141. The Crystal Structure of [1.1.1]Propellane at 138 K

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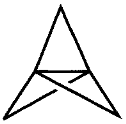
The molecular structure of [1.1.1]propellane has been determined from single-crystal X-ray diffraction measurements at 138 K. The crystals of this reactive compound were grown from the melt at *ca.* 263 K. The space group is *C*2, and the asymmetric unit contains four molecules. All have large thermal motion and two show orientational disorder as well. Because of these problems, the atomic positions cannot be determined with high accuracy. Within the experimental limits, the two ordered molecules have D_{3h} symmetry, with corrected lengths of central and side bonds of *ca.* 1.60 Å and 1.53 Å, respectively. At lower temperature, the crystals undergo a phase transition. The transition temperature, in the range of 100 to 132 K, varied from one crystal sample to another. All crystals obtained of the low-temperature phase were twinned, and its space group could not be established.

Introduction – The molecular geometry of [1.1.1]propellane (tricyclo[1.1.1.$0^{1,3}$]-pentane) **A** was calculated by *ab initio* MO methods (4-31G basis set) [1], long before its actual preparation [2][3]. More recently, the geometry of **A** has been redetermined by higher-level calculations (6-31G* basis set) [4], by analysis of its vibrational spectrum [4], and by a gas-phase electron-diffraction study [5].

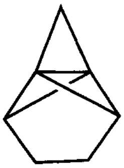
Our interest in this molecule was primarily not the confirmation of its structure, but the experimental determination of its electron-density distribution. In principle, the electron-density distribution can provide information about the nature of the central bond, the crucial bond in this highly strained molecule. *Wiberg et al.* [6] have analyzed the total (calculated) electron density of **A**, by examining its second derivative, the *Laplacian*. According to this analysis, 'the valence shell of an inverted C-atom exhibits five local charge concentrations, four bonded and one nonbonded'. The nonbonded charge concentration, exposed outside the bridgehead bond, is designated as a site of electrophilic attack. *Wiberg et al.* also find appreciable accumulation of charge between the bridgehead nuclei and conclude that the bridgehead atoms are bonded to one another, in contrast to bicyclo[1.1.1]pentane, where the bridgehead atoms are separated by 1.89 Å.

In our recent X-ray analysis (81 K) of two [1.1.1]propellane derivatives **B** and **C**, electron-density difference maps showed no positive density between the bridgehead atoms [7]. On the other hand, we observed a diffuse, positive difference-density peak close to each inverted C-atom, outside the bridgehead bond, in the region of the nonbonded charge concentration found in the *Laplacian* analysis. Due to the low melting points and the high reactivity, the crystal specimens of **B** and **C** could not be measured to very high resolution, and thus the difference-density maps are not of highest quality. Much effort has, therefore, been invested in obtaining crystals of the parent compound **A**. Unfortunately, its scattering behavior turns out to be even worse; all crystals obtained up till now are disordered, and an accurate electron-density study seems out of question. At lower temperature, the crystals of **A** undergo a phase transition. The crystals, obtained by cooling trough the transition point, are highly twinned and not usable for a structure analysis.

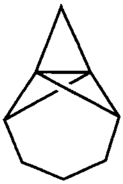
Here, we report structure and packing of **A** in the high-temperature phase, and some experiments carried out with the low-temperature crystal modification.



A



B



C

Experimental. – All our experiments were done with a sample of [1.1.1]propellane prepared by Mr. *U. Bunz* in the laboratory of Prof. *G. Szeimies*. The X-ray measurements were made on an *Enraf-Nonius CAD4* diffractometer equipped with graphite monochromator (Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å) and a locally modified *Enraf-Nonius* gas-stream low-temperature device. Temperature fluctuations, as monitored by a Pt 100 Ω resistor, were less than 0.05 K during the crystallization experiments and less than 0.3 K during data collection.

The crystals of **A** were obtained from the melt by slow cooling from *ca.* 263 K to 261 K (~1 K / 3 h) of one drop of liquid enclosed in a glass capillary mounted on the diffractometer. Since **A** is unstable in presence of traces of humidity, and because it polymerises slowly at the melting temperature, all manipulations were carried out under N_2, and the crystals were grown in a relatively short time (*ca.* 6 h). The first few specimens obtained were all twinned. The formation of twinned crystals was influenced by short-term temperature fluctuations of the cooling device. After reducing the temperature fluctuations below 0.05 K, we were able to produce a few single crystals of good optical quality (linear dimensions *ca.* 0.5×0.5×0.5 mm, mosaic spread < 0.3°).

Cell dimensions of the high-temperature phase (138 K), listed in *Table 1* and plotted in *Fig. 1* as a function of temperature, measured before and after data collection, were obtained by least-squares refinement of setting angles for 18 reflections with 2θ values in the range 20 to 26°. Three standard reflections were monitored at intervals of 2.8 h X-radiation time. The intensity decrease of these reflections, after a two-week exposure time, was *ca.* 5%. This decrease, probably caused by radiation damage, was accompanied by a small increase of the unit cell volume of *ca.* 0.12%. Similar observations were made during the data collection of two [1.1.1]propellane derivatives **B** and **C** [7]. The intensity decrease, as well as the increase of the unit cell volume, may be connected with an increase of defects and accompanying disorder [7][8]. An appropriate scaling correction was made to compensate for the intensity drift.

