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The Crystal and Molecular Structure of an Octacycloheneicosane Inert Towards Lewis Acid Isomerization

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Hydride transfer reduction (with 96% H_2SO_4 and methylcyclohexane) of norbornadiene trimer (**1**) gives *exo,exo*-octacyclo[8.8.1.1^{3,6}.1^{12,15}.0^{2,9}.0^{4,8}.0^{11,18}.0^{13,17}]heneicosane (**4**). The *X*-ray structural details of **4** and those calculated by force field methods are in excellent agreement. Further rearrangement of **4** to more stable $C_{21}H_{28}$ isomers (e.g., **2** or **3**) does not take place even with highly active Lewis acid catalysts. This exceptional behavior is attributed mechanistically to energetically unfavorable "bottlenecks", i.e., intermediates with quaternary carbons and highly strained structures lying along the rearrangement pathway, which cannot be achieved under the reaction conditions without decomposition taking place.

Die Struktur eines gegenüber Umlagerungen mit Lewis-Säuren inerten Octacycloheneicosans

Bei der Hydrid-Transfer-Reduktion (96proz. Schwefelsäure in Methylcyclohexan) von trimerem Norbornadien (**1**) entsteht *exo,exo*-Octacyclo[8.8.1.1^{3,6}.1^{12,15}.0^{2,9}.0^{4,8}.0^{11,18}.0^{13,17}]heneicosan (**4**). Die aus der Röntgenstrukturanalyse von **4** erhaltenen Bindungslängen und Bindungswinkel stimmen gut mit denen aus Kraftfeldrechnungen überein. Auch mit hochaktiven Lewis-Säuren als Katalysatoren erfolgt keine weitere Umlagerung von **4** zu stabileren $C_{21}H_{28}$-Isomeren wie z.B. **2** oder **3**. Dieses ungewöhnliche Verhalten wird mit der erforderlichen Bildung energetisch ungünstiger, hochgespannter Zwischenprodukte mit quartären Kohlenstoffatomen erklärt, die unter diesen Reaktionsbedingungen nicht entstehen können.

Adamantane¹⁾, diamantane²⁾, triamantane³⁾, and numerous other cage ring systems are best prepared by Lewis acid catalyzed isomerization of polycyclic hydrocarbon precursors⁴,⁵⁾. Such reactions are remarkably general and almost invariably lead to the thermodynamically most stable saturated isomers, the "stabilomers"⁵⁾. Only a few instances are known in which a less

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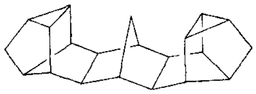
stable isomer fails to rearrange to the most stable one under such conditions[5,6]. Such exceptional molecules (one of which is the subject of this paper) are of interest since their structures should reveal why further rearrangement is precluded.

Preparation of 4 and Determination of Structure

Various tetrahydronorbornadiene dimers have proven to be useful precursors for isomerization to diamantane[2,4]. Norbornadiene trimer ($C_{21}H_{24}$, **1**[7,8]), formed by the action of Rh/C catalyst on bicycloheptadiene[7], appeared to be a promising starting material for synthesis of higher cage hydrocarbons. Tetrahydro-**1** might serve as $C_{21}H_{28}$ rearrangement precursor for triamantane derivatives, e.g. **2** or **3**. The latter is expected to be the octacycloheneicosane stabilomer[5].

Accordingly, **1** was subjected to hydride transfer reduction[9] (concentrated sulfuric acid and methylcyclohexane), and a white crystalline saturated hydrocarbon, **4** ($C_{21}H_{28}$, m.p. 197 – 198 °C), was obtained. Under these conditions only limited rearrangement generally is observed[9]. However, more vigorous catalysts ($AlBr_3$[1–5] and chlorinated Pt/Al_2O_3 with HCl gas[10]) failed to alter **4**. More vigorous conditions lead to loss of starting material through destructive side reactions, but no further rearrangement occured.



