

## The Crystal Structure of a Pyrazomycin Analogue: 4,5-Dimethoxycarbonyl-3-(2,3-*O*-isopropylidene- $\beta$ -D-erythrofuransyl)-1-*p*-nitrophenylpyrazole (CPOP)

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Pyrazomycin analogue  $C_{20}H_{21}N_3O_9$ , CPOP, is monoclinic,  $P2_1$ ,  $a=14.276$  (7),  $b=12.852$  (6),  $c=5.735$  (5) Å,  $\beta=95.06$  (4)°,  $U=1048.14$  Å<sup>3</sup>,  $Z=2$ , F.W. 447.4,  $D_x=1.417$  g cm<sup>-3</sup>,  $F(000)=468$ . Counter technique, direct methods, least-squares refinement,  $R=6.2\%$  ( $R_w=2.2\%$ ) for 1258 reflexions measured at 20°C. The *C*-nucleoside CPOP is of interest as an analogue of pyrazomycin, an antitumour and antiviral antibiotic. In this  $\beta$ -anomer, the erythrofuransyl moiety is found in an unusual conformation with a torsion angle N(2)-C(1)-C(1')-O(1') [ $\chi$ ] equal to 122.8°. The arrangement and conformation of the substituents on the pyrazole ring are discussed. A pseudo plane of symmetry through the erythrofuransyl moiety is present.

### Introduction

CPOP ( $C_{20}H_{21}N_3O_9$ ) was supplied by Dr Françoise Perret and Professor J. M. J. Tronchet.\* This paper forms part of several studies on the syntheses of *C*-nucleosides (Tronchet & Perret 1970, 1971, 1972; Perret, 1974; Tronchet, Perret, Barbalat-Rey & Nguyen-Xuan, 1976). The structure is of interest because of its relation to pyrazomycin( $\beta$ ) which has considerable medicinal potential due to its antiviral and antitumor activity (Gerzon, Williams, Hoehn, Gorman & Delong, 1969). The structure of pyrazomycin( $\beta$ ) was solved by Jones & Chaney (1972) and the pyrazomycin B( $\alpha$ ) isomer by Gutowski, Chaney, Jones, Hamill, Davis & Miller (1973). Both compounds could be isolated from the same strain of *Streptomyces candidus*. However, CPOP and pyrazomycin show noticeable differences. For example in CPOP there are bulky substituents such as the *p*-nitrobenzene and methoxycarbonyl groups. But still more significant seems to be that CPOP has no free hydroxyl groups.

These differences can be expected to modify both the molecular and crystal structures, and the biological activity.

### Experimental

CPOP was obtained as fine crystals. Reciprocal-lattice explorer photographs allowed the determination of possible space groups  $P2_1$  or  $P2_1/m$  (systematic absences  $0k0$  with  $k \neq 2n$ ). 1544 intensities ( $1258 \geq 3\sigma$ ) were collected at 20°C on a Philips PW 1100 automatic diffractometer ( $\omega$ - $2\theta$  scan, Mo  $K\alpha$  radiation,  $\lambda=0.7107$  Å, graphite monochromator). The crystal data are shown in Table 1.

Table 1. Crystal data of CPOP

$C_{20}H_{21}N_3O_9$	F.W. 447.4
Monoclinic	$P2_1$ (No. 4)
$a=14.276$ (7) Å	$U=1048.14$ Å <sup>3</sup>
$b=12.852$ (6)	$Z=2$
$c=5.735$ (3)	
$\beta=95.06$ (4)°	$F(000)=468$
$D_x=1.417$ g cm <sup>-3</sup>	$\lambda(\text{Mo } K\alpha)=0.7107$ Å

