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Original Scientific Paper

(1-Adamantyl)methyl esters: whole-molecule disorder in the crystal structure of (1-adamantyl)methyl-1-adamantanecarboxylate*

Dalibor Milić,[a] Marija Alešković,[b] Dubravka Matković-Čalogović,[a,*] and Kata Mlinarić-Majerski[b,*]

[a]*Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, Horvatovac 102a, 10000 Zagreb, Croatia*
[b]*Department of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, POB 180, 10002 Zagreb, Croatia*

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Abstract. Two (1-adamantyl)methyl esters, (1-adamantyl)methyl-1-adamantanecarboxylate (**1**) and bis[(1-adamantyl)methyl]-1,3-adamantanedicarboxylate (**2**) were prepared in good yields and characterized by spectroscopic methods. The structure of **1** was determined by single-crystal X-ray diffraction structural analysis. The structure shows two kinds of whole-molecule disorder: the ester molecule statistically occupies two different sites in the crystal asymmetric unit with occupancies of 95 and 5 % (positional disorder), and at each of the sites there is additional disorder over a crystallographic 2-fold rotation axis (orientational disorder). Analysis of diffuse scattering patterns in the diffraction images revealed the positional disorder as stacking disorder of molecular layers with two-dimensional translational symmetry. In the absence of other, more directional interactions, the molecules in the crystal structure of **1** are held together only by van der Waals interactions which provide the rationale for the observed whole-molecule disorder.

Keywords: adamantane, (1-adamantyl)methyl esters, X-ray diffraction analysis, whole-molecule disorder, stacking disorder, diffuse scattering

INTRODUCTION

Adamantane molecules are highly symmetrical (point group symmetry T_d) which allows them to be disordered in their crystals,[1–3] as well as in the solid-state structures of several clathrates.[4–6] The whole-molecule disorder is also found for the crystal structures of few adamantane derivatives including adamantanone,[2] fluoroadamantane[3] and, somewhat surprisingly, 1-adamantanecarboxylic acid.[7]

Whole-molecule disorder is a phenomenon occasionally encountered in the crystal structures (for some "classical" (early) examples of whole-molecule disorder in crystals see references[8–13]). In an ideal case, each molecule assumes the energetically most favorable orientation in the molecular crystal. But, if two or more orientations are very close in energy, it may happen that during the crystal growth each molecule randomly assumes one of these possible orientations. According to a Boltzmann distribution, if two molecular orientations in the crystal have exactly the same energy, the occupancies for the corresponding sites will be exactly the same resulting in a 50:50 whole-molecule disorder. On the contrary, if the possible orientations are somewhat different in energy, the occupancy ratio will be different and the orientation with the lowest energy will be the most probable one. The crystal structures of (C_{60}-I_h)[5,6]fullerene are one of the most studied systems showing a whole-molecule disorder.[14–18] The disorder is due to the highly symmetrical character of C_{60} molecules (point group symmetry I_h) and a lack of other intermolecular interactions except for the van der Waals contacts.

Compounds containing the adamantane moiety have long been of interest due to its diverse biological activity, rigid structure, and well defined chemistry.[19–22] For example, the very bulky adamantyl group has been used as a protecting group of the carboxyl function and has received considerable attention in several fields of chemistry. To avoid the synthesis of side products in various reactions the ester bond is very often the choice of protection for the carboxyl group.[23] In particular, 1-adamantyl and 2-adamantyl groups were used as the protection groups to render peptide intermediates soluble in organic solvents.[24–26] In addition, the adamantyl protected amino acids may be applicable to solid phase peptide synthesis in combination with either 9-fluorenylmethyloxycarbonyl (Fmoc) or *tert*-butyloxycarbonyl (Boc) as N-protecting groups.[27]

* Authors to whom correspondence should be addressed. (E-mail: dubravka@chem.pmf.hr; majerski@irb.hr)

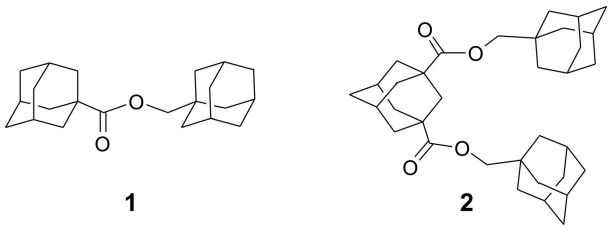

Figure 1. Structural diagrams of (1-adamantyl)methyl-1-adamantanecarboxylate (**1**) and bis[(1-adamantyl)methyl]-1,3-adamantanedicarboxylate (**2**).

