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INFLUENCE OF HYDROGEN BONDS ON THE MOLECULAR STRUCTURE AND CONFORMATIONS OF TWO ($C_{30}H_{48}O_2$) PENTACYCLIC TRITERPENE ISOMERS

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The structural study of two ($C_{30}H_{48}O_2$) pentacyclic triterpene (PCTT) isomers is presented. These terpenes, known as 30-hydroxy-lup-20(29)-en-3-one (**1**) and (11α)-11-hydroxy-lup-20(29)-en-3-one (**2**), were isolated from *Maytenus imbricata* Mart. Ex Reissek (Celastraceae). The molecular structure of **1** and **2** differs in the position of the hydroxyl group. Both compounds crystallize in non-centrosymmetric space groups with two molecules in the asymmetric unit. The crystal structure of **1** shows a triclinic $P1$ space group (a = 9.5518(1) Å, b = = 9.7083(1) Å, c = 14.4696(2) Å, α = 93.832(1)°, β = 102.833(1)° and γ = 103.307(1)°), while compound **2** crystallizes in a monoclinic $P2_1$ one (a = 13.4439(16) Å, b = 14.4463(14) Å, c = = 13.5224(9) Å and β = 99.703(8)°). The two molecules independent by symmetry of **1** differ slightly due to the presence of static disorder in oxygen atoms. In addition, the intermolecular geometries of **1** and **2** were analysed, and in each isomer the crystal packing is stabilized by O—H···O intermolecular hydrogen bonds and van der Waals forces.

K e y w o r d s: *Maytenus imbricata*, pentacyclic triterpene, crystal structure, molecular conformation, static disorder, hydrogen bond.

INTRODUCTION

Maytenus is a well-known genus of the Celastraceae family with several specimens largely used in traditional medicine in Brazil. Previous chemical investigations of this genus have resulted in the isolation of several secondary metabolites including glycosides, flavonoids, alkaloidic and non alkaloidic sesquiterpenes, friedelanes, oleananes, lupanes, quinonoid triterpenes and other pentacyclic triterpenes (PCTTs) [1]. In general, PCTTs compose a class of chemical compounds commonly obtained from plants that belong to the Celastraceae family [2]. These terpenes and their derivatives have shown many interesting biological properties, such as anti-inflammatory [3], anti-HIV [4], anticancer [5], nematostatic effects [6].

As part of our ongoing search for new biologically active compounds [6—14] from plants, we have investigated *Maytenus imbricata* (Celastraceae), a plant native in the savana region of Minas Gerais and Bahia states in Brazil. Three PCTTs named as 30-hydroxy-lup-20(29)-en-3-one (**1**) and (11α)-11-hydroxy-lup-20(29)-en-3-one (**2**), and 3β,30-dihydroxy-lup-20(29)-ene (**3**) [2] have previously been isolated from *M. imbricata*.

Recently, we have reported the crystal structure of **3** and 3β-lup-20(29)-en-3-ol (or lupeol) isolated from *Maytenus imbricata* [2, 10] and *Garcinia brasiliensis* (the Guttiferae family) [11] respec-

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tively. Surprisingly, based on the X-ray diffraction analysis of **3** [10] and lupeol [11], we found that they crystallize in an enantiomorphous space group with almost identical cell parameters and supramolecular structures.

For all PCTTs studied by single crystal X-ray diffraction cited above, the molecular structure and, in some cases, the relative stereochemistry have also been established by a detailed NMR spectral data analysis [2, 10—13]. Due to the importance of weak intermolecular interactions on the macroscopic properties of solids such as solubility, chemical stability, melting point, density, etc., in addition to their intramolecular geometry, it is important to know the crystal packing forces or intermolecular bonding motifs such as hydrogen bonds, aromatic π—π stacking, steric repulsion, and van der Waals forces. Single crystal X-ray diffraction represents one of the best techniques available to obtain this type of data [5, 10—14]. It is important to emphasize that among intermolecular forces, hydrogen bonding plays important roles both in chemistry and biology, but it is still poorly understood. Recent progress both in theoretical and experimental methods has shown many new interesting facts about the H-bonding [15—17].

