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Thermolabile Hydrocarbons, XXVII[1]

2,3-Di-1-adamantyl-2,3-dimethylbutane; Long Bonds and Low Thermal Stability

Manuela A. Flamm-ter Meer[a], *Hans-Dieter Beckhaus*[a], *Karl Peters*[b], *Hans-Georg von Schnering*[b], and *Christoph Rüchardt**[a]

Institut für Organische Chemie und Biochemie der Universität Freiburg[a], Albertstr. 21, D-7800 Freiburg i. Br., und

Max-Planck-Institut für Festkörperforschung[b], Heisenbergstr. 1, D-7000 Stuttgart 80

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The title compound **2** was prepared by a Wurtz procedure. Its highly deformed structure was determined by *X*-ray analysis and matched with high precision by MM2 force field calculations. The three neighbouring C_qC_q bonds are longer than 164 pm and the $C_qC_qC_q$ bond angles are 118°. According to MM2 calculations and a kinetic investigation **2** is the most strained and least stable member of the C_qC_q alkane series investigated previously[2].

Thermolabile Kohlenwasserstoffe, XXVII[1]

2,3-Di-1-adamantyl-2,3-dimethylbutan; lange Bindungen und geringe thermische Stabilität

Die Titelverbindung **2** wurde durch Wurtz-Synthese dargestellt und eine Kristallstrukturanalyse durchgeführt. Die Strukturdaten des sehr stark deformierten Molekülgerüstes – drei benachbarte C_qC_q-Bindungen sind länger als 164 pm, $C_qC_qC_q$-Bindungswinkel sind bis 118° aufgeweitet – werden durch Rechnungen mit dem MM2-Kraftfeld sehr gut wiedergegeben. Nach den Kraftfeldrechnungen ist **2** der am stärksten gespannte, nach kinetischen Messungen der thermisch labilste Vertreter der bereits früher bearbeiteten C_qC_q-Alkane[2].

Previously we discussed the factors which influence the strengths and the lengths of CC bonds between two quaternary carbons in open-chain structures[2–6]. Substituents stabilizing the radicals, which are formed on bond homolysis, decrease the bond strength but apparently have little effect on the bond length[4–8]. Increasing ground state strain H_s on the other hand results in a decrease in bond strength and also in an increase in bond length[4–6]. The most highly strained and thermally most labile known member of the unsubstituted aliphatic C_qC_q series is octamethylhexane **1**[2], the structure and thermochemistry of which were so far investigated only by molecular mechanics and NMR[2,9]. A crystal structure analysis was prevented by the low melting point of **1**, the experimental determination of its heat of formation by the poor yield of its preparation. It was an unfortunate situation in the context of our search for relationships between structure, strain, and thermal stability of highly strained compounds[4–6] that the MM2 force field[10]

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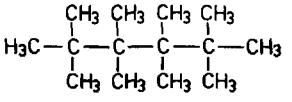
like other force fields was not originally parametrized for highly strained compounds like **1**.



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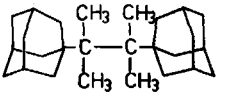
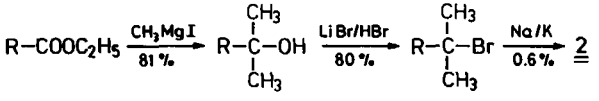


2

We investigated, therefore, the synthesis of the title compound **2** hoping, that it would be crystalline. In addition **2** would contribute in extending our ongoing research of comparing the steric effects of adamantyl and *tert*-butyl groups[1b].

Synthesis and Spectra of 2

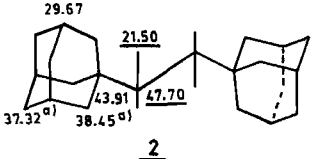
Ethyl 1-adamantanecarboxylate (**3**) on treatment with methylmagnesium iodide gave the tertiary alcohol **4** in 81% yield[11] from which the bromide **5** was obtained in 80% yield by the recently proposed reagent LiBr/HBr[12] in benzene. Despite extensive attempts to improve the yield of the last dimerisation step[1b] analytical pure **2** was obtained from **5** and sodium-potassium alloy[13] in only 0.6% yield as high melting colourless needles by column chromatography and by crystallisation from CCl_4.



