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Structure of 7,8-Dihydro-4,7,7-trimethyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione

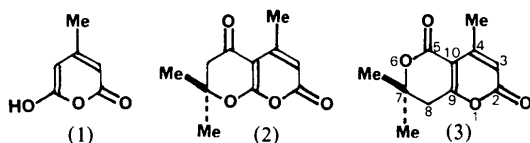
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Abstract. C₁₁H₁₂O₄, *M_r* = 208.2, monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 11.908 (5), *b* = 9.611 (4), *c* = 9.437 (6) Å, β = 107.99 (5)°, *V* = 1027.2 Å³, *D_x* = 1.35, *D_m* = 1.34 (1) g cm⁻³; Mo *K*α radiation, μ = 1.11 cm⁻¹, λ = 0.71073 Å. Final *R* = 0.043 for 1095 observations. The structure consists of one crystallographically independent molecule separated from its neighbors by ordinary van der Waals distances. The structure of the title compound was not the expected dimerization product.

Introduction. In the course of a reaction with 6-hydroxy-4-methyl-2-pyrone (1) (Bland & Thorpe, 1912) a dimerization occurred to yield a crystalline product, m.p. 426 K, which was thought to be (2) or (3). The preparation is described by Burke, Saunders & Murtiashaw (1981). Mechanistic and spectroscopic evidence favored structure (2), but (3) could not be eliminated. The structure analysis was undertaken to settle this issue.



The ring-closure product (2) or (3) was prepared as described by Burke *et al.* (1981). The crystals were grown from a hexane–ether solution over a period of two weeks. A single parallelepiped-shaped crystal of ~0.31 × 0.07 × 0.08 mm was mounted on a glass fiber on a goniometer head on a CAD-4 diffractometer

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Table 1. *Data collection and refinement parameters*

Graphite monochromator
Faces: (010), (0 $\bar{1}$ 0), ($\bar{1}$ 00), (110), (011), (0 $\bar{1}$ $\bar{1}$)
Absorption corrections made and max./min. transmission factors found were 0.997–0.985 (Frenz, 1980)
<i>P</i> factor = 0.030 in $\sigma(F_o^2) = [\sigma(I_{\text{rao}})^2 + (P \times I_{\text{rao}})^2]^{1/2}/Lp$ and $w = 1/\sigma(F_o)^2$
Data considered non-zero if $F^2 > 4\sigma(F^2)$
4509 independent <i>hkl</i> 's measured in ω -2 θ mode
1095 reflections used to solve and refine structure (data collection could have been terminated at lower 2 θ)
Three standard reflections monitored every 100 reflections, decay less than 2% <i>I</i>
Room temperature ~291 K
Structure refined by full-matrix least squares, including anisotropic temperature factors and anomalous-dispersion corrections with weights based upon intensity statistics (Frenz, 1980); function refined was $\sum_i w_i (F_o - F_c)^2$
Final least squares performed on Amdahl V6 with weights as per option 5 and $F_{\text{min}} = 3.5$ (Stewart, 1979)
Final <i>R</i> = 0.043, weighted <i>R</i> = 0.052
Error of observation of unit weight = 1.55

interfaced to a PDP-11/40 computer. The crystal was aligned and intensity data were collected by standard techniques (Enraf–Nonius, 1980). Details are found in Table 1.

The structure was solved with direct methods *via MULTAN 78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978; Main, 1976) in which the overall molecular geometry was utilized to generate starting phases. Without the molecular geometry, the phase sets generated *E* maps of continuous hexagonal geometry in which the structure was not readily apparent regardless of various levels of sin θ data truncations. Refinement was by full-matrix least squares

Table 2. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
O(6)	0.3437 (2)	0.0736 (2)	-0.0139 (2)	4.15 (7)
C(8)	0.2025 (3)	-0.0388 (3)	0.0871 (4)	4.8 (1)
O(1)	0.0789 (2)	0.1072 (2)	0.1767 (2)	4.46 (7)
C(3)	0.0828 (3)	0.3562 (3)	0.1698 (3)	4.2 (1)
C(2)	0.0320 (2)	0.2340 (3)	0.2065 (3)	4.3 (1)
C(10)	0.2145 (2)	0.2200 (3)	0.0772 (3)	3.3 (1)
C(4)	0.1704 (2)	0.3542 (3)	0.1063 (3)	3.7 (1)
C(9)	0.1672 (2)	0.1039 (3)	0.1142 (3)	3.6 (1)
O(2)	-0.0474 (2)	0.2224 (2)	0.2608 (3)	6.0 (1)
C(5)	0.3039 (2)	0.2025 (3)	-0.0003 (3)	3.8 (1)
C(11)	0.2190 (4)	0.4888 (4)	0.0708 (5)	5.2 (2)
C(13)	0.3497 (4)	-0.1711 (4)	-0.0008 (5)	5.7 (2)
O(5)	0.3404 (2)	0.2966 (2)	-0.0582 (3)	5.8 (1)
C(7)	0.3285 (2)	-0.0424 (3)	0.0801 (3)	3.9 (1)
C(12)	0.3215 (3)	0.9739 (4)	0.2300 (4)	5.6 (2)