During the course of our investigation of adamantane derived retropeptides[28,29] and different 1- and 1,3-adamantane derivatives[30,31] we have prepared and characterized ester derivatives of adamantanecarboxylic acid and adamantane-1,3-dicarboxylic acid: (1-adamantyl)methyl-1-adamantanecarboxylate (**1**), and bis[(1-adamantyl)methyl]-1,3-adamantanedicarboxylate (**2**) (Figure 1). In this paper, we also report an unusual four-fold whole-molecule disorder in the crystal structure of **1**.

EXPERIMENTAL

General: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300 or 600 Spectrometer. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as a reference. Infrared spectra were recorded from KBr-discs. Melting points were obtained using a Kofler apparatus and are uncorrected. For thin-layer chromatography (TLC) analysis, precoated TLC plates (Kieselgel 60 F254) were used, and column chromatography was done by using Kieselgel 60 (70-230 mesh) as the stationary phase. Literature procedures were used for the synthesis of 1-(hydroxymethyl)adamantane,[32] adamantanecarboxylic acid, and adamantane-1,3-dicarboxylic acid.[33]

Synthesis of (1-adamantyl)methyl-1-adamantanecarboxylate (1)

A solution of adamantanecarboxylic acid (0.1 g, 0.5 mmol) in $SOCl_2$ (3 cm^3) was refluxed for 2 h. Evaporation of excess of $SOCl_2$ afforded adamantane-1-carboxylic acid chloride as a white solid (0.11 g, 99 %), the compound was used in the next step without further purification due to its instability.[33]

A solution of adamantane-1-carboxylic acid chloride (0.11 g, 0.5 mmol) in dichloromethane (2 cm^3) was added to a solution of 1-(hydroxymethyl)adamantane (0.09 g, 0.5 mmol) and 4-(dimethylamino)pyridine[34] (0.271 g, 2.2 mmol) in dichloromethane (3 cm^3). The solution was stirred overnight at room temperature. The reaction was monitored by TLC (CH_2Cl_2). The reaction mixture was filtered through silica gel with dichloromethane as solvent. Further purification by column chromatography on silica gel (CH_2Cl_2 – R_f = 0.63) yielded **1** (0.116 g, 64 %) as a white microcrystalline solid; m.p. 247–248 °C (lit.[35] 247–250 °C); IR(KBr) $\tilde{\nu}_{max}$/cm^{-1}: 2904 (s), 2887 (s), 1725 (s), 1241 (m) 1241 (m) 1087 (m); ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 1.51–1.56 (m, 6H), 1.65–1.68 (m, 14H), 1.88–1.92 (m, 6H), 1.96–2.05 (m, 4H), 3.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm: 27.8 (d, 3C), 27.9 (d, 3C), 33.3 (s, 1C), 36.4 (t, 3C), 36.9 (t, 3C), 38.8 (t, 3C), 39.2 (t, 3C), 40.9 (s, 1C), 73.3 (t, 1C), 177.6 (s, 1C); *Anal.* Calcd. for $C_{22}H_{32}O_2$ (M_r = 328.49): C 80.44, H 9.82 %; found C 80.37, H 9.87 %. Suitable single crystal was obtained from acetone/dichloromethane (1:1) mixture by slow evaporation at room temperature.

Synthesis of bis[(1-adamantyl)methyl]-1,3-adamantanedicarboxylate (2)

A solution of adamantane-1,3-dicarboxylic acid (0.07 g, 0.3 mmol) in $SOCl_2$ (0.5 cm^3) was refluxed overnight. Evaporation of excess of $SOCl_2$ afforded adamantane-1,3-dicarboxylic acid dichloride as a white solid (0.07 g, 88 %), which was characterized by IR spectroscopy: IR(KBr) $\tilde{\nu}_{max}$/cm^{-1} 2915 (m), 2863 (m), 1794 (s), 1455 (s), 1446 (s), 1061 (s), 1040 (s), 943 (s), 833 (s), 670 (s). The compound was used in the next step without further purification due to its instability.