3 **4** **5**

R=

The ^1H NMR spectrum of **2** consists of a singlet signal for methyl and two separate broad absorptions for the adamantyl protons. The signals of the more complex ^{13}C NMR spectrum were assigned to the corresponding carbons by decoupling and spin echo experiments[14] (see Fig. 1), and the two triplet signals were assigned to the methylene groups by analogy[15]. There is a large downfield shift of the signals of the central C-atoms of **2** very close to that observed previously



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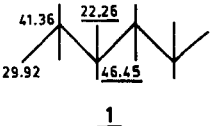


1

[a] Presumed assignment.

Fig. 1. ^{13}C NMR chemical shifts of **1**[2] and **2**; δ(ppm)

for **1** (see Fig. 1). This shift is obviously caused by strong van der Waals interactions.

This assumption is supported by the fact that the chemical shifts of the central C_q atoms in the series of aliphatic hydrocarbons $R(CH_3)_2C-C(CH_3)_2R$ increase continuously when R is changed from primary to secondary and tertiary alkyl groups[2,9]. The largest shift is found in **2** which is also the most strained member of the series.

In the mass spectrum of **2** (chemical ionisation with methane) the $M/2^+$ peak had the highest intensity and the only larger mass observed was $(M/2 + 1)^+$. The fragmentation pattern was simple as in similar cases[2].

Structure of 2

2 crystallizes monoclinically in the space group $P2_1/n$ (no. 14) with a = 2282(1), b = 674.9(2), c = 1359.6(7) pm and β = 102.12(4)°, Z = 4, d_c = 1.150 g · cm^{-3}. The positional and thermal parameters of the atoms of **2** are given in Table 3 and the bond lengths and angles in Table 4. The perspective drawing of **2** and a Newman projection along its central bond are shown in Fig. 2. Selected bond lengths and bond angles are compared with results from force field calculations with Allingers MM 2 force field[10] (see Table 1).

Despite the very unusual features of the structure of **2**, the agreement between the experimental results and the calculated predictions is remarkable.

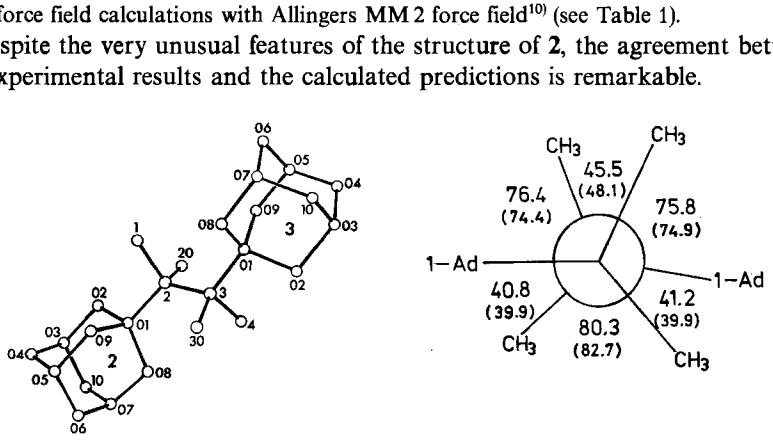


Fig. 2. Left: Stereographic projection of the molecule of **2** and numbering of atoms. Right: Newman projection of **2** along the C(3)–C(2) bond and torsional angles from *X*-ray analysis (MM 2 results in brackets)

Table 1. Selected bond lengths and bond angles of **2** as obtained by crystal structure analysis (exp.) and by MM 2 force field calculations (calcd.)[10] (numbering from Fig. 2)

Bond Lengths [pm]	exp.	calcd.[a]	Bond Angles (Degree)	exp.	calcd.
C(2)–C(3)	163.9	164.0	C(201)–C(2)–C(1)	106.1	105.8
C(2)–C(201)	164.7	165.5	C(201)–C(2)–C(20)	107.1	105.8
C(3)–C(301)	164.0	164.5	C(2)–C(3)–C(30)	108.2	108.5
C(2)–C(1)	154.6	155.7	C(2)–C(3)–C(4)	109.5	109.0
C(2)–C(20)	153.9	155.2	C(3)–C(2)–C(201)	117.4	120.9
			C(2)–C(3)–C(301)	117.8	120.9

[a] MM 2 force field[10].

