$C_{16}H_{18}N_2O_3$

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# Methyl 1,6-Dihydro-1-(dimethylcarbamoyl)-4-methyl-6-oxo-2-phenyl-3-pyridinecarboxylate

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Abstract. $C_{17}H_{18}N_2O_4$, $M_r = 314\cdot34$, monoclinic, $P2_1/n$, $a = 8\cdot494$ (1), $b = 18\cdot303$ (3), $c = 10\cdot364$ (2) Å, $\beta = 101\cdot51$ (1)°, $V = 1578\cdot8$ (4) Å^3, $Z = 4$, $D_x = 1\cdot322$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71069$ Å, $\mu = 8\cdot9$ mm^{-1}, $F(000) = 664$, room temperature, final $R = 0\cdot041$ for 2051 observed reflections with $I > \sigma(I)$. Crystal grown by evaporation from ethyl ether and *n*-hexane. The title compound is an unexpected product of the alcoholysis of a substituted 6*H*-1,3-oxazin-6-one. The heterocyclic ring has an envelope conformation with C(2) out of the plane of the other atoms. The deviation from planarity is due to intermolecular interactions.

Introduction. As part of a continuing investigation on the structure and reactivity of 1,3-oxazin-6-ones and of their reaction products (Becalli, Benincori & Marchesini, 1988; Becalli & Marchesini, 1987; Becalli, Marchesini & Pilati, 1989; Pilati, 1988, 1989), we report the crystal and molecular structure of the title compound (III), obtained by Marchesini (1989), from the substituted 1,3-oxazin-6-one (I), according to the following scheme.
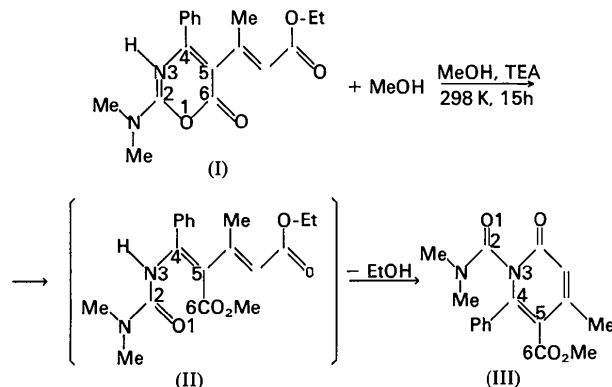
The title compound was completely unexpected; in fact, under the same conditions, the reaction of other 4,5-substituted 2-(*N,N*-dimethylamino)-1,3-oxazin-6-ones gives acyclic compounds like (II), or products in which the dimethylamino group is shifted from position 2 to position 6. This X-ray crystal analysis was undertaken to confirm the structure of this new product.

Experimental. IR data (Nujol): 1716, 1668, 1602 cm^{-1}; ^{1}H NMR data (CHCl$_3$): 7·4 (5*H,m*), 6·4 (1*H,s*), 3·43 (3*H,s*), 2·85 (3*H,s*), 2·80 (3*H,s*), 2·3 (3*H,s*); melting point 396–397 K. Crystal size 0·35 × 0·25 × 0·075 mm. Nonius CAD-4 diffractometer with graphite monochromator; lattice parameters determined using 25 reflections in the θ range 13–15°; data collection $0 < \theta < 25°$; *hkl* range: 0→10, 0→21, −12→12; three standard reflections, no significant variation of intensity. Of 2765 independent data collected, 2051 with $I > \sigma(I)$ were considered observed. Data were corrected for Lorentz and polarization coefficients, not for absorption. The structure was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). All heavy atoms were obtained from the 'best' E map. H atoms placed in calculated positions, refined isotropically, non-H anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4I_o/[\sigma^2(I_o) + 0\cdot0001I_o^2]$ and I_o is the intensity on an absolute scale. A secondary-extinction parameter g [Larson (1967), equation (3)] was refined [final value $6\cdot0$ (7) × 10^{-6}]. The range of the final difference Fourier map was $\pm 0\cdot2$ e Å^{-3}; in the last cycle, $(\Delta/\sigma)_{max}$ was 0·05; $S = 1\cdot90$, $R = 0\cdot041$ and $wR = 0\cdot034$ for 2051 observed reflections. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

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Programs used include Enraf–Nonius *SDP* (Frenz, 1983), *ORTEP*II (Johnson, 1976), *PARST* (Nardelli, 1983), and various in-house programs for refinement and geometrical analysis running on a Gould NP1 computer.