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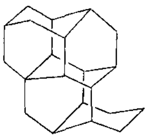

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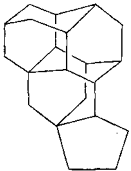

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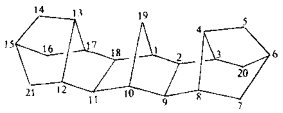

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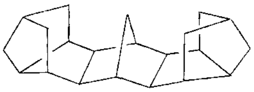

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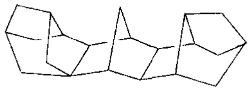

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Spectroscopic methods provide clues to the structure of **4**. The eight ^{13}C NMR signals observed indicate a species like **4** or **5** with two planes of symmetry or similar equivalence of carbon atoms. The structure of **5** is closer to that of the starting material (**1**), but stereoisomeric **4** can arise from **1** readily *via* Wagner-Meerwein rearrangements of the outer norbornane units. The proton NMR spectrum shows signals for *four* protons at unusually high field ($\delta = 0.75 - 1.0$)[11]. IR C – H stretching bands are observed at unusually high frequencies (ca. 3000 cm^{-1}). These can be ascribed to nonbonded interactions of congested hydrogens[12]; structure **4** has four and **5** has six such hydrogens.

Since thousands of $C_{21}H_{28}$ isomers are possible, we resorted to *X*-ray analysis to establish structure **4** for the rearrangement product. The *X*-ray analysis was carried out independently and did not benefit from structural conjectures based on the spectroscopic data.

Force Field Calculations

Molecular mechanics calculations, easily carried out, are a reliable method for estimating energies and exact structures, particularly of saturated hydrocarbons[13-15]. The results of both EAS[14] and Allinger's 1971 force fields[15] (Table 1) agree within 2 kcal/mol for the **2**, **3**, and **6** in heat of formation and strain energies. For the remaining two structures, larger differences between the force field results are found, but **4** is found by both methods to be 14.4 ± 0.2 kcal/mol more stable than **5**. The reason that **4**, rather than **5**, was obtained experimentally is clarified by these results.

As expected from their largely diamondoid structures, **2** and **3** are indicated to be over 40 kcal/mol more stable than **4**. Despite this large driving force, further rearrangement of **4** does not occur under the conditions investigated. A likely first step along such a hypothetical rearrangement path involves **6**, indicated to be 14.1 ± 2.4 kcal/mol less stable than **4**. Qualitative analysis with models indicates that further rearrangements of **6** along pathways which might eventually lead to **2** or **3** must involve increasingly less stable structures.

Table 1. Heats of formation and strain energies (kcal/mol) calculated by EAS[14] and *Allinger* 1971[15] force fields

Compound	ΔH_f° (gas, 25 °C) EAS	All.'71	Strain Energy EAS	All.'71
2	−44.59	−43.68	22.67	23.98
3	−46.17	−45.59	22.20	23.23
4	−3.08	2.88	63.07	69.38
5	11.46	17.21	77.61	83.71
6	13.45	14.60	80.71	82.26
Norbornane (**7**)[14]	−12.99	−13.48	16.98	16.78
Brendane (**8**)[14]	−11.72	−10.31	22.57	24.26

Discussion of the Structure

The structure of **4** (point group C_{2v}) is comprised of two outer brendane (**8**) units connected *cis,exo* to a central norbornane moiety (**7**) by common edges. The strain energy of **4**, 66 ± 3 kcal/mol (Table 1) corresponds closely to the sum (63.7 ± 1.6 kcal/mol) obtained by simply adding the strain energy of norbornane (**7**) to twice that of brendane (**8**), despite the repulsive interactions among the transannular hydrogens.

The experimental *X*-ray geometry of **4**, and those calculated with the two force fields[14,15], are in close agreement. Figure 1 gives the experimental bond lengths and angles. Tables 2 and 3 compare the calculated with the experimental bond lengths and bond angles, respectively. Very few deviations greater than 0.02 Å in lengths or 2° in angles are found. Figure 1 also gives the arbitrary numbering employed.