The *anti*-conformation ($\Delta H_f^\circ = -58.1$ kcal · mol^{-1}) is favored over the *gauche*-conformation ($\Delta H_f^\circ = -54.4$ kcal · mol^{-1}) by 3.7 kcal · mol^{-1} according to the force field calculations. It is, indeed, the conformation found in the crystal. Due to the bulkiness of the adamantyl groups the $C_qC_qC_q$ bond angles in the central region are increased to 117.6° (120.9°, MM2) and consequently the torsional angles deviate appreciably from the ideal 60° angle. The 163° torsional angles between the two adamantyl groups apparently allow the best reduction of repulsive van der Waals interactions between vicinal groups. This distortion reduces the symmetry to the C_2 point group very similar to the situation in the distorted structure of hexamethylethane, which was determined by electron diffraction[16d]. Force field calculations predict a similar deviation from the 180° torsional arrangement for most of the C_qC_q alkanes investigated previously[2,9]. The agreement between the experimental and the calculated torsional angles in Fig. 2 is particularly remarkable. Obviously they are not determined by the inherent force constants which are small compared to those of bond stretching and bond angle deformations; steep torsional potentials are rather caused by strong non-bonded repulsions.

The most remarkable feature in the structure of **2** are the 164 pm long C_qC_q bonds in the central region of the molecule. 164 pm matches the longest CC bonds reported in alicyclic compounds[16] and there are three of them adjacent to each other in **2**, one of them being almost 165 pm in length. The ability of the MM2 force field to match these unusual structural deformations is quite impressive.

This supports the validity of the calculated structure of **1**[2] because the structures of **1** and **2** have much in common. Both prefer the *anti*-conformation while for other members of the series $R-C(CH_3)_2-C(CH_3)_2-R$ (R = C_2H_5, *neo*-C_5H_{11}) a slight preference of the *gauche*-arrangement over the *anti*-conformation was found by dynamic NMR spectroscopy as well as force field calculations[9]. Fig. 3 shows for comparison some typical bond lengths, bond angles, and torsional angles for octamethylhexane **1**.

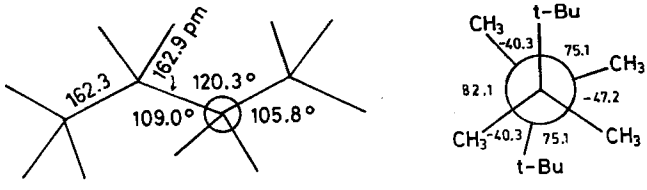


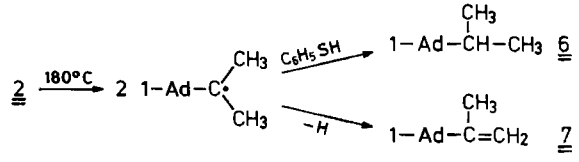
Fig. 3. Bond lengths, bond angles, and torsional angles of **1** (MM2 results[2])

The bond angle deformations in **1** and **2** are almost identical, the torsional deformations are similar, but in **2** larger than in **1**. The bond stretching in the center of **2** surpasses that in **1** by 1–2 pm for each C_qC_q bond.

Thermal Stability and Strain

2 is the most crowded member of the aliphatic C_q-C_q ethane series. It was of interest to find out whether **2** still follows the relationship between thermal stability and strain reported for this series[2,4–6].

When a sample of **2** was heated to 180°C for 5 h in a mixture of toluene and thiophenol a quantitative yield of 2-(1-adamantyl)propane (**6**) (1.82 mol/mol **2**) and 2-(1-adamantyl)propene (**7**) (0.18 mol/mol **2**) were analysed by capillary gc and mass spectroscopy. The yield of adamantane was less than 0.1% indicating that **2** decomposes almost exclusively by the cleavage of the bond between the central two quaternary carbon atoms. This is energetically the favoured pathway of homolytic cleavage because the intermediate 2-(1-adamantyl)propyl radicals are less strained than 2-(1-adamantyl)-1,1,2,2-tetramethylethyl radicals which would be formed in the cleavage reaction of the other long bonds.