A solution of adamantane-1,3-dicarboxylic acid dichloride (0.07 g, 0.2 mmol) in dichloromethane (2 cm^3) was added to a solution of 1-(hydroxymethyl)adamantane (0.08 g, 0.5 mmol) and 4-(dimethylamino)pyridine[34] (0.122 g, 1 mmol) in dichloromethane (2 cm^3). The solution was stirred for 24 h at room temperature. The reaction was monitored by TLC (CH_2Cl_2 – R_f = 0.41). The reaction mixture was filtered through silica gel with dichloromethane as solvent. Further purification by column chromatography on silica gel (CH_2Cl_2) yielded **2** (0.086 g, 72 %) as a white microcrystalline solid; m.p. 153–155 °C; IR(KBr) $\tilde{\nu}_{max}$/cm^{-1}: 2917 (s), 2887 (s), 2851 (m), 1727 (s), 1263 (m), 1217 (m) 1021 (m); ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 1.49–1.58 (m, 8H), 1.59–1.79 (m, 16H), 1.84–2.02 (m, 16H), 2.07 (br. s, 2H), 2.13–2.21 (m, 2H), 3.66 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm: 27.8 (d, 2C), 27.9 (d, 6C), 33.3 (s, 2C), 35.3 (t, 1C), 36.9 (t, 6C), 38.0 (t, 4C), 39.2 (t, 6C), 39.9 (t, 1C), 41.2 (s, 2C), 73.6 (t, 2C), 176.8 (s, 2C); *Anal.* Calcd. for $C_{34}H_{48}O_4$ (M_r = 520.74): C 78.42, H 9.29 %; found C 78.62, H 9.11 %. Unfortunately, we were not able to grow suitable single crystals from dichloromethane, chloroform, methanol, ethanol, benzene, toluene, xylene, ethyl acetate, or either from their mixtures. The obtained crystals were in the form of very thin needles and were not suitable for single-crystal X-ray diffraction measurements.

X-ray structural analysis

The X-ray data for **1** were collected at 100(1) K on the Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal data for **1**: $C_{22}H_{32}O_2$, M_r = 328.48, colorless plate, 0.12 × 0.25 × 0.27 mm^3, orthorhombic, *Pbcn* (No. 60), a = 18.129(2) Å, b = 9.9360(4) Å, c = 9.9744(7) Å, V = 1796.7(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.215 Mg m^{-3}, μ = 0.075 mm^{-1}, $2\theta_{max}$ = 50°, $-21 \le h \ge 18$, $-11 \ge k \ge 11$, $-11 \ge l \ge 11$, 5557 measured reflections, 1574 independent reflections, 905 reflections with $I > 2\sigma(I)$, R_{int} = 0.0387, 128 parameters refined, 163 restraints used, R_1 = 0.0589 [$F^2 > 2\sigma(F^2)$] and 0.1070 (all data), wR_2 = 0.1421 [$F^2 > 2\sigma(F^2)$] and 0.1705 (all data), S = 1.007, the largest difference peak and hole 0.38 and –0.26 e Å^{-3}. Data reduction (including the numerical absorption correction, T_{min} = 0.983; T_{max} = 0.990) was performed using the CrysAlis software package.[36] The space group was unambiguously established from the systematic absences in the diffraction data and there were no signs of crystal twinning. Solution, refinement and analysis of the structure was done using the programs integrated in the WinGX software system.[37] The structure was solved by direct methods (SHELXS)[38] and refined by the full-matrix least-squares method based on F^2 against all reflections (SHELXL).[38] All non-hydrogen atoms were refined anisotropically by using the restraints on displacement parameters of the disordered ones. A molecule lying in the second, less occupied, position was refined as a rigid body using the molecular geometry found in the first, more occupied, position (prior to the final refinement). All hydrogen atoms in the first position were found in the difference map. Due to the low data-to-parameter ratio, all hydrogen atoms in the structural model were placed in idealized positions, with d(C−H) of 1.00 Å for methine and 0.99 Å for methylene groups, and refined using the riding model with U_{iso}(H) = 1.2 U_{eq}(C). Geometry calculations were done using PLATON,[39] while the structure drawings were prepared using ORTEP[40] and MERCURY.[41]

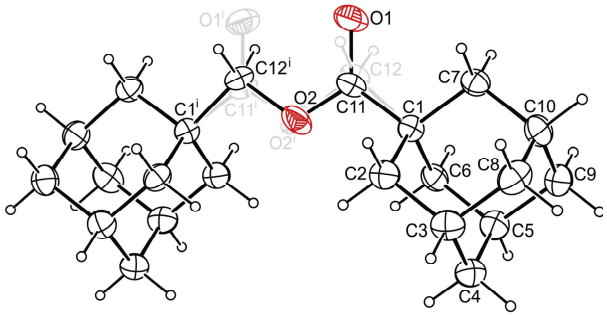

Figure 2. A disordered ester molecule of **1** in the major site [population parameter = 0.954(2)] disordered over a crystallographic 2-fold rotation axis passing almost through O2 [symmetry operator (i) $-x$, y, ½ − z]. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 50 % probability level. The atoms in the other orientation around the 2-fold axis are shown in gray.