The C – H bond lengths are given in table 4; because of known difficulties in locating hydrogen atoms exactly by *X*-ray methods, the calculated values probably are more

Table 2. C – C Bond lengths (Å) in **4** (numbering of atoms see fig. 1)

Bond Length	Experimental Values	EAS Values[a)]	All. '71 Values[b)]
C(1) – C(2)	1.525	1.521	1.526
C(1) – C(3)	1.539	1.522	1.526
C(2) – C(5)	1.542	1.543	1.543
C(3) – C(4)	1.542	1.543	1.543
C(4) – C(5)	1.575	1.531	1.532
C(4) – C(6)	1.549	1.539	1.536
C(5) – C(8)	1.545	1.540	1.537
C(6) – C(7)	1.545	1.532	1.534
C(6) – C(9)	1.560	1.542	1.544
C(7) – C(8)	1.554	1.534	1.534
C(7) – C(11)	1.531	1.521	1.526
C(8) – C(12)	1.560	1.541	1.544
C(9) – C(10)	1.536	1.532	1.533
C(10) – C(11)	1.525	1.515	1.524
C(10) – C(12)	1.537	1.533	1.533

a) EAS force field[14)]. – b) *Allinger* 1971 force field[15)].

Table 3. Bond angles in **4**, in degrees

Bond Angle	Experimental Values	EAS Values[a)]	All. '71 Values[b)]
C(2) – C(1) – C(3)	94.6	92.3	93.2
C(1) – C(2) – C(5)	102.4	102.8	102.1
C(5') – C(2) – C(5)	106.7	108.4	108.4
C(1) – C(3) – C(4)	102.4	103.0	102.2
C(4') – C(3) – C(4)	106.6	108.1	108.1
C(3) – C(4) – C(5)	102.6	102.4	102.8
C(3) – C(4) – C(6)	116.6	117.7	119.2
C(5) – C(4) – C(6)	104.7	105.7	105.3
C(2) – C(5) – C(4)	102.8	102.4	102.9
C(2) – C(5) – C(8)	116.2	117.5	119.0
C(4) – C(5) – C(8)	105.2	105.7	105.2
C(4) – C(6) – C(7)	107.2	107.4	107.2
C(4) – C(6) – C(9)	112.4	111.9	113.3
C(7) – C(6) – C(9)	101.4	100.1	101.1
C(6) – C(7) – C(8)	99.9	100.8	99.4
C(6) – C(7) – C(11)	104.7	106.4	105.8
C(8) – C(7) – C(11)	104.7	106.6	105.9
C(5) – C(8) – C(7)	106.9	107.4	107.3
C(5) – C(8) – C(12)	112.8	112.0	113.4
C(7) – C(8) – C(12)	101.4	100.0	101.1
C(6) – C(9) – C(10)	104.2	103.8	103.6
C(9) – C(10) – C(11)	101.0	101.1	101.3
C(9) – C(10) – C(12)	108.7	110.6	109.2
C(11) – C(10) – C(12)	101.2	101.0	101.3
C(7) – C(11) – C(10)	94.5	92.1	92.9
C(8) – C(12) – C(10)	103.8	103.8	103.6

a) EAS force field[14)]. – b) *Allinger* 1971 force field[15)].