The kinetics of this thermolysis reaction were measured by following the heat flow during the decomposition of **2** dissolved in two weight equivalents of 9,10-dihydroanthracene (scavenger) in a differential scanning calorimeter[7,8]. The results are recorded in Table 2 together with data for octamethylhexane **1** for comparison.

Table 2. Activation parameters for the thermal decomposition of 2,3-di-1-adamantyl-2,3-dimethylbutane (**2**) and of octamethylhexane (**1**)[2]

	n/T[a]	$\Delta G^{\neq}$ (300°C) [kcal · mol^{-1}]	$\Delta H^{\neq} \pm \sigma$[b]	$\Delta S^{\neq} \pm \sigma$[b] [e.u.]	H_s[c] [kcal · mol^{-1}]	T[d] [°C]
1[e,f]	6/45	34.4	42.1 ± 0.8	13.6 ± 1.7	41.2[e]	195
2	3/47	30.5	43.7 ± 0.1	23.1 ± 0.1	42.1[g]	167

[a] For **1** n = number of independent rate constants (by gc), for **2** n = number of independent dsc experiments with separate evaluation[7,8], T = temperature range of measurements and dsc analysis, respectively. — [b] σ = standard deviation. — [c] $H_s = \Delta H_f^{\circ}(g) - \Delta H_f^N$; $\Delta H_f^{\circ}(g)$ = standard heat of formation obtained from calculations using the MM2 force field[10] ΔH_f^N = normal value calculated according to *von Schleyer*s group increment formalism[17]. — [d] Temperature at which the half time of decomposition is 1 h. — [e] See ref.[2]. — [f] The activation parameters were calculated with the improved statistical analysis of the program „Kinetic 80" by *Hellmann*[18]. — [g] The ring strain oft two adamantyl rings[3,19] 2 × 7.9 = 15.8 kcal · mol^{-1} was substracted as a correction term.

It is obvious from these data that the exchange of 1-adamantyl for *tert*-butyl results in a decrease of thermal stability. $T(\tau_{1/2} = 1\ h)$ of **2** is almost 30°C lower than for **1** and the difference in $\Delta G^{\neq}$ (300°C) amounts to almost 4 kcal/mol. The difference in $\Delta G^{\neq}$, however, is mainly due to the much larger entropy of activation $\Delta S^{\neq}$ of **2** than for **1**. The 23.1 e.u. value of $\Delta S^{\neq}$ for **2** is much larger than the mean value 15 e.u. of $\Delta S^{\neq}$ for the aliphatic $C_q - C_q$ series[2]. This increased entropy of activation is probably due to the rigid structure of the adamantyl group which leads to increased barriers for rotation about the C-1 – adamantyl bond in **2** as

compared to the C–*tert*-butyl bond in **1**. This hindered rotation is apparently liberated on thermal bond dissociation.

The close agreement of $\Delta H^{\neq}$ on the one hand and of H_s on the other for **1** and **2** supports the wide scope of validity of the relationship between strain and thermal stability in this series when it is based on $\Delta H^{\neq}$. For several reasons, however, which were discussed in other context the $\Delta G^{\neq}$ (300°C) vs H_s correlation

$$\Delta G^{\neq}\ (300\,^{\circ}\mathrm{C}) = 62.1\ (\pm 0.7) - 0.63\ (\pm 0.03)\ H_s\ [\mathrm{kcal \cdot mol^{-1}}]$$

turned out to be preferred for the analysis of this relationship[5–7]. For H_s = 42.1 kcal · mol^{-1} of **2** this results in an expected free enthalpy of activation of the decomposition of **2** $\Delta G^{\neq}$ (300°C) calcd. = 35.5 kcal · mol^{-1} which deviates by as much as 5 kcal/mol from the experimental value.