Continuing our X-ray diffraction studies applied to establish the structural details of natural products, in this paper, we report the results of intra- and intermolecular geometry investigations of isomers 30-hydroxy-lup-20(29)-en-3-one (**1**) and (11α)-11-hydroxy-lup-20(29)-en-3-one (**2**), emphasizing the effects of hydrogen bonds on molecular conformations.

EXPERIMENTAL

Compounds **1** and **2** were isolated from stems and branches of *M. imbricata* Mart. Ex Reissek (Celastraceae). The plant material was collected in the ″Morro de Santana″ region, Ouro Preto city, Minas Gerais, Brazil. A voucher specimen was deposited (Collection No. 27780) at the *Herbarium* of the Department of Botany, Federal University of Viçosa (UFV), Viçosa, Minas Gerais, Brazil. The previous molecular structures of compound **1** and **2** were deduced from spectroscopic experiments reported elsewhere [2].

The single crystals of **1** and **2** were obtained by recrystallization in chloroform: ethanol mixture (1:1 v/v) and in hexane:ethyl acetate (1:1 v/v) respectively. In both compounds, crystal diffraction data were collected at 150 K on an Enraf-Nonius Kappa-CCD diffractometer using MoK_α radiation (0.71073 Å) monochromated by graphite. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program [18]; integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [19].

The structures of **1** and **2** were solved by direct methods using the SHELXS-97 program [20] and refined by full-matrix least squares on F^2 with the SHELXL-97 program [20] considering anisotropic temperature factors for all atoms except for hydrogen atoms that had their positional parameters fixed stereochemically and refined with a riding model [20]. Hydrogen atoms of CH and CH_2 groups were set isotropic with a thermal parameter larger by 20 % than the equivalent isotropic displacement parameter of the atom isotropic temperature factor common for all hydrogen atoms to which each one was bonded. This percentage was set to 50 % for the hydrogen atoms of the CH_3 and OH groups.

Despite the fact that both compounds crystallized in non-centrosymmetric space groups, the Flack parameter [21] was not refined during the X-ray crystallographic analysis neither for **1** nor for **2**. In both molecules, the most electron-rich atom is oxygen, which does not have an anomalous scattering large enough to permit the determination of the absolute structure using X-ray diffraction (using MoK_α radiation). Therefore, Friedel pairs were averaged before the refinement.

The WinGX program [22] was used to prepare materials for the publication. The MERCURY [23] and ORTEP-3 [24] programs were used to generate the molecular graphics. For structural analyses was used Mogul [25], a valuable knowledge base for analyzing the conformational and geometric features of a molecule. It searches for the substructures of compounds deposited at the Cambridge Crystallographic Data Centre (CCDC) [26], which are similar to those of a target molecule. A summary of the crystal data and refinement conditions of **1** and **2** are presented in Table 1.

Table 1

Summary of crystal data collection and structure refinement results for triterpenes **1** *and* **2**

Parameters	Triterpene **1**	Triterpene **2**
Molecular formula	$C_{30}H_{48}O_2$	$C_{30}H_{48}O_2$
Empirical formula	$C_{15}H_{24}O_1$	$C_{15}H_{24}O_1$
Formula weight	440.68	440.68
Temperature, K	150	150
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P1$	$P2_1$
Unit cell dimensions (a, b, c, Å; α, β, γ, deg.)	9.5518(1), 9.7083(1), 14.4696(2); 93.832(1), 102.833(1), 103.307(1)	13.4439(16), 14.4463(14), 13.5224(9); β = 99.703(8)
Volume, Å^3	1263.27(7)	2588.7(4)
Z, Z'	1, 2	2, 4
Calc. Density, Mg/m^3	1.159	1.131
Absorp. coefficient, mm^{-1}	0.070	0.068
F(000)	488	976
Crystal size, mm	0.08×0.18×0.24	0.32×0.36×0.40
θ range for data collection, deg.	2.97—27.48	3.38—26.38
Reflections collected	33641	6920
Independent reflections	5778 [R(int) = 0.0435]	4882 [R(int) = 0.1835]
Completeness to θ, %	99.6	88.5
Data / restraints / parameters	5778 / 6 / 594	4882 / 1 / 580
Goodness-of-fit on F^2	1.012	1.037
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0438, $wR2$ = 0.1157	$R1$ = 0.0977, $wR2$ = 0.2337
R indices (all data)	$R1$ = 0.0494, $wR2$ = 0.1207	$R1$ = 0.1507, $wR2$ = 0.2692
Largest diff. peak and hole, e·Å	0.254 and –0.272	0.403 and –0.470