RESULTS AND DISCUSSION

*Synthesis of **1** and **2***

The most convenient method for preparation of esters is the reaction of acid chlorides and alcohols. However, hydrogen chloride formed in such reactions often precludes substantial ester formation and a base should be used to react with the intermediary formed hydrogen chloride. (1-Adamantyl)methyl esters **1** and **2** (Figure 1) were prepared from the corresponding acid chlorides: adamantane-1-carboxylic acid chloride and adamantane-1,3-dicarboxylic acid dichloride, respectively, and 1-(hydroxymethyl)adamantane in the presence of 4-(dimethylamino)pyridine[34] which allowed us to carry out the reaction at room temperature. Although esters **1** and **2** are relatively hindered, the obtained yields were 64 and 72 %, respectively.

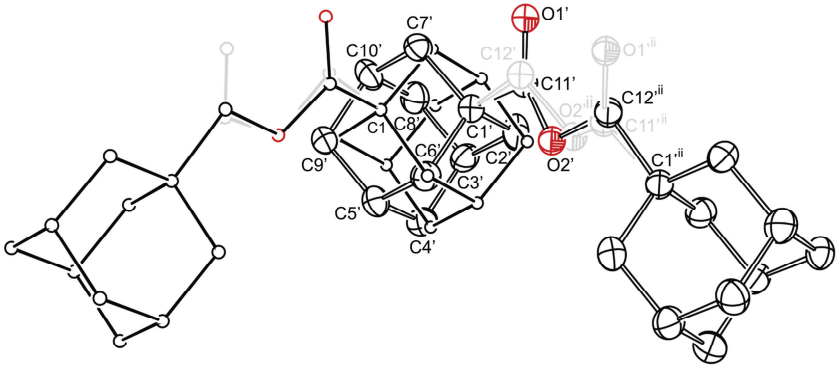

Figure 3. The two types of disorder in the crystal structure of **1**. For both the major and minor sites the disorder about crystallographic twofold axes is shown. Atoms in the major site (yellow in Figure 4) are shown as spheres of arbitrary radius, while atoms in the minor site (population parameter = 0.046(2); gray in Figure 4) are shown as displacement ellipsoids at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected geometric parameters in **1** (in Å and degrees)[(a)]

1st site		2nd site	
C1−C11	1.476(16)	C1'−C11'	1.48(3)
C1−C12	1.547(15)	C1'−C12'	1.55(3)
O1−C11	1.274(10)	O1'−C11'	1.27(3)
O2−C11	1.33(2)	O2'−C11'	1.33(3)
O2−C12^{i}	1.46(2)	O2'−C12'^{ii}	1.38(3)
O1−C11−O2	118.1(13)	O1'−C11'−O2'	118(2)
O2−C11−C1	115.9(13)	O2'−C11'−C1'	116(2)
O2−C12−C1	104.5(11)	O2'−C12'−C1'	105.2(17)
C11−O2−C12^{i}	116.4(8)	C11'−O2'−C12'^{ii}	110(2)
O1−C11−C1−C7	3.2(16)	O1'−C11'−C1'−C7'	3(3)
O1−C11−O2−C12^{i}	−6(2)	O1'−C11'−O2'−C12'^{ii}	12(3)
C11−O2−C12^{i}−C1^{i}	−179.7(12)	C11'−O2'−C12'^{ii}−C1'^{ii}	176.4(19)
C7−C1−C12−O2^{i}	179.6(8)	C7'−C1'−C12'−O2'^{ii}	163.2(17)

[(a)] Symmetry codes: i = −*x*, *y*, 1/2 − *z*; ii = −*x*, *y*, −1/2 − *z*.

Crystal Structure of ***1***

The ester molecules **1** crystallize in the orthorhombic space group *Pbcn* with four molecules in the unit cell. The most interesting feature in the crystal structure of **1** is existence of two different types of whole-molecule disorder: an ester molecule statistically occupies two different sites unrelated by crystallographic symmetry (positional disorder), and in each of the sites the molecule, which lacks 2-fold rotation symmetry, is additionally disordered over a crystallographic 2-fold rotation axis (orientational disorder).