Discussion. Table 1 lists final refined coordinates and U_{eq} values for non-H atoms.* Fig. 1 shows the molecule with the numbering scheme of heavy atoms. Table 2 reports bond distances and bond angles. The heterocyclic ring has an envelope conformation, with atoms N(1), C(3), C(4), C(5) and C(6) strictly on the same plane A; atoms C(2) and O(7) are out of the plane in the same direction by 0·050 (2) and 0·138 (2) Å, respectively. This small but significant distortion from planarity is probably due to the intermolecular interactions between O(7) and two C(12) methyl groups located at (i) $-\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$ and (ii) $-x$, $-y$, $1 - z$, respectively; the short distances involved are: O(7)···C(12^i) 3·284 (4), O(7)···C(12^{ii}) 3·358 (3), O(7)···H(122^i) 2·54 (3) and O(7)···H(123^{ii}) 2·59 (3) Å. With O(7) on the plane A, these distances would become much more asymmetric (3·171, 3·495, 2·44 and 2·72 Å, respectively). The atoms of the benzene ring (plane B) are coplanar, within a maximum deviation of 0·005 (2) Å. The closeness of the benzene ring to the methoxycarbonyl and dimethylaminocarbonyl groups prevents much conjugation between the heterocyclic ring and these three groups; in fact, the dihedral angle between the planes A and B is 49·66 (7)°; those between A and the least-squares planes through C(5), C(9), O(10), O(11) and through N(1), C(19), O(20) and O(21) are even greater, being 70·71 (8) and 75·65 (8)°, respectively.

* Lists of structure factors, anisotropic thermal parametrs and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52975 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
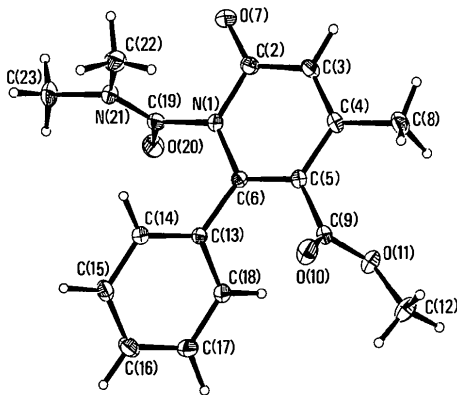

Fig. 1. *ORTEP*II (Johnson, 1976) plot of the molecule with numbering scheme. Thermal ellipsoids at 20% of probability; H atoms not to scale.

Table 1. *Final atomic coordinates and equivalent isotropic temperature factors* (Å²)

$$U_{eq} = (1/6\pi^2)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(7)	−0·0159 (2)	0·21940 (8)	0·3288 (2)	0·0490 (6)
O(10)	−0·1985 (2)	−0·10244 (9)	0·1680 (2)	0·0589 (7)
O(11)	−0·1446 (2)	−0·11290 (8)	0·3865 (1)	0·0454 (5)
O(20)	0·3216 (2)	0·12775 (9)	0·3352 (2)	0·0553 (7)
N(1)	0·0491 (2)	0·10527 (9)	0·2685 (2)	0·0334 (6)
N(21)	0·1946 (2)	0·1746 (1)	0·1393 (2)	0·0437 (7)
C(2)	−0·0531 (3)	0·1543 (1)	0·3176 (2)	0·0383 (8)
C(3)	−0·1922 (3)	0·1214 (1)	0·3505 (2)	0·0407 (9)
C(4)	−0·2198 (2)	0·0489 (1)	0·3447 (2)	0·0367 (8)
C(5)	−0·1079 (2)	0·0022 (1)	0·2985 (2)	0·0327 (7)
C(6)	0·0254 (2)	0·0303 (1)	0·2611 (2)	0·0319 (7)
C(8)	−0·3680 (3)	0·0170 (2)	0·3822 (3)	0·055 (1)
C(9)	−0·1521 (3)	−0·0764 (1)	0·2750 (2)	0·0371 (8)
C(12)	−0·2141 (4)	−0·1855 (2)	0·3742 (3)	0·058 (1)
C(13)	0·1447 (2)	−0·0159 (1)	0·2114 (2)	0·0315 (7)
C(14)	0·1934 (3)	−0·0011 (1)	0·0938 (2)	0·0370 (8)
C(15)	0·3008 (3)	−0·0469 (1)	0·0487 (2)	0·0452 (9)
C(16)	0·3587 (3)	−0·1083 (1)	0·1193 (3)	0·0507 (9)
C(17)	0·3101 (3)	−0·1239 (1)	0·2353 (3)	0·0497 (9)
C(18)	0·2050 (3)	−0·0780 (1)	0·2812 (2)	0·0404 (8)
C(19)	0·2024 (3)	0·1377 (1)	0·2508 (2)	0·0392 (8)
C(22)	0·0483 (4)	0·1906 (2)	0·0439 (3)	0·054 (1)
C(23)	0·3445 (4)	0·2055 (2)	0·1139 (4)	0·070 (1)