Table 3. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

O(1)—C(2)	1.405 (4)	C(7)—O(6)	1.470 (4)
C(2)—C(3)	1.413 (5)	O(6)—C(5)	1.347 (4)
C(3)—C(4)	1.354 (5)	C(5)—C(10)	1.475 (4)
C(4)—C(10)	1.451 (4)	C(5)—O(5)	1.205 (4)
C(10)—C(9)	1.344 (4)	C(2)—O(2)	1.211 (4)
O(1)—C(9)	1.356 (4)	C(4)—C(11)	1.497 (5)
C(9)—C(8)	1.480 (4)	C(7)—C(12)	1.512 (4)
C(8)—C(7)	1.523 (5)	C(7)—C(13)	1.515 (5)
C(9)—O(1)—C(2)	121.1 (2)	O(1)—C(9)—C(8)	113.3 (3)
O(1)—C(2)—C(3)	116.4 (3)	C(9)—C(8)—C(7)	111.3 (3)
O(1)—C(2)—O(2)	114.6 (3)	C(8)—C(7)—O(6)	108.5 (2)
O(2)—C(2)—C(3)	129.1 (3)	C(8)—C(7)—C(13)	111.1 (3)
C(2)—C(3)—C(4)	123.0 (3)	C(8)—C(7)—C(12)	113.8 (3)
C(3)—C(4)—C(10)	118.0 (3)	O(6)—C(7)—C(13)	104.1 (3)
C(3)—C(4)—C(11)	119.4 (3)	O(6)—C(7)—C(12)	107.1 (2)
C(11)—C(4)—C(10)	122.6 (3)	C(13)—C(7)—C(12)	111.7 (3)
C(4)—C(10)—C(9)	118.9 (3)	C(7)—O(6)—C(5)	121.8 (2)
C(4)—C(10)—C(5)	123.6 (3)	O(6)—C(5)—C(10)	118.7 (3)
C(5)—C(10)—C(9)	117.3 (3)	O(6)—C(5)—O(5)	117.4 (3)
C(10)—C(9)—C(8)	124.1 (3)	C(10)—C(5)—O(5)	123.8 (3)
C(10)—C(9)—O(1)	122.5 (3)		

including anomalous-dispersion corrections, absorption corrections and anisotropic temperature factors for the non-H atoms. The H atoms were found from difference maps and were refined isotropically. The final *R* factor was 0.043. See Table 1 for details.* The atomic-coordinate parameters and errors are listed in Table 2. Important bond distances and angles are listed in Table 3. Least-squares-plane data are in Table 4. An *ORTEP* (Johnson, 1970) drawing of the structure is shown in

* Lists of structure factors, anisotropic thermal parameters H-atom parameters and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36842 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Least-squares plane

Equation of plane involving atoms O(1), C(2), C(3), C(4), C(10), C(9), C(11), O(2) = $Px + Qy + Rz = S$ where $P = 4.9506$, $Q = 0.1357$, $R = 6.9508$, $S = 1.6321$. Largest deviation from plane: ± 0.02 (1) Å.

Distances (Å) from other atoms to plane

C(5)	-0.10 (1)	C(7)	0.54 (1)
O(5)	-0.31 (1)	C(12)	2.19 (1)
C(8)	-0.03 (1)	C(13)	0.07 (1)
O(6)	-0.02 (1)		

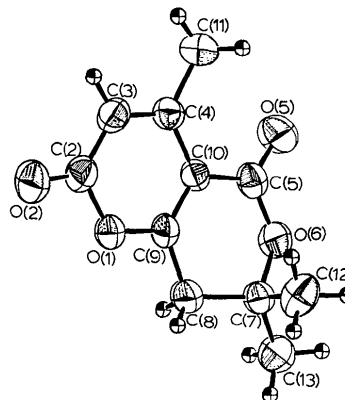


Fig. 1. An *ORTEP* (Johnson, 1970) drawing of the title molecule including the H atoms. The notation is consistent with the tables and molecular drawing (3). The ellipsoids of the non-H atoms are drawn at the 50% probability level. One H atom on C(11) is hidden by C(11). See Fig. 2.