1 = 30-hydroxy-lup-20(29)-en-3-one and **2** = (11α)-11-hydroxy-lup-20(29)-en-3-one.

RESULTS AND DISCUSSION

Crystal structure of 30-hydroxy-lup-20(29)-en-3-one (1). Pentacyclic triterpene **1** crystallizes in the non-centrosymmetric $P1$ space group. Based on the analysis of the crystal structure of **1**, it was possible to establish two molecules in the asymmetric unit (hereafter called **1A** and **1B**). Fig. 1 is an Ortep-3 [24] type displaying the structure of **1A** with non-hydrogenous atoms labelled. During the

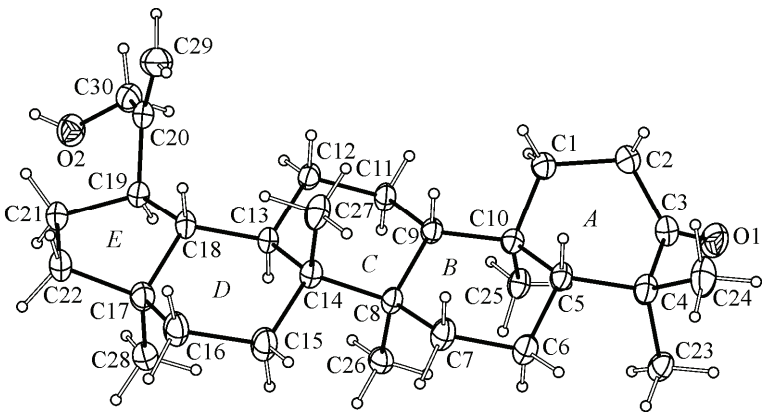

Fig. 1. ORTEP-3 view of **1A** showing the thermal ellipsoids at the 40 % probability level and atom labeling. H atoms are shown as small spheres of arbitrary radii

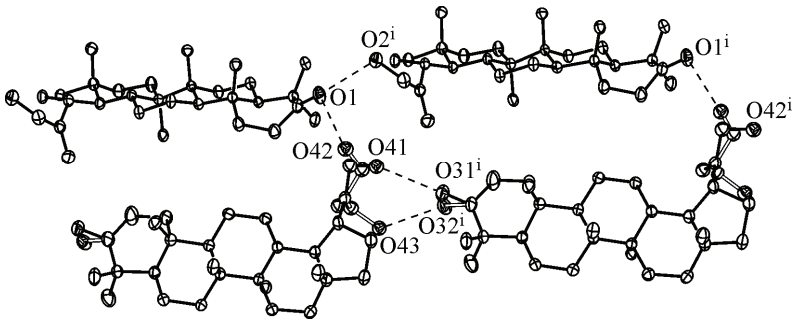

Fig. 2. Representation of hydrogen bonds in **1** showing the interaction between electronegative oxygen atoms to give rise to an infinite two dimensional chain parallel to the [001] direction [Symmetry code: $x+1, y-1, z$]

structure determination disordered sites around the carbonyl and hydroxyl groups of **1B** were found (Fig. 2). Trial refinements were used with the split-atom approach for these extra sites. From a statistical and convergence point of view, the classical split-atom model with two carbonylic oxygen atoms and three hydroxyl groups resulted in the best structural refinement. The model splitting each oxygen atom of the carbonyl group over two positions, O21 and O22, with a constrained 50 % occupancy each, was found to be the best one. For the three disordered sites found to the hydroxyl group, labelled as O41, O42 and O43, the SHELXL [20] restraints were applied, enabling one atom to be distributed over more than two sites so that the elemental composition corresponded (within suitable standard deviations) to an experimental chemical analysis. This means that the sum of site occupation factors was restrained to be equal to one oxygen atom. The refined occupation values found for O41, O42, and O43 sites were 0.368(3), 0.341(4) and 0.291(4) respectively.