Table 2. *Bond distances* (Å) *and angles* (°)

O(7)—C(2)	1·232 (2)	O(10)—C(9)	1·200 (3)
O(11)—C(9)	1·326 (2)	O(11)—C(12)	1·450 (4)
O(20)—C(19)	1·213 (3)	N(1)—C(2)	1·412 (3)
N(1)—C(6)	1·387 (2)	N(1)—C(19)	1·475 (3)
N(21)—C(19)	1·329 (3)	N(21)—C(22)	1·455 (3)
N(21)—C(23)	1·464 (4)	C(2)—C(3)	1·427 (4)
C(3)—C(4)	1·345 (3)	C(4)—C(5)	1·431 (3)
C(4)—C(8)	1·508 (4)	C(5)—C(6)	1·368 (3)
C(5)—C(9)	1·493 (3)	C(6)—C(13)	1·489 (3)
C(13)—C(14)	1·390 (3)	C(13)—C(18)	1·389 (3)
C(14)—C(15)	1·387 (3)	C(15)—C(16)	1·377 (3)
C(16)—C(17)	1·377 (5)	C(17)—C(18)	1·378 (4)

C(9)—O(11)—C(12)	116·0 (2)	C(6)—N(1)—C(19)	120·9 (2)
C(2)—N(1)—C(19)	114·2 (2)	C(2)—N(1)—C(6)	123·8 (2)
C(22)—N(21)—C(23)	117·1 (2)	C(19)—N(21)—C(23)	117·3 (2)
C(19)—N(21)—C(22)	125·5 (2)	O(7)—C(2)—N(1)	118·9 (2)
N(1)—C(2)—C(3)	114·6 (2)	O(7)—C(2)—C(3)	126·5 (2)
C(2)—C(3)—C(4)	123·4 (2)	C(3)—C(4)—C(8)	121·2 (2)
C(3)—C(4)—C(5)	118·9 (2)	C(5)—C(4)—C(8)	119·9 (2)
C(4)—C(5)—C(9)	117·9 (2)	C(4)—C(5)—C(6)	120·8 (2)
C(6)—C(5)—C(9)	120·7 (2)	N(1)—C(6)—C(5)	118·4 (2)
C(5)—C(6)—C(13)	122·9 (2)	N(1)—C(6)—C(13)	118·7 (2)
O(11)—C(9)—C(5)	112·2 (2)	O(10)—C(9)—C(5)	124·1 (2)
O(10)—C(9)—O(11)	123·6 (2)	C(6)—C(13)—C(18)	119·4 (2)
C(6)—C(13)—C(14)	122·4 (2)	C(14)—C(13)—C(18)	118·2 (2)
C(13)—C(14)—C(15)	120·6 (2)	C(14)—C(15)—C(16)	120·2 (2)
C(15)—C(16)—C(17)	119·7 (2)	C(16)—C(17)—C(18)	120·2 (2)
C(13)—C(18)—C(17)	121·1 (2)	N(1)—C(19)—N(21)	114·9 (2)
O(20)—C(19)—N(21)	126·4 (2)	O(20)—C(19)—N(1)	118·7 (2)

There are a few other short intermolecular contacts; the most significant are between O(10) and the hydrogen atoms H(223)$(-x, -y, -z)$ and H(14)$(-x, -y, -z)$ [2·40 (4) and 2·53 (2) Å, respectively], and O(20)···H(82)$(x - 1, y,z)$ [2·48 (2) Å].

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Structures of Double-Hydrogen-Bonded Adducts of 1,8-Biphenylenediol and Related Compounds

