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Synthesis and X-ray diffraction study of triamantane

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ABSTRACT

Triamantane was synthesized in 80% yield by skeletal isomerization of a mixture of heptacyclo(8.8.0.0^{2,17}.0^{3,11}.0^{4,9}.0^{12,16}.0^{13,18})octadecane and heptacyclo(8.8.0.0^{2,13}.0^{3,11}.0^{4,9}.0^{12,17}.0^{14,18})octadecane under the action of the ionic liquid 2AlCl$_3$–Et$_3$N·HCl and mild conditions (50 °C, 8 h). X-ray diffraction analysis confirms the structure of the obtained product.

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Polycyclic cage hydrocarbons of the triamantane series are of considerable interest for the manufacture of pharmaceutical drugs[1] and materials for microelectronics[2] and non-linear optics.[3]

Triamantane (**1**) and its derivatives are found in crude oils, but only in trace amounts of 0.0001–0.03%. The relative contents of diamondoids in crude oils have been reported: adamantane (100), diamantane (50) and triamantane (15).[4] Under laboratory conditions, triamantanes are prepared by skeletal isomerization of polycyclic hydrocarbons having the same composition, induced by acid catalysts, specifically Lewis acids (AlCl$_3$, AlBr$_3$), superacids [B(OSO$_2$CF$_3$)$_3$, CF$_3$SO$_3$H] and Pt-containing catalysts.

The most efficient method for the synthesis of triamantane (**1**) is based on skeletal isomerization of the C$_{18}$H$_{24}$ polycyclic hydrocarbons **2** and **3**; these are obtained in three steps from the [4π+4π]-dimer of norbornadiene (binor-S) (Scheme 1).

The isomerization of hydrocarbons **2** and **3** into triamantane (**1**) has been catalysed by Lewis and Brønsted acids: AlCl$_3$ (refluxing in cyclohexane for 5 days, 60% yield),[5] B(OSO$_2$CF$_3$)$_3$ (0 °C, Freon-113, 74 h, 70% yield), CF$_3$SO$_3$H-SbF$_5$ (0 °C, Freon-113, 74 h, 71% yield) and CF$_3$SO$_3$H-B(OSO$_2$CF$_3$)$_3$ (0 °C, Freon-113, 74 h, 69% yield).[6]

Inorganic ionic liquids have become more common in synthetic practice. They have found wide use in organic synthesis and catalysis. Some inorganic ionic liquids are known to exhibit Brønsted or Lewis acidity or superacidic properties. In particular, superacidic behaviour was found for aluminium chloride containing melts, which makes them attractive for use in catalysis.[7] For example, the high catalytically active ionic liquid, 2AlCl$_3$ + Et$_3$N·HCl has been shown to isomerize cyclohexane into methylcyclopentane.[8]

We have found that the ionic liquid 2AlCl$_3$ + Et$_3$N·HCl can serve as an effective catalyst for the isomerization of cyclic hydrocarbons (**2** and **3**) into triamantane (**1**).[9] The reaction proceeded under mild conditions (50 °C) to give a yield of **1** being dependent on the reactant molar ratio. Using an equimolar ratio of [**2**+**3**]/[ionic liquid] = 1:2, the yield of **1** was 50%. With a twofold increase in the concentration of the ionic liquid ([(**2**+**3**)]/[2AlCl$_3$ + Et$_3$N·HCl] = 1:4), the yield of **1** was 80% under the same conditions (Scheme 2).

The ionic liquid 2.5AlCl$_3$ + Et$_3$N·HCl showed lower catalytic activity. Under the same conditions (50 °C, 8 h), the yield of the end product did not exceed 40%. The reaction mixture was heterogeneous, so the experiments were performed with vigorous stirring. The high yield of triamantane while using 2AlCl$_3$ + Et$_3$N·HCl can be explained by the fact that this compound is a homogeneous liquid whilst 2.5AlCl$_3$ + Et$_3$N·HCl is a viscous, heterogeneous mass, which mixes poorly with the initial hydrocarbons **2** and **3**.

It is noteworthy that the ionic liquid performs two functions in this reaction, being both the catalyst and the reaction medium. The use of solvents is undesirable because the addition of a solvent (hexane, dichloromethane) decreased the triamantane yield to 10%.

In 1969, X-ray diffraction data for triamantane were reported for the first time.[10] However, no detailed analysis of its structure was given. Only the unit cell parameters were described and the structure was found to exist as an orthorhombic system with an

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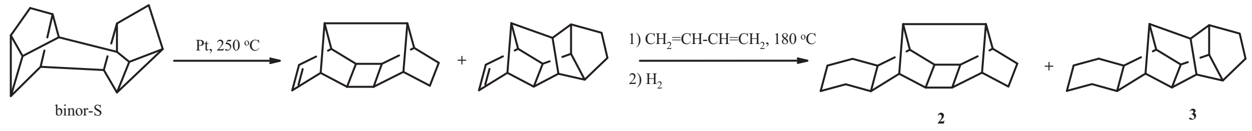
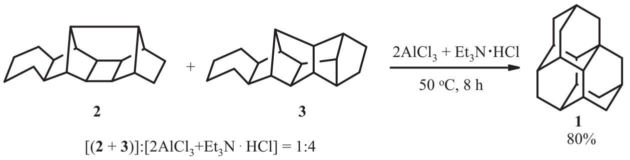


Scheme 1. Multistep synthesis of the $C_{18}H_{24}$ polycyclic hydrocarbons **2** and **3** from binor-S.