A weak point of the $\Delta G^{\neq}/H_s$ analysis is the fact, that it ignores residual strain in the radicals being formed. Therefore $\Delta G^{\neq}/D_s$-correlations were introduced[5–7,20,21] in which $D_s = H_s$ (dimer) − 2 H_s (radical fragments).

The strain enthalpies of the radicals were obtained from force field calculations using *Beckhaus*'s force field for radicals[22]. For the 2-(1-adamantyl)propyl radical a strain enthalpy of 10.2 kcal · mol^{-1} is obtained in this way which corresponds to 2.3 kcal · mol^{-1} after correction for the ring strain of the adamantyl ring (7.9 kcal · mol^{-1})[19]. From the correlation

$$\Delta G^{\neq}\ (300\,^{\circ}\mathrm{C}) = 62.2\ (\pm 1.1) - 0.72\ (\pm 0.05)\ D_s\ [\mathrm{kcal \cdot mol^{-1}}]$$

$\Delta G^{\neq}$ (300°C) = 35.2 kcal · mol^{-1} is expected for **2** which deviates even more from the experimental value in Table 2.

There are two obvious reasons for this discrepancy. Either it is due to the anomalous high entropy of activation for the decomposition of **2**. As a consequence a full compensation of the temperature function of $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ may no longer be guaranteed[5–7]. This compensation effect[23] is responsible for the high quality of the $\Delta G^{\neq}/H_s$-correlations in these systems.

More important on the other hand is that the precise reliability of the thermochemical results of force field calculations by the MM 2 force field may no longer be achieved for a compound as highly strained as **2**. The limit of the reliability of thermochemical MM 2 results was encountered previously for tetra-*tert*-butylethane[1a] and for hexacyclopropylethane[24]. For tetra-*tert*-butylethane the experimental heat of formation (66.3 kcal · mol^{-1}) did deviate from the MM 2 result (57.7 kcal · mol^{-1}) by about 8 kcal · mol^{-1}. Due to lack of material an experimental determination of the heat of formation of **2** was so far not possible. It is planned to collect this information in the near future.

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Experimental Part

IR spectra: Perkin Elmer spectrometer 398 and 421. – ^{1}H NMR spectra: Bruker WM 250 and Varian EM 390 instruments. – ^{13}C NMR spectra: Bruker WP 80 spectrometer; δ-scale,

internal reference TMS. – Mass spectra: Finnigan MAT 44 S spectrometer. – Gas chromatography: Fractometer 3700 Varian (gc-MS coupling); Fractometer F 20 B and Sigma B Perkin Elmer. – Differential scanning calorimeter: Perkin Elmer DSC-2.

2-(1-Adamantyl)-2-propanol (**4**) was prepared in 81% yield from ethyl 1-adamantanecarboxylate (**3**)[25] and methylmagnesium iodide[11] and crystallized from toluene below 60°C or sublimed in small portions at 60°C/12 Torr. M. p. 75–78°C (lit.[11] 81.0–81.4°C). – IR and ^{1}H NMR spectra agreed with data in the literature[11].

2-(1-Adamantyl)-2-bromopropane (**5**): A mixture of 13.0 g (67 mmol) of **4** and 8.7 g (100 mmol) of LiBr in 85 ml of benzene[12] was cooled in an ice bath and 15.4 ml (129 mmol) of 74% HBr in 85 ml of acetonitrile was slowly added with stirring. After 3 h of stirring, the phases were separated and the aqueous phase was extracted twice with benzene. The combined organic phase was then extracted twice with 20 ml of glycol each time and dried with anhydrous $MgSO_4$. After the solvent had been evaporated in vacuo the remaining solid residue was crystallized from petrolether (40–60°C). The colourless platelets turned yellow on standing for a few days. Yield: 17.0 g (80%); m. p. 109–111°C (lit.[11] 124°C). – IR (KBr): 595 (C–Br) cm^{-1}. – The ^{1}H NMR spectrum agreed with that reported earlier[11].