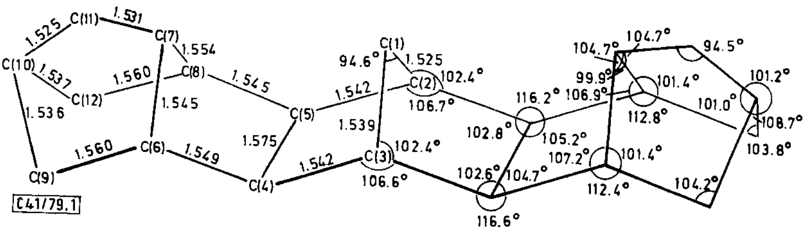


Fig. 1. Experimental bond lengths (Å) and angles of **4**

reliable. All five-membered rings have half chair conformations. The angles between the two planes (designated A and B) defining each chair are given in table 5. The larger angle of 142.3° for C(6), C(4), C(5), C(8)/C(6), C(7), C(8) probably is due to the repulsion of hydrogens H(7) and H(1), which are only around 2 Å apart (*X*-ray 2.02 Å, EAS 2.04 Å, All.'71 2.18 Å). This transannular repulsion also explains the large values for bond angles C(3) – C(4) – C(6) and C(2) – C(5) – C(8): 116.4° (average *X*-ray), 117.6° (EAS), 119.0° (All.'71). The small C – C – C angle at the bridging methylene

Table 4. C – H Bond lengths (Å) in $C_{21}H_{28}$ (4)

Bond Length	Experimental Values	EAS Values[a]	All.'71 Values[b]
C(1) – H(1)	0.95(4)	1.091	1.085
C(2) – H(2)	0.97(4)	1.102	1.101
C(3) – H(3)	1.03(4)	1.102	1.100
C(4) – H(4)	1.00(3)	1.101	1.098
C(5) – H(5)	1.00(3)	1.101	1.097
C(6) – H(6)	0.98(3)	1.103	1.100
C(7) – H(7)	1.05(3)	1.100	1.099
C(8) – H(8)	1.02(3)	1.103	1.100
C(9) – H(9)	1.03(3)	1.101	1.096
C(9) – H(10)	1.00(3)	1.103	1.099
C(10) – H(11)	1.00(3)	1.103	1.105
C(11) – H(12)	1.03(3)	1.102	1.099
C(11) – H(13)	1.09(4)	1.102	1.099
C(12) – H(14)	0.97(3)	1.101	1.097
C(12) – H(15)	1.02(3)	1.102	1.099

[a] EAS force field[14]. – [b] *Allinger* 1971 force field[15].

Table 5. Angles between planes A and B in **4**

Plane A	Plane B	Experimental Angle	EAS Angle[a]	All. '71 Angle[b]
C(1), C(2), C(3)	C(3), C(4), C(5), C(2)	124.7°	123.9°	123.8°
C(3), C(4), C(5), C(2)	C(6), C(4), C(5), C(8)	122.2°	123.7°	125.4°
C(6), C(4), C(5), C(8)	C(6), C(7), C(8)	142.3°	145.8°	142.9°
C(7), C(6), C(9), C(10)	C(7), C(11), C(10)	125.8°	125.3°	125.9°
C(7), C(8), C(12), C(10)	C(7), C(11), C(10)	125.9°	131.2°	126.0°

[a] EAS force field[14]. – [b] *Allinger* 1971 force field[15].

(C-7) position of norbornane has long been a feature of interest[16–18)]. In 4 (Figure I), C(1) and C(ll) present this structural feature; C-C-C angles of 94.6” and 94.5” are found by X-ray, respectively, and slightly smaller values by the force field calculations. The C-C single bond lengthenings of C(4) – C(5), 1.575(4) Å, and of C(6)- C(9), 1.560(4) Å, indicated by X-ray, are not reproduced by the force field results.

