

Fig. 11. Schematic description of epitaxial growth of (a) the K<sub>2</sub>Pc(CN)<sub>8</sub>-K crystal on a KCl (001) surface and (b) the MPc(CN)<sub>8</sub>-M crystal on a metal film.

complex take a random orientation on the Cu film constructed with a single crystal and there is no specific relation between the deposit and substrate crystals.

Fig. 11 shows a schematic description of the epitaxial growth of the K<sub>2</sub>Pc(CN)<sub>8</sub>-K and MPc(CN)<sub>8</sub>-M complex crystals on the substrates. In the case of the K<sub>2</sub>Pc(CN)<sub>8</sub>-K crystal on a KCl (001) surface, [K<sub>2</sub>Pc(CN)<sub>8</sub>] molecules make flat contact with the substrate surface owing to interaction between their cyano groups and K<sup>+</sup> ions on a KCl surface as shown in Fig. 11(a). Square lattices of the crystals take three different orientations depending on multiple positioning of [K<sub>2</sub>Pc(CN)<sub>8</sub>] molecules on the ionic lattice of the KCl crystal. Molecular columns of these crystals stand perpendicular to the substrate. In the case of the MPc(CN)<sub>8</sub>-M complex crystal on a metal film, [MPc(CN)<sub>8</sub>] molecules come into contact with the substrate surface at different angles because there is no anisotropic interaction between the cyano

groups and the metal surface. These crystals do not show a specific mutual orientation with the substrate crystal and the molecular columns of the MPc(CN)<sub>8</sub>-M complex grow in random directions.

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## Structure of 1-Methyl-5-(D-galacto-1,2,3,4,5-pentaacetoxypentyl)-3-phenylpyrazole

BY C. F. CONDE AND A. CONDE

*Departamento de Física de la Materia Condensada, Instituto de Ciencias de Materiales, Universidad de Sevilla-CSIC, Sevilla, Spain*

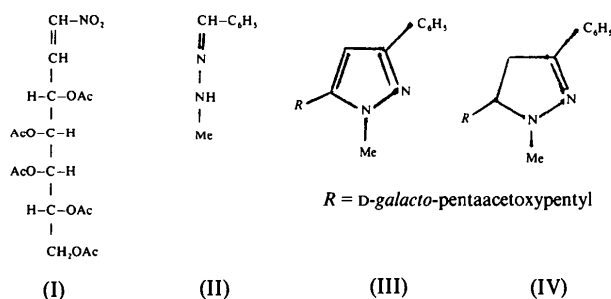
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**Abstract.** C<sub>25</sub>H<sub>30</sub>N<sub>2</sub>O<sub>10</sub>, *M<sub>r</sub>* = 518.5, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 12.303 (2), *b* = 25.071 (4), *c* = 8.823 (5) Å, *V* = 2721.4 (16) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.265 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.7107 Å, μ = 0.09 mm<sup>-1</sup>, *F*(000) = 1076, room temperature, final *wR* = 0.040 for 1424 observed reflexions. Bond distances and angles are all within the expected ranges. The pyrazole and phenyl planes are twisted by 18°. Torsion angles between the acetoxy groups and the

pentyl chain range from 45 to 80°. The crystal cohesion is mainly due to van der Waals interactions but there are two possible hydrogen bonds along [100] and [001]. Molecular-packing analysis in the atom-atom approach yields an equilibrium configuration close to the experimental structure.

**Introduction.** The structure determination of 1-methyl-5-(D-galacto-1,2,3,4,5-pentaacetoxypentyl)-3-

phenylpyrazole was undertaken as part of a continuing research project on C-nucleosides and their precursors. The biological properties of pyrazomycin and other pyrazole C-nucleosides have propitiated the development of synthesis methods for these and also for precursors and analogous compounds. The title compound (III) was prepared (Gómez-Guillén & Lassaletta, 1987, 1988) by reaction of the sugar nitroalkene (I) with aromatic benzaldehyde methylhydrazone (II). The proposed structure was assigned on the basis of chemical and spectroscopic properties and the X-ray analysis was suggested in order to eliminate the 2-pyrazoline form (IV) and to establish the conformational details of the molecule in the solid state.