Except the aforementioned disorder, the intramolecular geometry of **1A** and **1B** is similar. A comparison of **1A** and **1B** through the method of Kabsch [27] (disordered atoms were not considered) showed them to be similar with a root mean square deviation between homologous atoms of 0.10(7) Å. In both structures, the ring A adopts a *half-boat* conformation, whereas the rings B, C, and D adopt a *chair* conformation. The remaining ring E presents an *envelope* shape with the quaternary carbon at the ring-corner in the flap position.

The intramolecular conformation of **1A** and **1B** was analyzed using MOGUL [25], which confirmed that all bond lengths and bond angles agree with the expected values reported in the literature. According to the Mogul analysis [25], there are small variations among the C—C single bond lengths (average value of 1.52(3) Å). The C2—C3 (1.508(4) Å) and C3—C4 (1.521(3) Å) single bond lengths, which contain the C3 atom belonging to a carbonyl group, are shorter than the remaining C—C bond lengths, such as C13—C14 (1.562(3) Å) and C8—C14 (1.598(3) Å) bond lengths, in which carbon atoms are completely substituted. In the first case, electronegative oxygen removes the electronic density from C3 resulting in a stronger interaction with either the C2 or C4 atoms, shortening the bond lengths. In the second case, the neighboring atoms are electron density donors, making them slightly longer. In addition, steric hindrance occurs around the most substituted carbon atoms. Concerning the bond lengths of the C30—O2 hydroxyl group with 1.420(3) Å and the C3=O1 carbonyl group with 1.221(3) Å, these values represent an evidence of single (average value of 1.41(3) Å) and double (average value of 1.22(2) Å) bonds respectively, when looking at the similar entries returned by the Mogul search [25]. In the structure, C20 and C29 atoms are separated by 1.328(4) Å, as expected based on sp^2 hybridization. Except the C3 atom, all other carbon atoms in the six- and five-membered rings adopt sp^3 hybridization. Some angle bonds slightly deviate from the ideal geometry, which can be explained by ring tensions. In the six-membered rings, the distortions on angle bonds are minimized by the *chair* conformation, whereas the five-membered rings are more tensioned, explaining the angular range observed from 100.1(2)° to 106.3(2)°.

The molecular assembly of **1** is stabilized by four independent hydrogen bonds that give rise to an infinite double chain parallel to the $[1\,\bar{1}\,0]$ direction (Fig. 2; Table 2). In crystal packing, the **1A** molecules are linked in a tail-head fashion by carbonyl at C3 and the hydroxyl group at C30 (Fig. 1). The **1B** molecules are linked along the $[1\,\bar{1}\,0]$ direction in the same fashion. However, either the hydroxyl or carbonyl group is split in two positions: the O41 atom is a hydrogen bond donor to O31, whereas

Table 2

Hydrogen bonding analysis of **1**

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (deg.)
O2[i]—H2...O1	0.82	2.24	3.053(1)	174
O41—H41...O31[i]	0.82	2.23	3.000(8)	157
O43—H43...O32[i]	0.82	2.21	3.004(9)	164
O42—H42...O1[i]	0.82	2.86	3.025(6)	104

Symmetry codes: [i] $x+1, +y-1, +z$.

the O42 one is a hydrogen bond donor to O32. The two single chains are also linked together by a fourth hydrogen bond, in which O43 acts as an intermolecular hydrogen bond donor to the O1 atom in **1A**. Therefore, the presence of the disordered sites in **1A** can be explained as a result of the supramolecular requirements in order to stabilize the packing of molecules in the solid state (Fig. 2).