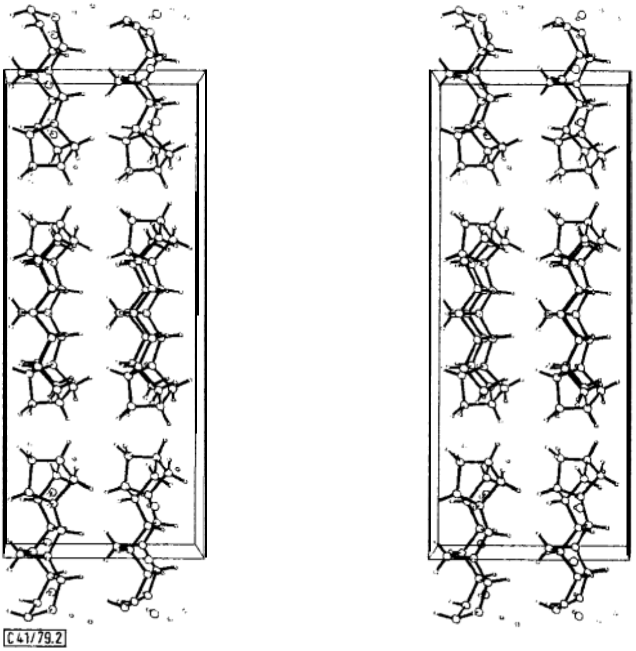


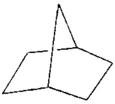
Fig. 2. Stereo diagram showing the packing of the molecule of 4 in the unit cell

A stereo diagram of the packing arrangement in the unit cell is shown in figure 2. The shortest intermolecular C ··· C distance is 3.68 Å. The molecules present opposite “sides” to one another in order to optimize van der Waals contacts.

Discussion of the Rearrangement Results

The formation of 4 rather than 5 by hydride transfer reduction of 1 finds analogies in related systems. When 9 is reduced with two moles of H_2 and then rearranged partially with $AlBr_3$, **10** (similar structurally to 4) is formed rather than **11**[9c)]. The hydride transfer reduction of Binor-S (12) with H_2SO_4 in methylcyclohexane gives 13 (rather than a stereoisomer) as the major product[9c)]. 13 has also been found as a rearrangement intermediate in reactions leading to diamantane **(14)**[9c)]; computer-assisted graph theoretical analysis supplies a detailed explanation for this behavior[19)].

The failure of 4 to rearrange further under Lewis acid catalysis to thermodynamically much more stable 2 or 3 is also precedented. Thus, **15,** with structural features similar to 4, could not be made to isomerize to ethanoadamantane **(16)**, the $C_{12}H_{18}$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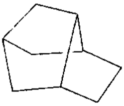
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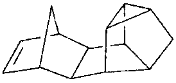
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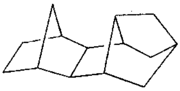
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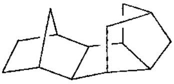
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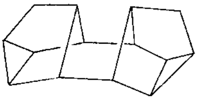
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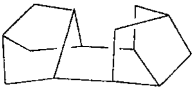
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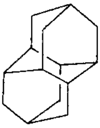
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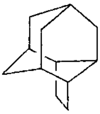
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stabilomer[5]. The simplest norbornane system with a fused five-membered ring, tetrahydrodicyclopentadiene (**17**), does give adamantane with $AlBr_3$, but with much more difficulty and in much lower yields than do almost all other tricyclodecane isomers[4,20]. Similarly, **10** is a poorer precursor for diamantane (**14**) than **13**.

The reason why **4** does not rearrange further is clear from our prior treatments of similar problems[19,20]. In order to rearrange to structures like **2** or **3**, 1,2-shifts must proceed to quaternary carbon-containing ring structures (e.g. **6**) which are too highly unfavorable energetically to be accessible under the conditions employed.

We conclude that norbornanes elaborated by fused five membered ring structures generally are *inferior* precursors for rearrangement to diamond-like isomers.

This work was initiated at Princeton University under support by the *National Institutes of Health*. The *Fonds der Chemischen Industrie* provided financial assistance at Erlangen.