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Abstract. X-ray crystal structures were determined for 1,8-biphenylenediol (1) and its 1:1 adducts with hexamethylphosphoric triamide (4), 2,6-dimethyl-4-pyrone (5) and 1,2,6-trimethyl-4-pyridone (6), for the adduct of 4,5-dinitro-1,8-biphenylenediol (2) with (5), for the adduct of 2,7-dimethyl-1,8-biphenylenediol (3) with (6), and for 1,8-dimethoxybiphenylene (7). 1,8-Biphenylenediol, (1), $C_{12}H_8O_2$, $M_r = 184\cdot20$, orthorhombic, $Pca2_1$, $a = 14\cdot056$ (2), $b = 4\cdot952$ (1), $c = 24\cdot134$ (3) Å, $V = 1680$ Å^3, $Z = 8$, $D_x = 1\cdot46$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0\cdot92$ cm^{-1}, $F(000) = 768$, $T = 150$ K, final $R = 0\cdot048$ for all 1985 unique reflections. 1,8-Biphenylenediol–hexamethylphosphoric triamide, (1.4), $C_{12}H_8O_2 . C_6H_{18}N_3OP$, $M_r = 363\cdot40$, monoclinic, $P2_1/n$, $a = 8\cdot527$ (1), $b = 15\cdot099$ (4), $c = 15\cdot354$ (3) Å, $\beta = 95\cdot17$ (1)°, $V = 1969$ Å^3, $Z = 4$, $D_x = 1\cdot23$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 1\cdot54$ cm^{-1}, $F(000) = 776$, $T = 217$ K, final $R = 0\cdot077$ for the 2351 unique reflections with $F_o^2 \geq 2\sigma(F_o^2)$. 1,8-Biphenylenediol–2,6-dimethyl-4-pyrone, (1.5), $C_{12}H_8O_2 . C_7H_8O_2$, $M_r = 308\cdot34$, triclinic, $P\bar{1}$, $a = 8\cdot983$ (1), $b = 13\cdot450$ (2), $c = 6\cdot926$ (1) Å, $\alpha = 85\cdot15$ (1), $\beta = 106\cdot19$ (1), $\gamma = 109\cdot72$ (1)°, $V = 756$ Å^3, $Z = 2$, $D_x = 1\cdot35$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0\cdot88$ cm^{-1}, $F(000) = 324$, $T = 148$ K, final $R = 0\cdot048$ for the 2592 unique reflections with $F_o^2 \geq 1\cdot5\sigma(F_o^2)$. 1,8-Biphenylenediol–1,2,6-trimethyl-4-pyridone, (1.6), $C_{12}H_8O_2 . C_8H_{11}NO$, $M_r = 321\cdot38$, monoclinic, $P2_1/n$, $a = 7\cdot639$ (1), $b = 22\cdot130$ (4), $c = 9\cdot411$ (1) Å, $\beta = 90\cdot66$ (1)°, $V =$ 1591 Å^3, $Z = 4$, $D_x = 1\cdot34$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0\cdot84$ cm^{-1}, $F(000) = 680$, $T = 150$ K, final $R = 0\cdot048$ for the 2188 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$. 4,5-Dinitro-1,8-biphenylenediol–2,6-dimethyl-4-pyrone, (2.5), $C_{12}H_6N_2O_6 . C_7H_8O_2$, $M_r = 398\cdot33$, monoclinic, $P2_1/n$, $a = 12\cdot298$ (4), $b = 9\cdot173$ (2), $c = 16\cdot247$ (6) Å, $\beta = 102\cdot59$ (2)°, $V = 1789$ Å^3, $Z = 4$, $D_x = 1\cdot48$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 1\cdot10$ cm^{-1}, $F(000) = 824$, $T = 292$ K, final $R = 0\cdot122$ for 1886 unique observed reflections with $F_o^2 \geq 0$. 2,7-Dimethyl-1,8-biphenylenediol–1,2,6-trimethyl-4-pyridone, (3.6), $C_{14}H_{12}O_2 . C_8H_{11}NO$, $M_r = 349\cdot43$, orthorhombic, $Cmca$, $a = 20\cdot489$ (5), $b = 7\cdot736$ (1), $c = 24\cdot930$ (6) Å, $V = 3951$ Å^3, $Z = 8$, $D_x = 1\cdot17$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0\cdot73$ cm^{-1}, $F(000) = 1488$, $T = 294$ K, final $R = 0\cdot130$ for the 921 unique observed reflections with $F_o^2 \geq 0$. 1,8-Dimethoxybiphenylene, (7), $C_{14}H_{12}O_2$, $M_r = 212\cdot25$, monoclinic, $P2_1/c$, $a = 15\cdot378$ (3), $b = 13\cdot360$ (3), $c = 10\cdot896$ (2) Å, $\beta = 109\cdot57$ (1)°, $V = 2109$ Å^3, $Z = 8$, $D_x = 1\cdot34$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0\cdot83$ cm^{-1}, $F(000) = 896$, $T = 159$ K, final $R = 0\cdot041$ for the 3011 unique observed reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Each molecule of (1) is hydrogen bonded through its two hydroxy groups, either as donor or acceptor, to four other molecules of (1). For each of the five adducts both hydroxylic H atoms of the diol are hydrogen bonded to the same basic O atom of the base. This basic O atom is within 0·45 Å of the least-squares plane of the biphenylene ring in all cases. In the adducts the distances between the two hydroxy O atoms are increased to an average 4·28 (4) from the average

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