Finally, the conformational comparison between **1** and **3** [10] carried out by the Kabsch method [27] revealed great similarity between both structures. A difference was observed in the A ring conformation, the substituent functional group at C3 (C—O is longer than C=O), and also in the torsional angle of the hydroxyl linked at C30. The root mean square deviation between the homologous atoms is 0.58(31) Å. On the other hand, their intermolecular structures are completely different. As discussed above, the packing of **1** is formed by double chains along the [1 $\bar{1}$ 0] direction, which are linked by van der Waals forces. As showed previously [10, 11], the crystal packing of **3** and lupeol is stabilized by intermolecular interactions forming infinite helical chains along the *c* axis. Since the molecular assembly depends on the intermolecular bonding motifs, the differences observed in the supramolecular chemistry of compounds **1**, **3** and lupeol can be explained by the absence of a strong proton donor linked at the C3 atom in **1**. On the other hand, either **3** or lupeol present a hydroxyl group linked at the C3 atom that is involved in hydrogen bonding acting as a donor and acceptor.

Crystal structure of (11α)-11-hydroxylup-20(29)-en-3-one (2). Pentacyclic triterpene **2** crystallizes in the non-centrosymmetric $P2_1$ space group. The single crystal X-ray crystallographic study of **2** also showed the presence of two molecules independent by symmetry in the asymmetric unit (hereafter called **2A** and **2B**). An ORTEP-3 view [24] of **2A** with the atom numbering scheme is showed in Fig. 3. An overlap of the two molecules performed by the method of Kabsch [27] emphasized their similarity, with a root mean square deviation between homologous atoms of 0.6(4) Å. Therefore, hereafter only the intramolecular geometry of the **2A** molecule will be discussed in detail. Since the crystallographic analyses for **1** and **2** were performed at the same temperature (150 K) and the molecular structure of both compounds differs only in the hydroxyl position, the geometric parameters found for **2** are similar to those found for **1**. As described for **1**, the molecular conformation was also analyzed

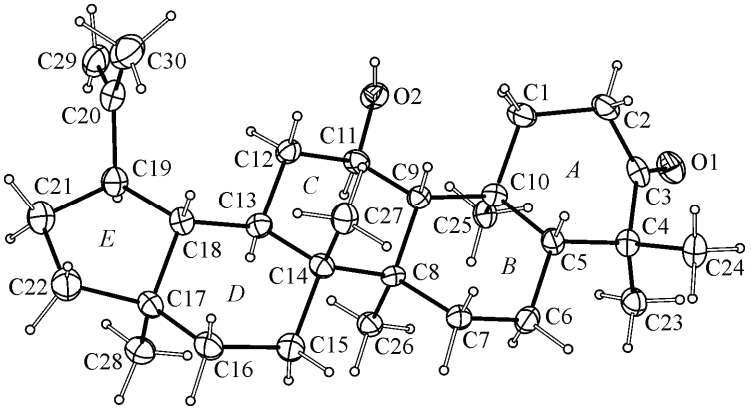

Fig. 3. ORTEP-3 view of **2A** with the atom labeling scheme. Displacement ellipsoids are drawn at the 50 % probability level while the H atoms are shown as small spheres of arbitrary radii

Table 3

Hydrogen bonding analysis of **2**

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (deg.)
O2—H2···O1^{ii}	0.82	2.11	2.821(8)	144
O4—H4···O3^{iii}	0.82	2.20	3.007(10)	169

Symmetry codes: ^{ii} $-x+2, y-1/2, -z+1$, ^{iii} $-x+1, y+1/2, -z+1$.

using MOGUL [25], and this study revealed that all bond lengths and bond angles were in agreement with the expected values for similar molecules, such as **3** and lupeol [10, 11].

The C11—O2 hydroxyl group linked at ring C is in the equatorial position. For triterpene **2**, the ring conformations are exactly equal to the one observed for **1**: *half-boat*, *chair*, *chair*, *chair*, and *envelope* for A, B, C, D, and E respectively (Fig. 3). This sequence agrees well also with the one found for 2β-methyl-3-oxolupane-28-nitrile [28]. As reported for 20(29)-lupen-3-one [29], it was expected that the six-membered rings adopted the most stable *chair* conformation, but for **1** and **2** this is not the case for the ring A. The *half-boat* conformation probably occurs due to the existence of the C3=O1 carbonyl and intermolecular forces acting on them (Table 3). Since the ring A is in the molecular extremity, it plays a role of intermolecular bonding motifs in the tail-head linkage. Thus, when hydrogen bonding interactions are present in these motifs, the outlying ring A can adopt a less stable conformation, as observed in **1** and **2**. Differently, the 20(29)-lupen-3-one compound [29] does not exhibit hydrogen bonds to provide energy for ring distortions.