Experimental Part

Norbornadiene Trimer $C_{21}H_{24}$ (**1**) was prepared according to the literature method[7]. – MS (*m/e*, %): 277 (19); 276 (100) $M^{+\cdot}$, 235 (34), 222 (13), 210 (31), 129 (29), 117 (55), 91 (82), 79 (34). – ^{13}C-NMR (25 MHz, $CDCl_3$): δ = 50.77 (4C); 46.97 (4C); 44.66 (2C); 39.02 (2C); 29.10 (1C); 27.67 (2C); 17.67 (2C); 12.87 (4C).

exo,exo-Octacyclo[8.8.1.$1^{3,6}$.$1^{12,15}$.$0^{2,9}$.$0^{4,8}$.$0^{11,18}$.$0^{13,17}$*]heneicosane* (**4**): A solution of 500 mg of **1** dissolved in 20 ml methylcyclohexane was added slowly to 15 ml of conc. sulfuric acid at 0°C. After vigorous stirring in the cold for 1.5 h, the mixture was poured (cautiously) onto ice. Pentane was added, the organic and water layers separated, and the latter extracted three times with pentane. The organic layer was washed with $NaHCO_3$ solution, twice with water, and dried over $MgSO_4$. After evaporation of the solvent and sublimation at 130 °C/5 mm, 395 mg of solid material remained. After two recrystallizations from ethanol, 310 mg (61%) of a single hydrocarbon (**4**), m.p. 197 – 198 °C, was obtained (GC on 5% SE 30 on Chromosorb W showed only one component).

IR (KBr, cm^{-1}): 3010 m, 3000 m, 2940 m, 2930 m, 2900 m, 2860 m, 1630 m, 1480 m, 1440 m, 1300 w, 1280 w, 1210 w, 1150 w, 920 w. – ^1H NMR: (60 MHz, CCl_4, numbering of atoms according to fig. 1): δ = 0.82 (4H *endo* at C(9), C(12), W_h = 12 Hz); 1.29 (6H at C(1), C(11); W_h = 7.5 Hz); 1.7 – 1.9 (16H); 2.40 (2H, W_h = 9 Hz). – ^{13}C NMR: (25 MHz, $CDCl_3$): δ = 57.97 (4C: C(4), C(5)); 49.02 (2C: C(2), C(3) or C(7)); 47.92 (2C: C(7) or C(2), C(3)); 44.60 (4C: C(6), C(8)); 42.25 (4C: C(9), C(12)); 40.48 (2C: C(11)); 34.71 (2C: C(10)); 30.62 (1C: C(1)). – MS (*m/e*, %): 281 (23), 280 (100) $M^{+\cdot}$, 159 (12), 121 (17), 120 (13), 91 (12), 79 (20).

$C_{21}H_{28}$ (280.4) Calcd. C 89.94 H 10.06 Found C 89.67 H 9.92

Attempt to rearrange **4** *with $AlBr_3$ in cyclohexane:* Pure hydrocarbon **4** (80 mg) and 160 mg $AlBr_3$ were dissolved in 5 ml cyclohexane. After vigorous stirring at room temperature for 15.5 h, 10 ml of water was added and the layers were separated. The water layer was extracted twice with cyclohexane. The combined organic solution was washed twice with water and dried over $MgSO_4$. After evaporation of the solvent and sublimation at 130 °C/5 mm, 56 mg (70%) of a solid material remained which was shown to be unchanged **4** by ^1H NMR.

Attempt to rearrange **4** *with chlorinated platinum-alumina catalyst and HCl gas:* During a seven hour period, pure hydrocarbon **4** (97.5 mg) was passed in a stream of HCl gas over a chlorinated platinum-alumina catalyst[10)] at 200 °C. (The activity of the catalyst had been established by a prior experiment involving rearrangement of tetramethylenenorbornane to methyladamantane.) The product (78.5 mg, 80%), collected in an ice-cooled trap, was shown to be unchanged **4** by ^1H NMR.

X-Ray Analysis

Data collection: Colorless crystals of plated shape were grown by slow evaporation of a solution in cyclohexane at 20 °C. A suitable crystal for *X*-ray investigation 0.2 × 0.2 × 0.15 mm in size was obtained by cutting a larger plate.