**Experimental.** Single crystals in the form of colourless prisms elongated along [001] prepared in the Organic Chemistry Department of this University and kindly supplied by Professor M. Gómez-Guillén. Crystal  $0.06 \times 0.15 \times 0.04$  mm. Unit-cell parameters from 25 reflexions  $5 < \theta < 20^\circ$ . Enraf-Nonius CAD-4 diffractometer, graphite monochromator,  $2 < 2\theta < 60^\circ$  ( $0 \leq h \leq 17$ ,  $0 \leq k \leq 35$ ,  $0 \leq l \leq 12$ ),  $\omega$ - $2\theta$  scan mode. Two standard reflexions ( $\bar{3}10$ ,  $3\bar{1}0$ ); variation in intensity less than 2% of the mean value. 2728 independent reflexions measured, 1304 considered unobserved [ $I < 2\sigma(I)$ ]. Lorentz and polarization correction, no correction for absorption or extinction. Structure solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement on  $F$ , anisotropic. Difference Fourier synthesis revealed the H-atom positions; isotropic temperature factor  $B = 4.0 \text{ \AA}^2$  for the H atoms. At final convergence  $\Delta/\sigma < 0.01$ ,  $R = 0.059$ ,  $wR = 0.040$ ,  $S = 1.72$  for 424 refined parameters,  $w = 1/\sigma^2(F_o)$ . Number of reflexions/number of variables = 3.4. Max. and min. values in final difference synthesis  $0.25$  and  $-0.20 e \text{ \AA}^{-3}$ , respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Crystallographic programs of the XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) used throughout.

Table 1. *Atom coordinates and equivalent isotropic thermal parameters* ( $\times 10^3$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \cos(a_i, a_j).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O41	1-0371 (7)	0-1756 (3)	0-5176 (10)	51 (4)
O42	0-8934 (8)	0-2283 (4)	0-5752 (12)	85 (5)
O51	1-1608 (7)	0-1282 (3)	0-2860 (10)	43 (4)
O52	1-1579 (8)	0-1439 (4)	0-0367 (11)	71 (5)
O61	0-9072 (7)	0-0651 (3)	0-3776 (10)	46 (4)
O62	0-9092 (9)	0-0379 (5)	0-6181 (11)	96 (6)
O71	1-0532 (6)	0-0254 (3)	0-1313 (9)	43 (3)
O72	1-2256 (6)	0-0057 (4)	0-0695 (11)	71 (4)
O81	1-1150 (7)	-0-0712 (3)	0-3057 (11)	55 (4)
O82	1-0053 (8)	-0-0952 (4)	0-1113 (13)	90 (5)
N1	0-9395 (9)	0-2428 (5)	0-1856 (13)	47 (5)
N2	0-9794 (9)	0-2881 (4)	0-1162 (12)	46 (4)
C1	1-0155 (11)	0-2205 (5)	0-2789 (16)	37 (5)
C11	0-8259 (9)	0-2273 (5)	0-1626 (17)	60 (6)
C2	1-0832 (11)	0-2944 (6)	0-1650 (16)	44 (5)
C21	1-1467 (12)	0-3350 (5)	0-0985 (19)	50 (6)
C22	1-1171 (12)	0-3614 (6)	-0-0277 (22)	77 (7)
C23	1-1846 (16)	0-4043 (9)	-0-0822 (32)	131 (12)
C24	1-2811 (21)	0-4132 (9)	-0-0242 (35)	130 (13)
C25	1-3132 (16)	0-3876 (8)	0-1015 (23)	118 (11)
C26	1-2442 (15)	0-3475 (6)	0-1640 (18)	90 (8)
C3	1-1082 (9)	0-2523 (5)	0-2706 (14)	44 (5)
C4	0-9899 (10)	0-1714 (5)	0-3666 (15)	42 (5)
C41	0-9768 (13)	0-2090 (7)	0-6074 (17)	59 (7)
C42	1-0337 (16)	0-2173 (9)	0-7621 (19)	130 (10)
C5	1-0442 (9)	0-1225 (5)	0-2938 (14)	38 (5)
C51	1-2114 (13)	0-1387 (6)	0-1476 (19)	67 (7)
C52	1-3293 (11)	0-1437 (7)	0-1631 (18)	86 (8)
C6	1-0256 (9)	0-0685 (5)	0-3722 (14)	39 (5)
C61	0-8588 (13)	0-0497 (6)	0-5123 (20)	64 (7)
C62	0-7381 (10)	0-0535 (5)	0-4931 (18)	67 (6)
C7	1-0783 (10)	0-0220 (6)	0-2959 (13)	36 (5)
C71	1-1382 (11)	0-0165 (6)	0-0325 (18)	59 (7)
C72	1-0939 (11)	0-0186 (6)	-0-1294 (15)	70 (7)
C8	1-0409 (10)	-0-0313 (5)	0-3551 (15)	48 (5)
C81	1-0882 (14)	-0-1010 (6)	0-1807 (20)	65 (8)
C82	1-1790 (13)	-0-1378 (5)	0-1415 (18)	74 (7)