The data were adjusted to an absolute scale by a Wilson plot and normalized structure factors were derived from the  $K$  curve ( $K=I/\langle I \rangle$ ). The cumulative distribution indicated the absence of a centre of symmetry and confirmed  $P2_1$ . The atoms of the *p*-nitrobenzene group and of the pyrazole ring were located with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Other atoms were subsequently found by the phase recycling process (Karle, 1968) provided in *SFCALC* of this program. The remaining heavy atoms were found from Fourier syntheses. Scattering factors computed from Hartree-Fock wave functions (Cromer & Mann, 1968) were used.\* In the preliminary stages of refinement the data set was limited to  $\sin \theta/\lambda < 0.3$  Å<sup>-1</sup>. Refinement was carried out with *CRYLSQ* (X-RAY system, 1974). The function minimized was  $\sum w(\Delta F^2)$  where  $w=1/\sigma^2(F_o)$ . Atomic positions and anisotropic thermal parameters of the heavy atoms, given in Table 2, were refined by full-matrix least squares. The positions of the H atoms found from difference maps and by calculations with *BONDAT* (X-RAY system, 1974) are given in Table

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31739 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Table 2. *Positional and thermal parameters of the heavy atoms* ( $\times 10^4$ )

The e.s.d.'s are in parentheses. The temperature parameters ( $\times 10^3$ ) have the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>31</sub>	<i>U</i> <sub>23</sub>
C(1)	2304 (4)	-6382 (6)	6774 (12)	36 (4)	16 (4)	45 (5)	7 (3)	8 (4)	8 (4)
C(2)	1734 (4)	-7225 (7)	7383 (12)	34 (4)	41 (4)	48 (5)	8 (4)	16 (4)	-3 (4)
C(3)	1992 (4)	-8045 (7)	6093 (12)	29 (4)	34 (4)	45 (5)	-4 (3)	4 (4)	10 (4)
C(4)	3286 (4)	-8277 (7)	3353 (12)	38 (4)	31 (4)	50 (5)	-13 (4)	9 (4)	-16 (4)
C(5)	3576 (5)	-9286 (6)	4014 (12)	62 (5)	28 (5)	55 (5)	-3 (4)	25 (4)	1 (4)
C(6)	4176 (5)	-9793 (8)	2620 (15)	44 (4)	26 (4)	78 (6)	1 (4)	14 (5)	2 (5)
C(7)	4478 (5)	-9289 (7)	694 (13)	32 (4)	42 (5)	61 (6)	-2 (4)	9 (4)	-13 (5)
C(8)	4206 (5)	-8294 (7)	103 (13)	44 (4)	60 (6)	47 (5)	-4 (4)	14 (4)	-2 (5)
C(9)	3595 (5)	-7787 (6)	1485 (13)	46 (6)	32 (4)	52 (5)	1 (4)	12 (4)	-8 (4)
C(1')	2283 (5)	-5300 (6)	7650 (14)	38 (4)	32 (4)	60 (5)	4 (4)	9 (4)	1 (4)
C(2')	2924 (5)	-4551 (6)	6401 (12)	47 (4)	31 (4)	43 (5)	5 (4)	-1 (4)	3 (4)
C(3')	2240 (5)	-3956 (6)	4603 (13)	64 (5)	37 (5)	46 (5)	-4 (4)	1 (4)	-11 (4)
C(4')	1291 (5)	-4503 (7)	4806 (14)	61 (5)	50 (5)	63 (6)	2 (5)	-21 (4)	-23 (5)
C(5')	3043 (5)	-2783 (6)	7069 (13)	67 (5)	30 (4)	53 (5)	4 (4)	-9 (4)	-1 (5)
C(6')	3814 (8)	-2375 (9)	5691 (19)	93 (7)	64 (6)	92 (7)	-19 (5)	16 (6)	14 (6)
C(7')	2865 (7)	-2037 (9)	9058 (18)	87 (6)	51 (6)	77 (6)	-1 (5)	11 (5)	-5 (5)
C(8')	1058 (5)	-7177 (8)	9148 (17)	55 (5)	43 (5)	84 (6)	12 (5)	21 (5)	20 (5)
C(9')	-310 (6)	-7908 (8)	10511 (18)	76 (6)	114 (8)	147 (9)	-41 (6)	49 (6)	9 (8)
C(10')	1640 (5)	-9171 (6)	5942 (15)	50 (4)	24 (4)	69 (6)	1 (4)	25 (4)	-7 (4)
C(11')	1037 (7)	-10479 (9)	3381 (21)	86 (6)	43 (5)	146 (9)	-21 (5)	-12 (6)	-31 (6)
N(1)	2698 (3)	-7721 (5)	4798 (9)	39 (4)	32 (4)	44 (4)	5 (3)	14 (3)	-1 (3)
N(2)	2901 (4)	-6682*	5240 (10)	37 (4)	18 (3)	56 (5)	-2 (3)	2 (3)	-8 (3)
N(3)	5151 (4)	-9848 (7)	-780 (13)	40 (4)	71 (5)	73 (5)	-3 (4)	13 (4)	-43 (5)
O(1)	5434 (4)	-10687 (5)	-10 (10)	95 (5)	54 (4)	120 (5)	27 (4)	41 (4)	-28 (4)
O(2)	5388 (3)	-9395 (6)	-2458 (9)	86 (4)	117 (5)	57 (4)	25 (4)	40 (3)	4 (4)
O(1')	1349 (3)	-4901 (5)	7127 (9)	47 (3)	36 (3)	81 (4)	3 (2)	21 (3)	-5 (3)
O(2')	3277 (3)	-3770 (5)	8025 (8)	53 (3)	31 (3)	54 (4)	-2 (2)	-7 (3)	-1 (3)
O(3')	2204 (3)	-2924 (5)	5610 (8)	62 (3)	27 (3)	72 (4)	8 (2)	-14 (3)	-5 (3)
O(4')	345 (3)	-7824 (5)	8585 (9)	70 (4)	65 (4)	96 (4)	-24 (3)	50 (3)	-18 (4)
O(5')	1141 (4)	-6650 (6)	10876 (10)	105 (4)	88 (5)	55 (4)	-15 (4)	32 (3)	-26 (4)
O(6')	1357 (3)	-9413 (5)	3751 (10)	64 (3)	34 (3)	92 (5)	-11 (3)	2 (3)	-11 (3)
O(7')	1624 (5)	-9707 (5)	7607 (10)	176 (5)	35 (3)	83 (5)	-15 (4)	34 (4)	11 (3)