Scheme 2. Isomerization of mixtures **2** and **3** into triamantane (**1**) in the presence of an ionic liquid catalyst at 50 °C ([(**2+3**)]/[$2AlCl_3$ + $Et_3N·HCl$] = 1:4).

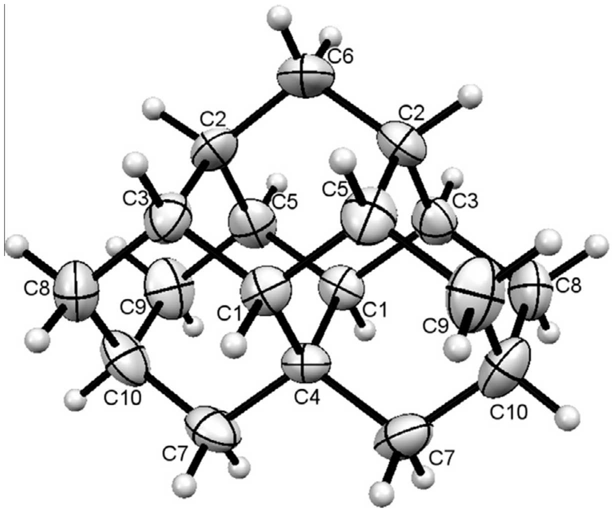


Figure 1. Molecular X-ray crystal structure of triamantane. The atoms are represented by thermal ellipsoids (p = 50%).

Fddd space group. Therefore, we report an X-ray diffraction study of triamantane with detailed analysis of the C—H bonds and bond angles.

The crystal structure of **1** (Fig. 1) is composed of single molecules held together by common van der Waals interactions. The bond distances (Å) distributed in accordance with the degree of substitution at the carbon atoms are given in Table 1. This classification distinguishes the following types of bonds: C—CH_2, C—CH, CH—CH_2, and CH—CH. The lengths of the CH—CH and CH—CH_2 bonds can also be classified into several types depending on the type of environment of the neighbouring groups. The bond angles can also be classified in several ways (Table 1). Considering the bond lengths, it should be noted that the CH—CH bonds, which contain in the local environment the carbon atoms bearing an equatorial hydrogen atom, have a bond length value of 1.540 Å. The lengths of the CH—CH bonds connected to carbons with both axial and equatorial orientations are, on average, 1.533 Å. The bond length dependence upon the environment of the neighbouring atoms is clearly seen in the examples of CH—CH_2 bonds. Indeed, the longest CH—CH_2 bond (1.529 Å) is observed if CH groups with an equatorial hydrogen are present in the local environment of this bond, whereas the presence of a CH group with an axial hydrogen or their absence leads to bond shortening (Table 1).

Analysis of the C—C—C bond angles demonstrated the greatest values for the CH_2—C—CH_2 and CH—CH_2—C angles, being 111.57° and 111.04°, respectively. The smallest value was found for the CH—C—CH angle (107.29°). Also noteworthy are the CH—CH_2—CH and CH—CH—CH angles, which vary depending on the local environment. For example, if the local environment contains CH groups with an axial hydrogen, these angles are the largest, whereas the presence of CH groups with an equatorial hydrogen in the local environment results in smaller values for these angles (Table 1).

The ^1H and ^{13}C NMR spectroscopic parameters of triamantane (**1**) are summarized in Table 2, and are simular to published data.[5] The accuracy of the assignments is supported by the cross-peak data in the homonuclear COSY and heteronuclear HMBC experiments (Table 2).

In conclusion, we have implemented the synthesis of triamantane via skeletal isomerization of a 1:1 mixture of heptacyclo$[8.8.0.0^{2,17}.0^{3,11}.0^{4,9}.0^{12,16}.0^{13,18}]$octadecane (**2**) and heptacyclo $[8.8.0.0^{2,13}.0^{3,11}.0^{4,9}.0^{12,17}.0^{14,18}]$octadecane (**3**) under mild conditions (50 °C, 8 h, 80% yield) using the inorganic ionic liquid [$2AlCl_3$ + $Et_3N·HCl$] as an effective catalyst. Single crystal X-ray analysis of triamantane has been performed to provide very detailed information on the bond distances and angles between atoms, being valuable supplements to the triamantane (**1**) characteristics already available in the literature.