A great majority of molecules [population parameter = 0.954(2)] are found in one site for which the 2-fold rotation crystallographic axis passes almost through the O2 atom (Figure 2) thus producing two equally populated molecular orientations. It was not possible to distinguish the positions of atoms of the two adamantyl groups in the molecule, so these were modeled by only one set of positions, *i.e.* the two adamantyl groups are related by a 2-fold rotation symmetry operator −*x*, *y*, 1/2 − *z*.

A minor portion of the ester molecules [population parameter = 0.046(2)] is found in the other site related to the first one by a non-crystallographic mirror symmetry parallel to the *ab*-plane and passing approximately through C7 and C4 atoms in the first position (Figure 3). Again, the molecule in this site is positioned on the crystallographic 2-fold axis passing near the O2' atom, and the two adamantyl groups are modeled as related by a 2-fold rotation symmetry operator −*x*, *y*, −1/2 − *z*. Even though the population parameter for the second site is very low, there were clear maxima in the difference Fourier map corresponding to the atomic positions

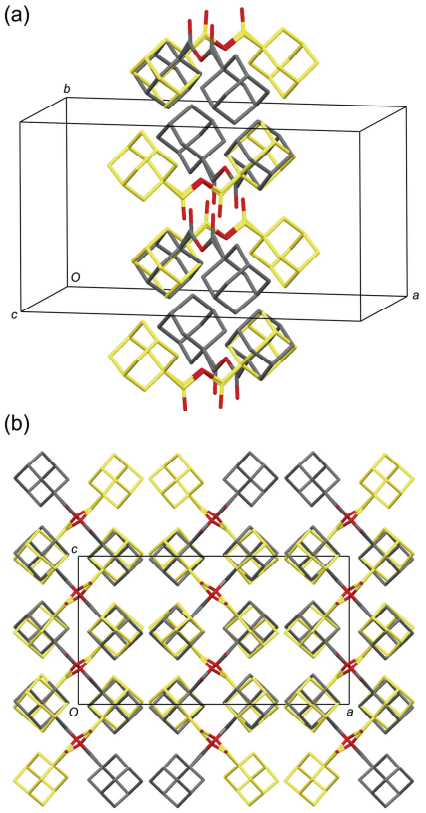

Figure 4. Crystal packing in the structure of **1**. Carbon atoms of the molecules in the major sites are colored gray and those in the minor sites are shown in yellow. If the major site is occupied, the two minor sites neighboring in the direction of the crystallographic *b*-axis cannot be occupied − otherwise, keto groups of molecules occupying these two different neighboring sites would be in a close contact [as shown in (a)]. View in (b) is along the crystallographic *b*-axis. Hydrogen atoms are omitted for clarity.

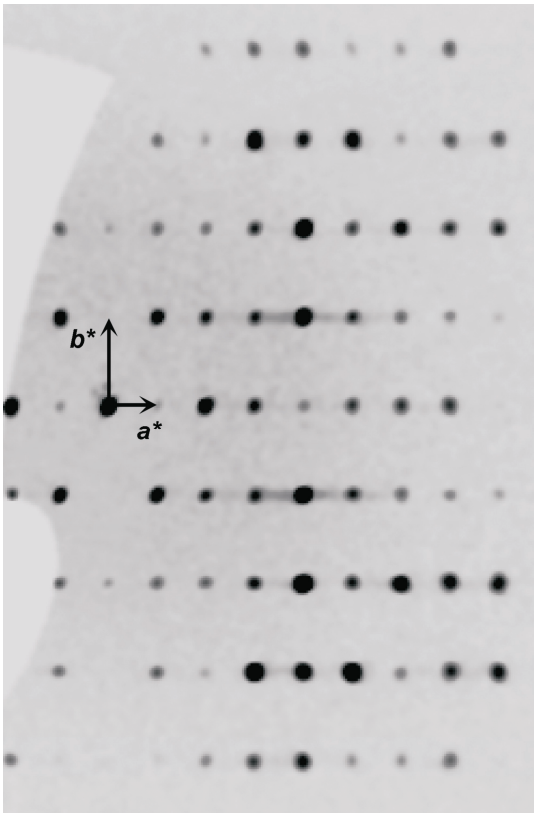

Figure 5. Reconstruction of the reciprocal-lattice plane $hk\bar{2}$. Lines of diffuse scattering are visible along the reciprocal a^*-axis.

in this site. If the population parameters for two molecular sites follow the Boltzmann distribution, the minor site is disfavored by 7.4 kJ mol^{-1} at 295 K in respect to the more populated major site.