\* The *y* coordinate of this atom was kept constant during refinement in order to fix the origin.

Table 3. *Positional and thermal parameters of the hydrogen atoms* ( $\times 10^3$ )

Isotropic temperature factors ( $\times 10^2$ ) are expressed as:  $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$ . E.s.d.'s are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(C5)	334 (3)	-982 (4)	592 (9)	8 (2)
H(C6)	441 (3)	-1044 (4)	314 (8)	5 (2)
H(C8)	442 (3)	-802 (3)	-161 (8)	4 (2)
H(C9)	330 (2)	-716 (3)	85 (6)	2 (2)
H(C1')	248 (2)	-543 (3)	946 (7)	2 (1)
H(C2')	368 (4)	-477 (5)	559 (10)	10 (2)
H(C3')	236 (3)	-394 (4)	263 (8)	5 (2)
H(C4')	54 (4)	-391 (5)	417 (11)	11 (2)
H'(C4')	128 (3)	-517 (4)	379 (8)	6 (2)
H(C6')	345 (3)	-167 (4)	440 (9)	5 (2)
H'(C6')	400 (4)	-263 (5)	473 (10)	9 (2)
H''(C6')	444 (4)	-192 (5)	613 (10)	10 (2)
H(C7')	237 (2)	-225 (3)	990 (6)	1 (2)
H'(C7')	268 (5)	-141 (6)	850 (12)	11 (3)
H''(C7')	351 (4)	-183 (6)	980 (11)	11 (3)
H(C11')	160 (4)	-1085 (4)	374 (10)	6 (2)
H'(C11')	60 (3)	-1075 (4)	488 (8)	5 (2)
H''(C11')	82 (3)	-1055 (4)	224 (9)	6 (2)
H(C9')*	-92	-749	1008	4.5
H'(C9')*	-48	-867	1080	4.5
H''(C9')*	9	-757	1208	4.5

\* Parameters of hydrogens around C(9') were not refined.