2,3-Di-1-adamantyl-2,3-dimethylbutane (**2**): The three necked flask used was dried by heating under reduced pressure and aerated with dry argon. In a countercurrent of argon 3.75 ml (75 mmol) of sodium-potassium alloy[13] was injected with a syringe and 50 ml of dry ether was added. Then a solution of 13.0 g (50 mmol) of **5** in 100 ml of anhydrous ether was steadily added which had been stored over molecular sieve (4 Å) for 24 h. The solution turned deep blue violet and the temperature rose to 32°C and slowly levelled off again after 1 h of stirring. The stirring was continued for 3 days till the solution had become light blue. 20 ml of ethanol was then slowly added with external cooling and afterwards the solution was hydrolyzed by adding ice water till two clear phases had separated. The aqueous phase was three times extracted with pentane and the combined organic phases were washed neutral, dried, and the solvent was evaporated. From the oily residue (8.0 g) the volatile components were distilled off at 54°C/0.2 Torr. The oily residue (300 mg) was chromatographed in CCl_4 over silica gel in order to remove olefinic impurities. From the remaining solid material 50 mg (0.6%) of colourless needles were isolated by crystallisation from CCl_4, m. p. 233–237°C (dec). – ^{1}H NMR (CCl_4, HMDS): δ = 1.79 (m; 9H), 1.53 (m; 6H), 0.92 (s; 6H, $C(CH_3)_2$). – ^{13}C NMR ($CDCl_3$, CCl_4, TMS): δ = 47.70 (s; C-2), 43.91 (s; C-3), 38.45 and 37.32 (2 t; C-4 and -6), 29.67 (d; C-5), 21.50 (q; C-1) (see Fig. 1 for numbering). – MS (CI-methane): m/z = 178 (16.6%, $M/2^+ + 1$), 177 (100, $M/2^+$), 176 (11, $M/2^+ - 1$), 175 (7.2, $M/2^+ - 2$), 135 (27.3, Ad^+).

$C_{26}H_{42}$ (354.3) Ber. C 88.06 H 11.94 Gef. C 87.73 H 11.59

Thermolysis of **2**

Products: A few ml of an 0.02–0.1 M solution of **2** containing 4 mol equivalents of thiophenol in toluene was heated in an ampule for 5 h in a thermostat to 180°C under nitrogen. The products were analyzed with *n*-dodecane as internal standard on a 25 m quartz capillary column coated with SE 30 and they were identified by comparison with authentic samples[1b] and by gc-MS coupling experiments.

2-(1-Adamantyl)propane (**6**), 1.82 mol/mol **2**.

MS: 178 (5%, M^+), 161, *135* (100 Ad^+), 79 (45, $C_6H_5^+$).

2-(1-Adamantyl)propene (**7**), 0.18 mol/mol **2**.

MS: 176 (78%, M^+), 161 (19, 1-Ad–C=CH_2^+), 135 (64, Ad^+), 79 (100, $C_6H_5^+$).

Kinetics were measured by following the heat flow of the non-isothermal decomposition reaction of **2** in a DSC-2 calorimeter[6,7,24]. The aluminum pan containing the sample was held in a steel container with a screw top which was made pressure tight with a silver gasket. Probe and standard were heated with the same rate of 5°C/min. The sensitivity of the instrument was 0.5 mcal · s^{-1}. For the evaluation and the statistical analysis a special computer program was developed. The shape factor was a good test for the order of the reaction (about 0.64 expected for a first order reaction)[26].

For each run 4–5 mg of a 1:2 mixture of **2** and 9,10-dihydroanthracene copressed to a pellet was used. The reference pan contained the same amount of 9,10-dihydroanthracene. In a typical run the peak due to the heat flow appeared between 166.0 and 212.8°C with a maximum at 200.5°C. The peak area corresponded to 166.4 mcal, the shape factor was 0.62 supporting first order kinetics. For the Eyring correlation 118 points of the curve were evaluated of which only 2 were eliminated as runaways by the Nalimov test[27]. The results are recorded in Table 2.