**Discussion.** The final atomic parameters are given in Table 1.\* An ORTEP (Johnson, 1965) drawing of the molecule with atomic labelling is shown in Fig. 1. Bond lengths and angles for non-H atoms are listed in Table 2. The pyrazole ring is planar with the largest displacement of any non-H atom from its plane being  $0.008 \text{ \AA}$ . The orientation of the phenyl ring to the pyrazole plane can be defined by the torsion angle  $C3-C2-C21-C22 = 161.0 (16)^\circ$ . The five acetoxy groups are planar and their torsion angles with respect to the main pentyl chain are  $C1-C4-O41-C41 = 76.3 (13)$ ,  $C4-C5-O51-C51 = -106.0 (13)$ ,  $C5-C6-O61-C61 = -133.7 (11)$ ,  $C6-C7-O71-C71 = 135.2 (11)$  and  $C7-C8-O81-C81 = -98.6 (13)^\circ$ . The Newman projections corresponding to C-C bonds of the main pentyl chain are shown in Fig. 2 where the configuration can be deduced.

#### Molecular-packing analysis

The crystal cohesion is mainly due to van der Waals interactions but some intermolecular contacts

\* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52078 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) for non-H atoms

O51—C5	1.444 (14)	O51—C51	1.395 (19)
O61—C6	1.460 (14)	O61—C61	1.385 (19)
O41—C4	1.457 (16)	O41—C41	1.371 (18)
O71—C7	1.487 (15)	O71—C71	1.380 (17)
O81—C8	1.422 (15)	O81—C81	1.373 (19)
O62—C61	1.159 (20)	N1—N2	1.379 (15)
N1—C1	1.366 (18)	N1—C11	1.465 (15)
O82—C81	1.198 (20)	O72—C71	1.156 (16)
N2—C2	1.357 (17)	C6—C7	1.495 (18)
C6—C5	1.538 (18)	C7—C8	1.507 (18)
C4—C1	1.487 (18)	C4—C5	1.536 (18)
C42—C41	1.549 (23)	C22—C21	1.345 (24)
C22—C23	1.440 (28)	C2—C21	1.412 (20)
C2—C3	1.443 (19)	C21—C26	1.367 (23)
C1—C3	1.394 (18)	C41—O42	1.168 (19)
C26—C25	1.429 (26)	C61—C62	1.497 (20)
C82—C81	1.489 (22)	C71—C72	1.530 (20)
C25—C24	1.341 (35)	O52—C51	1.187 (19)
C51—C52	1.462 (21)	C23—C24	1.312 (34)
C5—O51—C51	120.2 (10)	C6—O61—C61	118.3 (10)
C4—O41—C41	111.0 (10)	C7—O71—C71	116.7 (10)
C8—O81—C81	118.4 (11)	C1—N1—C11	128.8 (11)
N2—N1—C11	119.8 (10)	N2—N1—C1	111.2 (11)
N1—N2—C2	106.9 (10)	O61—C6—C5	102.4 (9)
O61—C6—C7	113.7 (10)	C7—C6—C5	114.8 (10)
O71—C7—C6	107.7 (9)	C6—C7—C8	113.7 (10)
O71—C7—C8	109.1 (9)	O41—C4—C5	105.5 (10)
O41—C4—C1	109.3 (10)	C1—C4—C5	110.5 (11)
O81—C8—C7	108.7 (10)	C21—C22—C23	119.2 (16)
N2—C2—C3	108.6 (11)	N2—C2—C1	118.3 (12)
C21—C2—C3	132.8 (12)	C22—C21—C2	123.3 (14)
C2—C21—C26	118.3 (14)	C22—C21—C26	118.4 (14)
N1—C1—C4	120.5 (12)	C4—C1—C3	132.4 (12)
N1—C1—C3	107.1 (11)	C6—C5—C4	116.7 (10)
O51—C5—C4	112.0 (9)	O51—C5—C6	104.8 (9)
C2—C3—C1	106.1 (11)	O41—C41—C42	110.3 (13)
C42—C41—O42	123.8 (15)	O41—C41—O42	125.9 (14)
C21—C26—C25	121.2 (16)	O61—C61—O62	122.1 (14)
O62—C61—C62	129.7 (15)	O61—C61—C62	108.1 (13)
O71—C71—O72	124.4 (14)	O72—C71—C72	127.1 (13)
O71—C71—C72	108.3 (11)	C26—C25—C24	118.7 (19)
O51—C51—O52	119.6 (14)	O52—C51—C52	128.2 (15)
O51—C51—C52	112.1 (13)	O82—C81—C82	126.5 (14)
O81—C81—C82	110.1 (13)	O81—C81—O82	123.2 (14)
C22—C23—C24	121.2 (22)	C25—C24—C23	120.5 (13)