3. For all the H atoms except those around C(9') the positional and isotropic thermal parameters could be refined. For H(C4') and H(C5), however, slightly abnormal distances were found. The final cycle gave  $R = \sum | \Delta F | / \sum | F_o | = 0.062$  for 1258 reflexions with  $F \geq 3\sigma$  (including those calculating greater than L-T threshold).

### Discussion

The bond distances and angles for the heavy atoms calculated with *BONDLA* (X-RAY system, 1974) are given in Table 4 and in Fig. 1. All values are in the expected range. Several torsion angles calculated with the same program are given in Table 5. The deviations of atoms from several least-squares planes are listed in Table 6.

Both the benzene and the pyrazole rings are nearly planar, as seen from the small deviations of the atoms included in planes 1 and 2. A deviation of 0.127 Å of C(4) out of plane 2 indicates a twist on the bond connecting the two rings. The angle between planes 1 and 2 is 38.4°, in good agreement with calculated values (Perret, 1974) based on UV data for CPOP analogues substituted on C(3).

Table 4. Bond angles ( $^{\circ}$ ) for all non-hydrogen atoms

E.s.d.'s are given in parentheses.

C(2)—C(1)—C(1')	127.3 (6)	C(3)—C(10')—O(6')	110.3 (6)
N(2)—C(1)—C(1')	121.9 (6)	C(3)—C(10')—O(7')	122.4 (7)
C(2)—C(1)—N(2)	110.8 (6)	O(7')—C(10')—O(6')	127.2 (8)
C(1)—C(2)—C(3)	105.7 (6)	C(10')—O(6')—C(11')	115.2 (7)
C(1)—C(2)—C(8')	124.6 (7)	C(2)—C(8')—O(5')	124.9 (8)
C(3)—C(2)—C(8')	129.7 (8)	C(2)—C(8')—O(4')	110.2 (7)
C(2)—C(3)—N(1)	107.9 (7)	O(4')—C(8')—O(5')	124.9 (8)
N(1)—C(3)—C(10')	120.7 (7)	C(9')—O(4')—C(8')	112.1 (7)
C(2)—C(3)—C(10')	131.4 (7)	C(1)—C(1')—C(2')	113.4 (6)
C(3)—N(1)—N(2)	110.2 (6)	C(1)—C(1')—O(1')	108.1 (6)
C(4)—N(1)—N(2)	117.8 (5)	O(1')—C(1')—C(2')	104.9 (6)
C(3)—N(1)—C(4)	131.6 (7)	C(1')—C(2')—O(2')	108.9 (6)
N(1)—N(2)—C(1)	105.3 (5)	C(1')—C(2')—C(3')	104.5 (5)
C(4)—C(9)—C(8)	119.9 (7)	C(3')—C(2')—O(2')	104.5 (5)
C(7)—C(8)—C(9)	118.3 (7)	C(2')—O(2')—C(5')	108.7 (5)
C(6)—C(7)—C(8)	122.2 (7)	O(2')—C(5')—O(3')	105.9 (6)
C(6)—C(7)—N(3)	118.8 (7)	C(6')—C(5')—C(7')	110.5 (8)
C(8)—C(7)—N(3)	118.9 (7)	O(2')—C(5')—C(6')	111.0 (7)
C(5)—C(6)—C(7)	119.6 (8)	O(2')—C(5')—C(7')	108.9 (6)
C(4)—C(5)—C(6)	117.5 (7)	O(3')—C(5')—C(6')	110.8 (7)
C(5)—C(4)—C(9)	122.4 (7)	O(3')—C(5')—C(7')	109.6 (7)
C(5)—C(4)—N(1)	118.8 (6)	C(3')—O(3')—C(5')	107.2 (6)
C(9)—C(4)—N(1)	118.6 (7)	O(3')—C(3')—C(2')	103.2 (5)
C(7)—N(3)—O(2)	117.1 (8)	O(3')—C(3')—C(4')	108.9 (6)
C(7)—N(3)—O(1)	115.0 (7)	C(4')—C(3')—C(2')	103.3 (6)
O(1)—N(3)—O(2)	127.7 (8)	O(1')—C(4')—C(3')	104.8 (6)
		C(1')—O(1')—C(4')	107.5 (5)