Concerning the conformation of the two isomers studied here, the similarity of both **1A** and **2A** molecules was highlighted by comparing the intramolecular structures using the Kabsch method [27], which found a root mean square deviation of only 0.10(9) between the homologous atoms. In this analysis, the C29 and C30 atoms of **1A** and **2A** were not considered, due to the opposite conformation of these substituents (Figs. 1 and 3). Indeed, this is the most important conformational difference between **1A** and **2A**, with the respective C18—C19—C20—C29 torsion angles of –29.3(2)° and 139.3(2)°. The opposite orientation of the C29 atom with respect to C30 in the **1A** molecule may be a consequence of the direction of intermolecular interactions occurring in the crystal packing. Meanwhile, in the crystal structure of **2** there is no hydrogen bond to modify the conformation of C29 and C30 atoms. Therefore these substituents adopt the less sterically hindered conformation stabilized by van der Waals forces (Fig. 4), such as that observed for lupeol [11].

The intermolecular hydrogen bond occurring between the hydrogen atom of the hydroxyl group linked to C11 (**2A** molecule) and the adjacent O1 carbonyl oxygen at $-x, y+1/2, -z+1$ stabilizes the packing of the **2A** molecule and gives rise to an infinite one-dimensional chain parallel to the [010] direction (Table 3, Fig. 4). A similar interaction in an antiparallel fashion occurs in the case of the **2B** molecule involving O4—H4···O3 atoms (Table 3). Both chains form a planar structure, connected by van der Waals interactions along the $[\bar{1}01]$ direction. Therefore, the chains are linked and form an infinite two-dimensional network parallel to the (101) plane.

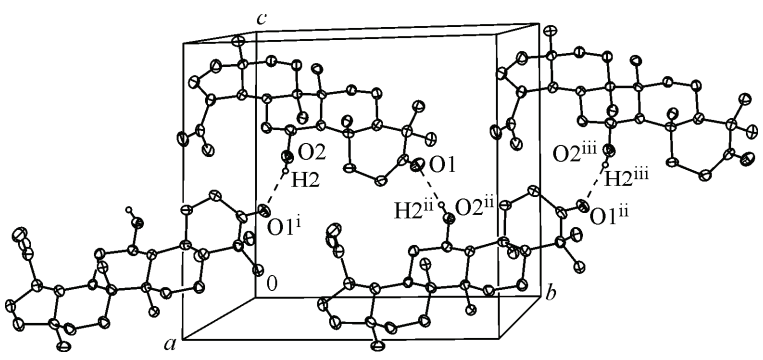

Fig. 4. View of the hydrogen bond network connecting **2A** molecules occurring along the *b* axis. Symmetry codes: (i) $x+2, y-1/2, -z+1$; (ii) $-x+2, y+1/2, -z+1$; (iii) $x, y+1, z$

CONCLUSIONS

In summary, the structural features of two pentacyclic triterpenes (30-hydroxy-lup-20(29)-en-3-one (**1**) and (11α)-11-hydroxy-lup-20(29)-en-3-one (**2**)), and the influence of hydrogen bonds on molecular conformations were studied in detail using the single crystal X-ray-diffraction data. The conformation of the six rings in both structures is shown to be similar. On the other hand, the opposite conformation of the chemical group linked at the C19 atom is the main difference between them, apart from the static disorder present in **1**, involving the hydroxyl group and the carbonyl one, which occurs due to hydrogen bonding orientations. In addition to the importance of the hydrogen bonding for packing stabilization, each triterpene structure is also kept together by van der Waals interactions.

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Supplementary material. Crystallographic data been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (**1**, CCDC 760694, and **2** CCDC 760695). Copies of the data can be obtained, free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk).

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