may be considered as possible hydrogen bonds. These interactions are C25—H25...O62( $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ ) linking molecules related by a screw axis parallel to [100] and C42—H423...O52( $x, y, z + 1$ ) linking neighbouring molecules along [001]. Details of these contacts are C25—H25 = 1.13 (5), C25...O62 = 3.32 (2), H25—O62 = 2.57 (3) Å, C25—H25...O62 = 122 (5)° and C42—H423 = 1.16 (6), C42...O52 = 3.40 (2), H423...O52 = 2.51 (3) Å, C42—H423...O52 = 132 (5)°, both satisfying the criteria of Taylor & Kennard (1982) for hydrogen bonds. The molecular geometry and crystal packing were computed by *PARST* (Nardelli, 1983).

Lattice-energy calculations in the atom-atom potential approach were performed using the computer program *PCK6* (Williams, 1972). The interaction between a pair of non-bonded atoms is in the form  $\phi = -Ar^{-6} + B \exp(-Cr)$  and the molecules are assumed to be rigid bodies but intramolecular rotations around selected bonds as axes were relaxed. The set of potential parameters is described elsewhere (Conde, Millán, Conde & Márquez, 1985). Lattice-energy minimization was performed with

respect to cell constants, molecular translation and rotation and also subrotation of the five acetoxy groups and the phenyl ring, starting from the experimental structure.

Representative results of the energy minimization are given in Table 3. As observed, the calculated equilibrium configuration is in good agreement with the experimental structure. The optimized structure remains very similar with regard to the molecular parameters as shown in Table 3. Shifts of the positional and orientational molecular parameters are 0.02 Å and 2.6°, respectively, and the variations in the torsion angles of intramolecular relaxed rotations are lower than 3° in all cases.

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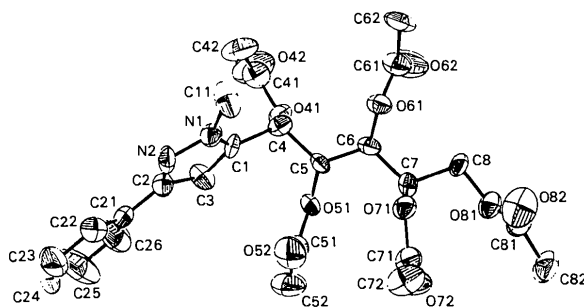


Fig. 1. An ORTEP plot of the molecule with atom labelling.