Table 5. Torsion angles ( $^{\circ}$ )

N(2)—N(1)—C(4)—C(9)	-38.8 (8)
C(8)—C(7)—N(3)—O(2)	-2.5 (9)
N(1)—C(3)—C(10')—O(6')	-56.7 (8)
C(3)—C(2)—C(8')—O(4')	-34.2 (10)
N(2)—C(1)—C(1')—O(1')	122.8 (6)
N(2)—C(1)—C(1')—C(2')	6.9 (9)
N(2)—C(1)—C(1')—H(C1')	-117 (2)
C(2')—C(3')—C(4')—O(1')	27.1 (8)
C(2')—C(3')—O(3')—C(5')	24.4 (7)

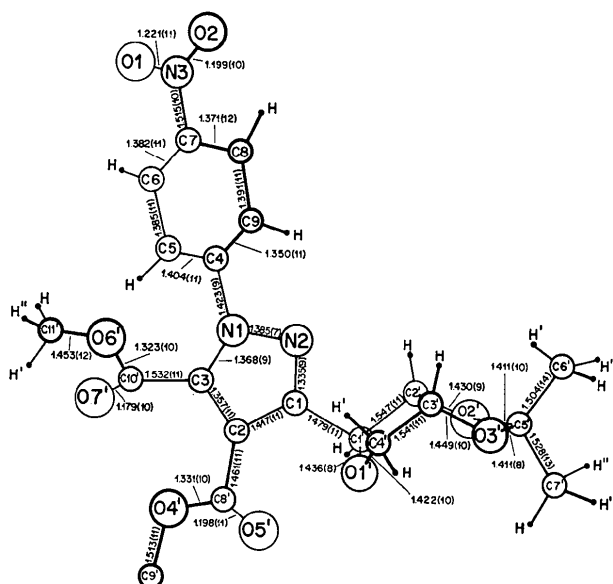


Fig. 1. A projection of CPOP ( $C_{20}H_{21}N_3O_9$ ) on a plane through the pyrazole ring. The numbering scheme and the intramolecular distances for the heavy atoms are given, with e.s.d.'s in parentheses.

Table 6. Deviations ( $\text{\AA}$ ) from least-squares planes through different sets of atoms

Dihedral angles calculated between some of the planes

Plane 1/Plane 2	38.4 $^{\circ}$	Plane 3/Plane 4	66.3 $^{\circ}$
Plane 3/Plane 2	80.6	Plane 4/Plane 5	30.7

Plane 1: C(4), C(5), C(6), C(7), C(8), C(9)

C(4)	-0.011	C(5)	0.010	C(6)	0.002
C(7)	-0.006	C(8)	-0.006	C(9)	0.003
N(1)	0.011	N(2)	0.052		

Plane 2: C(1), C(2), C(3), N(1), N(2)

C(1)	-0.010	C(2)	0.008	C(3)	-0.004
N(1)	-0.002	N(2)	0.008	C(4)	0.127
C(10')	-0.001	C(8')	0.095	C(1')	-0.039

Plane 3: C(1'), C(2'), C(3'), C(4')

C(1')	0.024	C(2')	-0.036	C(3')	0.036
C(4')	-0.024	O(1')	0.517		

Plane 4: C(2'), C(3'), O(2'), O(3')

C(2')	-0.038	C(3')	0.038	O(2')	0.027
O(3')	-0.026	C(5')	0.434	C(6')	1.931
C(7')	-0.237				

Plane 5: O(2'), O(3'), C(5')

O(2')	0.0	O(3')	0.0	C(5')	0.0
C(6')	1.213	C(7')	-1.279	C(2')	0.658
C(3')	0.766				

The conformation of the two methoxycarbonyl groups is indicated by the torsion angles: C(3)—C(2)—C(8')—O(4') of  $-34.2^{\circ}$  and N(1)—C(3)—C(10')—O(6') of  $-56.7^{\circ}$ . This is seen in Fig. 1 where the methoxy groups are located above the pyrazole ring.

