13.7 (8)° whereas that of the corresponding angle in the trioxolane ring (III), which has an identical conformation, is 45.2 (2)°. Why is there such a large difference? The answer is given by examination of the lengths of the bonds formed by the O atoms. While O(1)—O(2) and O(2)—C(2) are of typical single-bond length, O(1)—C(1) [1.352 (2) Å] is intermediate between the lengths of a single and a double bond, giving evidence of $\pi$-electron conjugation of O(1) with the fragment consisting of N, C(1) and the attached phenyl group. Two concomitant and interdependent effects reduce the puckering of the dioxazole ring: the O(1)—C(1) partial double bond pushes O(2) towards the ring plane and the $\pi$ conjugation withdraws electron charge from the lone pairs of O(1) resulting in a smaller repulsion between the lone pairs on the two adjacent O atoms.

In conclusion, the valence state of the peroxy O atoms appears to be the major factor in determining the puckering of this heterocyclic ring. The crystal packing is presented in Fig. 2.

The author is grateful to Professor R. Scarpati and her research group for stimulating interest in this work and for providing the crystals. The work was financially supported by Progetto Finalizzato Chimica Fine e Secondaria 2 of CNR (Rome).

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# Structure of Polymorph II of (1*R*,3*S*)-1,2,2-Trimethyl-3-(4-methylthiobenzoyl)-cyclopentanecarboxylic Acid

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**Abstract.** $C_{17}H_{22}O_3S$, $M_r = 306.407$, orthorhombic, $P2_12_12$, $a = 13.327$ (5), $b = 19.277$ (8), $c = 6.361$ (2) Å, $V = 1634$ (1) Å$^3$, $Z = 4$, $D_x = 1.245$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1.54178 Å, $\mu = 1.77$ mm$^{-1}$, $F(000) = 656$, $T = 293$ K, $R = 0.043$ for 2574 observed reflections. Two crystalline forms of the title compound have been obtained but only one (form II) has given suitable crystals for X-ray structure analysis. The five-membered ring has an envelope conformation with C(2) 0.60 (1) Å out of

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