The values of bond distances and angles (Table 1) are similar to those found in other related compounds,[7,42–48] however the observed disorder precludes a discussion of accurate molecular geometry. A carbonyl bond C11−O1 (C11'−O1') is synperiplanar in respect to C1−C7 (C1'−C7') and O2−C12^{i} (i = −*x*, *y*, 1/2 − *z*) [O2'−C12'^{ii} (ii = −*x*, *y*, −1/2 − *z*)] bonds, while C11−O2 (C11'−O2') is antiperiplanar in respect to C12^{i}–C1^{i} (C12'^{ii}–C1'^{ii}) bond (Figure 2).

In the crystal structure of **1** (Figure 4), the observed orientational disorder is possible because of a lack of any directional intermolecular interactions: the crystal packing is determined only by van der Waals interactions between the neighboring molecules. The exact molecular orientation in a particular molecular site is irrelevant, *i.e.* the two orientations related by the crystallographic 2-fold axis in the same site are equally probable.

It should be also noted that the ester molecules are arranged in layers parallel to the crystallographic *bc*-plane. Due to the steric limitations (Figure 4), all molecules in each such layer occupy either all major (gray in Figure 4) or all minor sites (yellow in Figure 4). Whatever the packing mode in a particular layer is, the layers are further stacked (in the direction of crystallographic *a*-axis) only by van der Waals interactions between adamantyl groups of the neighboring molecules. Due to the symmetry and metrics of the crystallographic unit cell ($c \approx a/2$), each molecular layer can be "misoriented" by the non-crystallographic glide plane *c* perpendicular to the crystallographic *a*-axis while apparently preserving van der Waals interactions between the layers. This results in stacking disorder (along the crystallographic *a*-axis) of the molecular layers with translational symmetry in the *b* and *c* directions. Interpretation of the positional disorder as stacking disorder of translationally symmetric layers parallel to the *bc*-plane is corroborated by observed lines of diffuse scattering along the reciprocal a^*-axis (clearly visible in the reconstructions of precession diffraction images; Figure 5). Such diffuse scattering pattern is characteristic for stacking disorder along one axis of the otherwise ordered layers.[49]

CONCLUSION

Two (1-adamantyl)methyl esters, **1** and **2**, were synthesized and characterized by spectroscopic methods. Single-crystal X-ray structural analysis of **1** revealed two types of whole-molecule disorder in the solid state: (1) the orientational disorder of each ester molecule, and (2) the stacking disorder of the molecular layers which are parallel to the crystallographic *bc*-plane. Both types of disorder are possible due to a lack of directional interactions between ester molecules.

Supplementary Materials. – CCDC 686710 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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SAŽETAK

(1-Adamantil)metilni esteri: nered cijele molekule u kristalnoj strukturi (1-adamantil)metil-1-adamantankarboksilata

Dalibor Milić,[a] Marija Alešković,[b] Dubravka Matković-Čalogović[a] i Kata Mlinarić-Majerski[b]

[a]*Zavod za opću i anorgansku kemiju, Prirodoslovno-matematički fakultet, Horvatovac 102a, 10000 Zagreb, Hrvatska*
[b]*Zavod za organsku kemiju i biokemiju, Institut Ruđer Bošković, POB 180, 10002 Zagreb, Hrvatska*

Dva (1-adamantil)metilna estera: (1-adamantil)metil-1-adamantankarboksilat (**1**) i bis[(1-adamantil)metil]-1,3-adamantandikarboksilat (**2**), pripravljena su u dobrom iskorištenju i okarakterizirana su spektroskopski. Struktura estera **1** određena je rentgenskom strukturnom analizom. Karakteriziraju je dvije vrste nereda cijele molekule: molekula estera zauzima jedno od dva različita položaja u asimetričnoj jedinici kristala (pozicijski nered), a u svakom položaju postoji još i dodatni nered preko kristalografske osi drugog reda (orijentacijski nered). Analizom difuznog raspršenja na difrakcijskim slikama otkriveno je da je pozicijski nered zapravo nered u slaganju molekulskih slojeva s dvodimenzijskom translacijskom simetrijom. U nedostatku drugih, usmjerenijih međudjelovanja, molekule u kristalnoj strukturi **1** povezane su samo van der Waalsovim interakcijama što objašnjava opaženi nered cijele molekule.