In the erythrofuransyl moiety, deviations of about 0.03 Å from plane 3 through C(1'), C(2'), C(3'), C(4') are found for these atoms. O(1'), located 0.517 Å out of this plane, characterizes an envelope form  $E_0$ , which is, however, slightly distorted, as shown by deviations of C(1') to C(4') from plane 3.

In the isopropylidene ring, the bond lengths and angles are in the same range as the values given by Riche & Pascard-Billy (1975) for similar rings in different molecules. This agreement becomes more pronounced when the average values of C(2')—O(2'), C(3')—O(3'), O(2')—C(5'), O(3')—C(5') and of angles around C(5') are compared. The average in CPOP for these bonds is 1.425 Å and for these angles  $110^{\circ}$ , compared with 1.425 Å and  $109.6^{\circ}$  calculated for seven different isopropylidene rings (Riche & Pascard-Billy, 1975). A possible explanation for this could be that the small variations due to different observed conformations cancel.

In the present investigation the isopropylidene ring has a slightly distorted envelope shape with C(5') located 0.435 Å from plane 4 through C(2'), C(3'), O(2') and O(3'). This conformation is also confirmed by plane 5 through O(2'), O(3'), C(5'), to which C(6') and C(7') are at nearly equal distances. As shown in Table 5, the angles between plane 3/plane 4 and plane

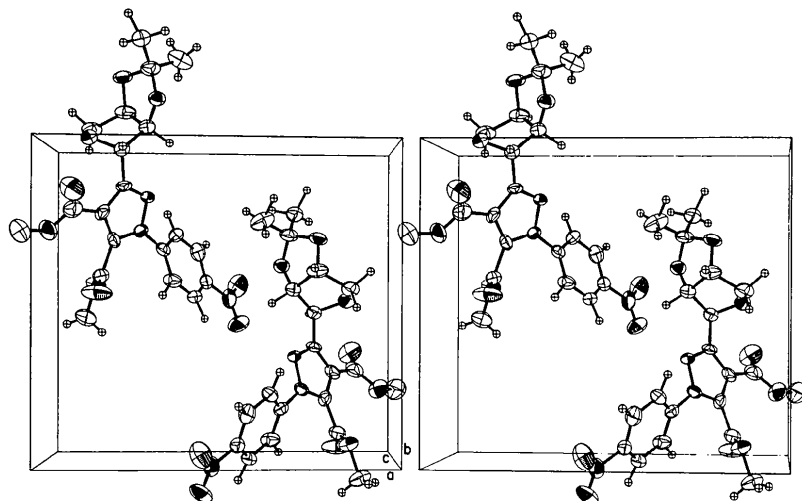


Fig. 2. Stereo view of the arrangement of CPOP ( $C_{20}H_{21}N_3O_6$ ) molecules in the unit cell (ORTEP, Johnson, 1971).

4/plane 5 are  $66.3$  and  $30.7^\circ$ . These features of the conformation are shown in both Figs. 1 and 2.

A pseudo mirror plane through  $O(1')$ ,  $C(5')$ ,  $C(6')$ ,  $C(7')$  of the erythrofuransyl moiety can be seen. From NMR data Tronchet & Perret (1972) showed that  $E_0$  was the most likely conformation of the furanoid ring, and also noted the presence of a plane of symmetry through it in solution. Therefore it is likely that there are only small differences of conformation in solution and in the crystalline state.

To describe the conformation in the *C*-nucleoside CPOP, between the furanoid and the pyrazole ring, the conventions proposed for *N*-nucleosides (Sundaralingam, 1969) were extended, and the torsion angle  $N(2)-C(1)-C(1')-O(1')$  taken as  $\chi$  was used to indicate the conformation. In CPOP this angle is  $122.8^\circ$  and corresponds to the *syn (+ac)* conformation. Such a conformation is rarely found in *N*-nucleosides. Only the X-ray analysis allowed the determination of this unusual conformation, different from both pyrazomycin( $\beta$ ) and pyrazomycin B( $\alpha$ ).

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