Preliminary Weissenberg photographs with Cu-K_α radiation indicate that the crystal belongs to the orthorhombic system. Systematic extinctions are hkl, $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$, defining the extinction unit[21)] $C - c -$ which comprises the three space groups $Cmc2_1 - C_{2v}^{12}$, $C2cm - C_{2v}^{16}$ (non-centrosymmetric) and $Cmcm - D_{2h}^{17}$ (centrosymmetric).

Accurate cell parameters were calculated by a least-square procedure from 22 reflections with $\Theta > 64°$ measured on double-radius (∅ = 114.6 mm) zero-layer Weissenberg photographs, calibrated with Si-powder lines[22)] (a_0 = 5.43088 Å), around the *a* and *b*-axis. The final lattice parameters are shown below.

Crystal Data:

Formula	$C_{21}H_{28}$, formula weight 280.4
Density (calculated)	1.23 gcm^{-3}
Space group	$Cmc2_1 - C_{2v}^{12}$
a, b, c	a = 23.91(2) Å, b = 6.353(5) Å, c = 9.929(5) Å
Z	4 molecules/unit cell
Radiation	Cu-K_α (λ_1 = 1.54051, λ_2 = 1.54433 Å)
μ(Cu-K_α)	5.14 cm^{-1}

The intensities were recorded with a Supper-Peace two-circle diffractometer using Ni-filtered Cu-$K_{\bar{\alpha}}$ radiation. In layers 0 – 13 around the *a*-axis and layers 0 – 7 around the *c*-axis a total of

2236 reflections to the value of $\Theta = 70°$ were recorded at 19 °C. The standard deviation was calculated according to $\sigma^2(I) = (P + m^2B)$. B is the background measurement for $1/m$ of the time of the peak scan P. Reflections with $I < 2.58\ \sigma(I)$ were assumed as unobserved, corresponding to the 1% error probability. Lorentz polarisation corrections were calculated but no absorption correction was applied. Relative scale factors for each layer were calculated according to *Hamilton, Rollet,* and *Sparks*[23] and equivalent reflections were averaged resulting a total of 726 unique refleitions. Statistical intensity tests indicated that the structure is non-centrosymmetric[24].

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle \lvert E \rvert \rangle$	0.876	0.798	0.886
$\langle E^2 \rangle$	1.032	1.000	1.000
$\langle \lvert E^2 - 1 \rvert \rangle$	0.824	0.968	0.736

High density in Patterson synthesis along the a-axis indicated a mirror plane perpendicular to this axis. Therefore, the space group $Cmc2_1 - C^{12}_{2v}$ was adopted and proved to be correct during the structure refinement. Since $Z = 4$ and the general position in $Cmc2_1$ is eightfold, the molecule has to lie at special position on the mirror plane.

Table 6. Fractional coordinates and isotropic and anisotropic temperature factors, $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ (Å^2) in the crystal of $C_{21}H_{28}$ (**4**)