The $C_{18}H_{24}$ hydrocarbons **2** and **3** were prepared by a reported procedure;[5] the chloroaluminate ionic liquid was prepared as described previously.[11]

Table 1
Classification of bond lengths and bond angles for **1**

Average bond lengths (Å) distributed according to the degree of substitution at the carbon atom				
CH_2—C	1.531	CH—CH	(eq)	1.540
			(ax and eq)	1.533
CH—C	1.545	CH—CH_2	(eq)	1.529
			(ax)	1.523
			(−)	1.522
			(ax and eq)	1.526
*Average bond angles (°) for **1** distributed according to the degree of substitution at the carbon atom*				
CH—CH—C		109.4	CH—C—CH	107.3
CH_2—CH—CH (eq)		110.4	CH_2—C—CH	109.5
(ax and eq)		110.7		
CH_2—C—CH_2		111.6	CH—CH_2—C	111.0
CH—CH_2—CH (ax)		110.0	CH—CH—CH (ax)	112.0
(eq)		109.4	(eq)	108.3

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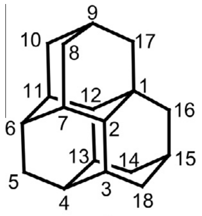
Table 2
^{1}H NMR (500.17 and 400.13 MHz) and ^{13}C NMR (100.62 MHz) spectroscopic data for **1**[a] ($CDCl_3$)



1

C	δ ^{13}C	δ ^{13}C (250 MHz)[15]	δ ^{1}H (*J*, Hz)	HMBC cross-peaks (CH)
1	33.6	33.9		
2, 12	47.0	47.1	1.49 s	C4, C6
3, 7, 11, 13	38.2	38.3	1.68 s	C4, C6
4, 6	35.3	35.4	1.66 s	C3, C7, C11, C13
5	38.6	38.7	1.66 s	C2, C12
8, 10, 14, 18	38.2	38.3	1.69–1.76 s	C3, C7, C11, C13
9, 15	27.9	28.0	1.86 sept (J = 3 Hz)	C8, C10, C14, C18
16, 17	45.4	45.5	1.28 d (J = 3 Hz)	C1, C15, C9, C18

[a] The chemical shifts are reported in δ (ppm), and the spin-spin coupling constants (J) in Hertz (Hz).

The X-ray diffraction study of triamantane (**1**) was carried out on an XCalibur Eos automated four-circle diffractometer (graphite monochromator, Mo$K\alpha$ radiation, λ = 0.71073 Å, ω-scan mode, $2\theta_{max}$ = 62°). The data were collected and processed using the CrysAlis^{Pro} (Oxford Diffraction Ltd) program, version 1.171.36.28. The structure was solved by direct methods and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were located in the difference Fourier synthesis and are included in the refinement with fixed thermal and positional parameters. The calculations were performed using the SHELX97 program package.[12] The key crystallographic data and X-ray experiment details for compound **1** are presented in Table 1 and in the Supplementary data. The CIF file has been deposited with the Cambridge Crystallographic Data Centre, CCDC-941276. Copies of these data are available free of charge from the CCDC on request: 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk)/http://www.ccdc.cam.ac.uk/data_request/cif.

Crystal data of **1**: $C_{18}H_{24}$, 240.37, orthorhombic, space group Fddd (no. 70), a = 12.8717(8) Å, b = 18.0852(11) Å, c = 21.9834(17) Å, V = 5117.5(6) Å^3, Z = 16, D_{calcd} = 1.248 g/mm^3, R = 0.0760, Rw = 0.2373, GOF = 1.037.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.12.006.

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9. *General procedure for the synthesis of triamantane* (**1**): A reactor (V = 50 mL) was charged under argon with 1.5 mmol of the $C_{18}H_{24}$ hydrocarbon mixture (**2** and **3**) and 6 mmol of the ionic liquid $2AlCl_3 + Et_3N{\cdot}HCl$. The reaction mixture was heterogeneous so the experiment was performed with continuous stirring for 8 h at 50 °C. The reactor was cooled to room temperature and the mixture was extracted with petroleum ether (3 × 50 mL) and filtered through a layer of silica gel (petroleum ether as the eluent). The solvent was distilled off and the residue was recrystallized from a 1:1 EtOAc/cyclohexane mixture. The yield of triamantane (**1**) was 80%. The structure of **1** was confirmed by NMR and mass spectrometry, X-ray diffraction analysis and also by comparison with authentic samples and reference data. Triamantane (**1**): mp. 221–221.5 °C (Lit. mp 221 °C).[13] ^{1}H NMR (400 MHz, $CDCl_3$).[14] ^{13}C NMR (100 MHz, $CDCl_3$)[15]: δ 27.9, 33.6, 35.3, 38.2, 38.2, 38.6, 45.4, 47.0 ppm. MS (EI, 70 eV) m/z (%): 240.1 $[M]^+$ (100.0), 239.1 (43.7), 143.1 (8.0), 131.1 (5.6), 129.1 (10.2), 128.1 (5.0), 117.1 (6.1), 115.1 (5.0), 105.1 (6.8), 91.1 (20.7), 79.1 (10.6), 77.1 (8.9).
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