X-ray Results and Operations[28]: A clear colourless crystal of dimensions 0.5 × 0.9 × 0.2 mm was optically centered on a Syntex P3 four-circle diffractometer. The orientation matrix and the cell parameters were determined on the basis of 15 reflections. The intensities of 3671 *hkl* reflections were measured at room temperature according to the ω-technique (Mo-K_α, graphite monochromator) using a scan range of 1° and a scan speed between 0.5 and 29.3° min^{-1} depending on the intensity of the measured reflections. In the range $3.0° \leq 2\Theta \leq 55.0°$, 3253 reflections *hkl* with $F > 3\sigma(F)$ were obtained which were used for the structure refinement. For the evaluation, the SHELXTL 83[29] system was employed. An

Table 3. Atom positions × 10^4; isotropic temperature coefficients U_{eq} × 10^3 in $Å^2$ (standard deviations). The isotropic temperature coefficients U_{eq} were calculated from the anisotropic temperature coefficients

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
C(1)	396(1)	7544(4)	812(2)	38(1)	C(208)	1564(1)	6621(4)	3384(2)	42(1)
C(2)	983(1)	6647(3)	1426(2)	29(1)	C(209)	758(1)	9158(4)	2825(2)	37(1)
C(3)	1559(1)	7504(4)	1012(2)	31(1)	C(210)	1038(2)	5494(5)	4731(2)	54(1)
C(4)	2101(1)	6129(5)	1399(2)	48(1)	C(301)	1491(1)	7725(4)	9791(2)	31(1)
C(20)	953(1)	4390(4)	1259(2)	44(1)	C(302)	2133(1)	8003(4)	9566(2)	43(1)
C(30)	1722(1)	9586(4)	1452(2)	41(1)	C(303)	2119(1)	8319(5)	8442(2)	49(1)
C(201)	972(1)	7038(4)	2617(2)	31(1)	C(304)	1846(1)	6498(5)	7855(2)	53(1)
C(202)	504(1)	5603(4)	2926(2)	41(1)	C(305)	1206(1)	6212(4)	8018(2)	46(1)
C(203)	440(1)	5889(4)	4022(2)	48(1)	C(306)	831(1)	8033(5)	7643(2)	49(1)
C(204)	239(1)	7996(5)	4173(2)	49(1)	C(307)	1112(1)	9849(4)	8217(2)	45(1)
C(205)	706(1)	9441(4)	3927(2)	46(1)	C(308)	1130(1)	9582(4)	9349(2)	38(1)
C(206)	1310(1)	9057(5)	4621(2)	54(1)	C(309)	1225(1)	5910(4)	9151(2)	38(1)
C(207)	1504(1)	6926(5)	4484(2)	50(1)	C(310)	1753(1)	151(5)	8058(2)	53(1)

Table 4. Bond distances in pm and bond angles in degrees (standard deviations)[a]

C(1) - C(2)	154.6(3)	C(1)	- C(2) - C(3)	110.1(2)	C(2)	- C(3) - C(4)	108.2(2)
C(2) - C(3)	163.9(4)	C(1)	- C(2) - C(20)	107.6(2)	C(2)	- C(3) - C(30)	109.5(2)
C(2) - C(20)	153.9(3)	C(1)	- C(2) - C(201)	106.1(2)	C(2)	- C(3) - C(301)	117.8(2)
C(2) - C(201)	164.7(3)	C(3)	- C(2) - C(20)	108.2(2)	C(4)	- C(3) - C(30)	107.7(2)
C(3) - C(4)	154.8(4)	C(3)	- C(2) - C(201)	117.4(2)	C(4)	- C(3) - C(301)	107.4(2)
C(3) - C(30)	154.2(4)	C(20)	- C(2) - C(201)	107.1(2)	C(30)	- C(3) - C(301)	105.9(2)
C(3) - C(301)	164.0(3)						

[a] The mean bond distances in the adamantane skeleton were 153.7 pm.

absorption correction was applied to all intensities on an Eclipse S/250 based on Ψ-scan measurements. The structure was solved by direct phase determination. The phases of 200 strong reflections were determined, and on the resulting *E* map approximate positions of all C atoms could be determined. Positional and thermal parameters could be refined by anisotropic least squares cycles to $R = 0.063$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements.

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