	x	y	z	B_{iso}	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
C(1)	0.5	0.2921(5)	0.0837(3)	3.2	0.00143(5)	0.0194(8)	0.0079(4)	0.0	0.0	0.0059(9)
C(2)	0.5	0.0714(4)	0.1449(3)	2.7	0.00135(5)	0.0144(6)	0.0068(3)	0.0	0.0	-0.0038(7)
C(3)	0.5	0.4057(4)	0.2205(4)	3.0	0.00132(5)	0.0116(6)	0.0103(3)	0.0	0.0	0.0005(8)
C(4)	0.44830(8)	0.3106(3)	0.2907(3)	2.8	0.00118(3)	0.0142(4)	0.0088(2)	0.0005(2)	-0.0000(2)	-0.0026(6)
C(5)	0.44824(8)	0.0771(3)	0.2375(2)	2.6	0.00117(3)	0.0130(4)	0.0074(2)	-0.0001(2)	-0.0003(2)	0.0002(5)
C(6)	0.39060(9)	0.3999(3)	0.2486(3)	3.2	0.00132(3)	0.0137(4)	0.0111(3)	0.0010(2)	-0.0002(2)	-0.0000(6)
C(7)	0.37050(9)	0.2710(4)	0.1259(2)	3.3	0.00127(4)	0.0216(6)	0.0088(3)	0.0007(2)	-0.0009(2)	0.0037(6)
C(8)	0.39096(9)	0.0483(3)	0.1680(3)	3.0	0.00130(3)	0.0163(5)	0.0088(2)	-0.0006(2)	-0.0007(2)	-0.0033(6)
C(9)	0.34396(9)	0.3499(4)	0.3536(3)	3.7	0.00137(4)	0.0240(6)	0.0106(3)	0.0013(2)	0.0003(2)	-0.0047(7)
C(10)	0.30836(9)	0.1799(4)	0.2848(3)	3.6	0.00111(3)	0.0239(6)	0.0114(3)	0.0001(2)	-0.0002(2)	0.0006(7)
C(11)	0.30682(9)	0.2619(4)	0.1405(3)	4.0	0.00126(4)	0.0276(7)	0.0116(3)	0.0011(3)	-0.0011(2)	0.0026(8)
C(12)	0.34399(8)	-0.0198(4)	0.2680(3)	3.7	0.00139(4)	0.0181(5)	0.0125(3)	-0.0010(2)	-0.0002(2)	0.0021(7)
H(1)	0.469(1)	0.331(4)	0.029(3)	1.7(6)						
H(2)	0.5	-0.047(7)	0.082(5)	2.5(9)						
H(3)	0.5	0.568(6)	0.222(5)	2.8(9)						
H(4)	0.455(1)	0.314(4)	0.390(3)	1.7(5)						
H(5)	0.454(1)	-0.029(4)	0.311(3)	1.6(5)						
H(6)	0.393(1)	0.550(4)	0.226(3)	1.9(6)						
H(7)	0.384(1)	0.324(4)	0.031(3)	1.7(6)						
H(8)	0.394(1)	-0.051(4)	0.088(3)	1.3(5)						
H(9)	0.319(1)	0.481(5)	0.365(3)	2.4(6)						
H(10)	0.362(1)	0.300(5)	0.439(3)	3.6(8)						
H(11)	0.271(1)	0.152(4)	0.329(3)	1.6(5)						
H(12)	0.288(1)	0.407(5)	0.127(3)	3.2(7)						
H(13)	0.282(1)	0.158(5)	0.075(4)	4.4(9)						
H(14)	0.360(1)	-0.080(4)	0.349(3)	2.7(6)						
H(15)	0.319(1)	-0.136(4)	0.231(3)	2.7(6)						

C 41/79.Tab.6

Determination of the structure: Direct phasing with a multisolution procedure did not give a clear shape of the molecule. Because at this stage of the work the molecular structure was completely unknown, it proved to be very difficult to select correct peaks in the initial E-Fourier synthesis. Different attempts with tangent-refinement finally showed a reasonable part of the molecule. A further Fourier synthesis revealed the whole molecule. The refinement of the crude structural model was carried out with a block-diagonal least-squares routine, the function minimized being

$$\sum w(F_o - \tfrac{1}{k}F_c)^2.$$

The weighting scheme adopted was

$$w(F_o) = \frac{4\,F_o^2}{\sigma^2(I)}$$

Atomic scattering factors were taken from the International Tables[25]. Isotropic and anisotropic refinement of the carbon atoms resulted in agreement factors

$$R = \sum |F_o - \tfrac{1}{k} F_c| / \sum F_o$$

of 0.103. A difference Fourier synthesis at this stage showed all hydrogen atoms which were included with isotropic temperature factors in the refinement. Final agreement factor on 762 reflections and 162 variables is $R = 0.038$. A final difference Fourier synthesis does not show any peak higher than $0.2\,e/\text{Å}^3$. The final positional and temperature parameters of the atoms appear in Table 6. Calculations and drawings were done using the program system KRIPROG[26].

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