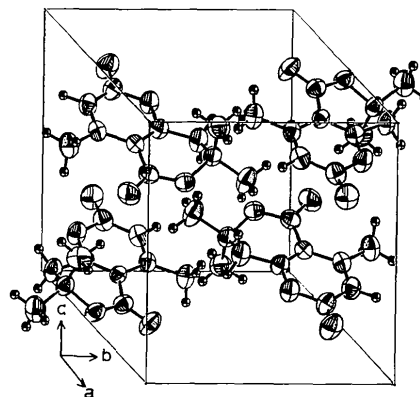


Fig. 2. An *ORTEP* (Johnson, 1970) drawing of the unit cell of the crystal structure of the title compound.

Fig. 1 and an *ORTEP* packing diagram is shown in Fig. 2.

Discussion. It was clear very early in the structure refinement that (2) was not the correct product of the reaction from the temperature factors of atoms at the 6 and 8 positions, and it was definitely established from

the H-atom locations. The correct structure of the reaction product is clearly (3). The mechanism to arrive at this product will be discussed by one of us (SDB) elsewhere. The structure consists, Fig. 2, of isolated molecules separated by ordinary van der Waals distances. The molecule is almost planar (see Table 4).

An examination of Table 4 reveals that the ring system containing O(1) is planar including the exocyclic atoms but the remainder of the molecule is considerably out of this plane. Therefore, there is considerable charge delocalization within the O(1) ring which must be responsible for the relatively short C(9)–O(1) distance of 1.356 (4) Å. In spite of the fact that C(5) is also bound to this same ring and one would expect it and its neighbor O(5) also to be planar with the ring, *vis à vis* its relationship to the C(9)–C(10) double bond, it is not. C(5) is –0.10 (1) Å and O(5) –0.31 (1) Å from this plane. This situation is probably due to the tetrahedral constraints imposed by C(8) and C(7). These geometrical factors in turn no doubt contribute to the shortening of the C(5)–O(6) distance to 1.347 (4) Å and are consistent with the C(5)–O(5) distance being observed shorter than the C(2)–O(2) distance. An additional factor contributing to the non-planarity of the O(6) ring is the relatively short non-bonded C(11)···O(5) distance of 2.842 (5) Å. The above delocalization, no doubt, exists in the starting material as well and probably contributes to the formation of the unexpected reaction product.

The remaining distances and angles are normal and have the expected values.

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Crystallographic Studies of High-Density Organic Compounds: 4-Amino-5-nitrobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]oxadiazole 3,8-Dioxide*

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Abstract. C₆H₂N₆O₆, *M_r* = 254.1, orthorhombic, *P*2₁2₁2₁, *a* = 13.6644 (6), *b* = 6.6969 (5), *c* = 9.5462 (8) Å, *D*_{calc} = 1.93 Mg m⁻³ for *Z* = 4; Cu *K*α(*λ* = 1.5418 Å) diffractometer data; 852 unique intensities; 747 intensities ≥ 3σ above background; final *R* = 0.034. The molecule is approximately planar; the largest out-of-plane deviations are associated with the

NH₂, NO₂ and two oxide groups. Bond lengths and angles in the five-membered rings are similar to values observed in other oxadiazoles and benzoxadiazoles. Benzene annelation has no significant effect on the basic oxadiazole structure. The molecules pack in sheets approximately perpendicular to *c*, the shortest contact being a 2.940 (5) Å C···O. Hydrogen bonding by one of the amino hydrogen atoms is limited to a strong intramolecular O···H–N contact with the neighboring nitro group, while the other hydrogen enters into somewhat weaker intra- and intermolecular contacts with oxygen.

* This name is the preferred one in line with IUPAC rules for organic nomenclature. The current *Chem. Abstr.* name is 5-nitrobenzo[1,2-*c*:3,4-*c'*]bis[1,2,5]oxadiazol-4-amine 3,8-dioxide. Our thanks to Dr K. L. Loening for this information.