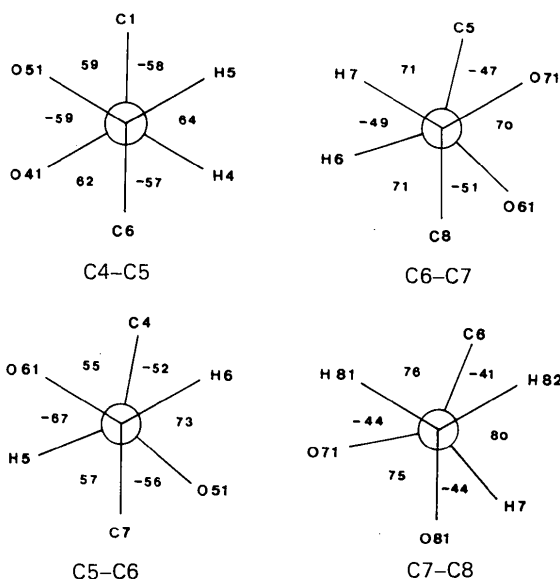


Fig. 2. Newman projections corresponding to the C—C bonds through the main chain. Torsion angles are in °; e.s.d.'s are in the range 0.8–1.4° (excluding those involving H atoms).

Table 3. Results of energy minimization

 $\bar{r}_c$ : molecular centre of mass,  $\theta$ : molecular rotation.

Cell constants	
$\Delta a$	0.4%
$\Delta b$	0.1
$\Delta c$	0.5
Molecular parameters	
$ \Delta r_c $	0.02 Å
$\theta$	2.6°
Subrotations ( $\Delta\tau$ )	
C1—C4—O41—C41	-1.1°
C4—C5—O51—C51	-2.3
C5—C6—O61—C61	-1.8
C6—C7—O71—C71	-0.6
C7—C8—O81—C81	-2.7
C3—C2—C21—C22	-1.3

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## Structure of 2-Methyl-1,3-cyclopentanedione

BY ANDRZEJ KATRUSIAK

Department of Organic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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**Abstract.**  $C_6H_8O_2$ ,  $M_r = 112.13$ , monoclinic,  $C2/m$ ,  $a = 12.766$  (2),  $b = 6.807$  (2),  $c = 6.4814$  (8) Å,  $\beta = 93.94$  (1)°,  $V = 561.9$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.33$  g cm<sup>-3</sup>, m.p. = 486–488 K,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 1.07$  cm<sup>-1</sup>,  $F(000) = 240$ ,  $T = 292$  K, final  $R = 0.040$  for 541 observed reflections. The structure consists of chains along  $z$  of hydrogen-bonded enol molecules [O...O distance 2.598 (2) Å]. The molecules lie on a mirror plane and the chains, in turn, are arranged in layers perpendicular to  $y$ . The positions of the H atoms of the methyl group are well defined and consistent with the constraints of the mirror plane, the H atom in the plane being on the side of the hydroxyl group; a metastable position of the methyl H atoms, corresponding to a 180° rotation of the methyl group, has also been detected.

**Introduction.** This study of 2-methyl-1,3-cyclopentanedione (MCPD) (enol form) was undertaken primarily to establish the arrangement of the MCPD molecules in the crystal and their intermolecular interactions. In the structures of cyclic  $\beta$ -diketo-

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methanes investigated so far the molecules are interconnected by strong —O—H...O= hydrogen bonds shorter than 2.6 Å, which form chains — as has been observed in 1,3-cyclohexanedione (CHD) (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986), 1,3-cyclopentanedione (Katrusiak, 1989) and dimedone (5,5-dimethyl-1,3-cyclohexanedione) (Semmingen, 1974; Singh & Calvo, 1975). It was demonstrated by Etter, Urbańczyk-Lipkowska, Jahn & Frye (1986) that, in the presence of suitable guest molecules, cyclomers can be formed from the hydrogen-bonded CHD molecules. We also wanted to investigate the intermolecular hydrogen bond and to compare it with those in similar structures, and look at the molecular dimensions of the MCPD molecule, the twofold symmetry of which is broken by the alternating HO—C=C—C=O  $\pi$ -bond system.

**Experimental.** Crystals of MCPD were recrystallized from ethanol. Colourless, elongated plates with  $y$  along the long and  $z$  along the short edges of the plates, dimensions 0.27 × 0.27 × 0.15 mm. The inten-