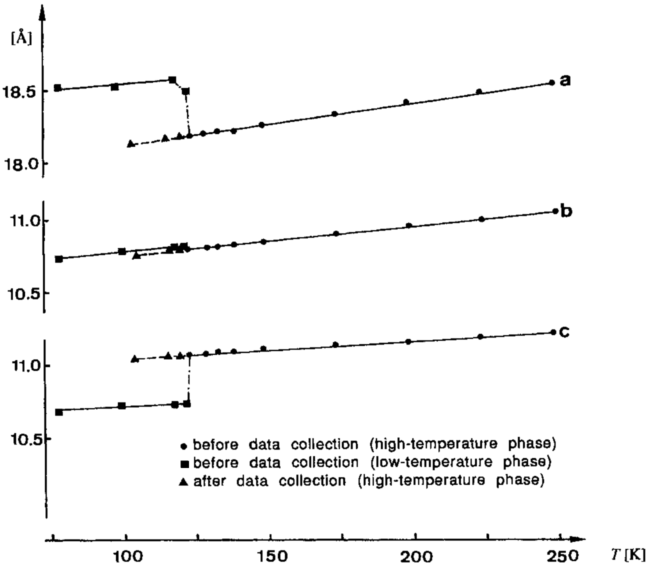


Fig. 1. *Temperature dependence of lattice parameters in the range 80–250 K for the crystal specimen used for data collection.* Before data collection the transition point occured at *ca.* 123 K; after data collection the high-temperature phase persisted to *ca.* 100 K. Below this temperature the crystal specimen transformed into a powder.

Table 1. *Experimental Details of the X-Ray Diffraction Measurements of [1.1.1]Propellane*

Temperature of data collection [K]	138
Melting point [K]	263
Approximate crystal dimensions [mm]	0.5×0.5×0.5
Space group	*C*2
Cell dimensions	
a [Å]	18.228(5)
b [Å]	10.833(3)
c [Å]	11.109(3)
β [°]	128.44(2)
Unit cell contents	16×C_5H_6
D_c [g/cm^3]	1.022
2 sin θ/λ range [Å^{-1}]	1.10
No. of symmetry equivalent orientations measured	2
No. of measured reflections	2573
$R_{\text{int}} = (\sum_{HN}\sum \mid I_{H,i} - \langle I_H \rangle \mid)/\sum_{H} N \langle I_H \rangle$	0.017
No. of unique reflections	1267
No. of observed reflections ($I > 3\,\sigma(I)$)	845
No. of variables in final least-squares analysis	233
Type of refinement	*F*
Scan mode	ω/θ
Weight	1.0
Extinction correction	non
R(*F*)	0.038

Analysis and Refinement of the High-Temperature Structure. – The diffraction pattern at 138 K can be indexed in terms of a centered monoclinic cell (*Table 1*). The systematic absences are compatible with the space groups *C*2, *Cm*, and *C*2/*m*. The structure was solved by direct methods [9] in the space group *C*2. The asymmetric unit contains two ordered propellane molecules (*Fig. 2*) with almost regular D_{3h} symmetry and two which are rotationally disordered about the central bonds (*Fig. 3*). All methylene C-atoms, including the disordered ones in molecules 3 and 4, were located in the first E map. In order to find out if the apparent disorder might have resulted from choice of a wrong space group, we tried to solve the structure in *Cm* and *C*2/*m*, but without success. Furthermore, we doubled all cell axes and measured an additional (low-order) data set at 138 K. A few new reflection peaks could be detected, and also some which violated the assumed C-centering. However, it was not clear if these peaks are real *Bragg* reflections, or higher harmonics of the strongest low-order reflections, or a mixture of both. They were not included in further refinements.

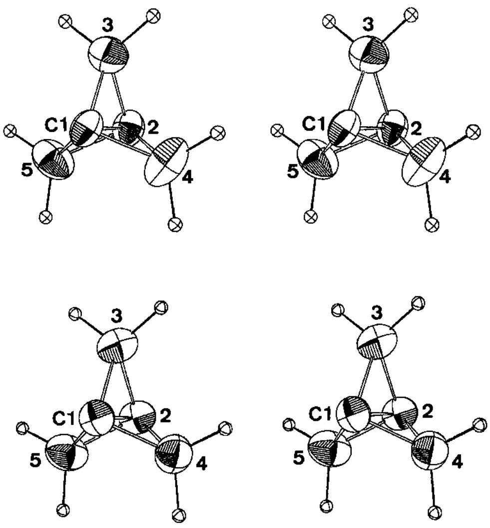


Fig. 2. *Stereoscopic view of the ordered molecules 1* (above) *and 2* (below) *at 138 K.* Vibrational ellipsoids for C-atoms are shown at the 30% probability level.

The scattering behavior at higher *Bragg* angles was poor, and only 843 reflections with $I > 3\,\sigma(I)$ could be measured out to $\mathbf{H} = 2\sin\theta/\lambda = 1.1$ Å^{-1}. The least-squares analysis was carried out with program SHELX76 [10]. The least-squares shifts were damped by a factor 10–20 to reduce the effect of correlation among the atomic parameters. First, a series of isotropic refinements were carried out, including all C-atoms. For the disordered molecules 3 and 4, the population parameters of the bridgehead atoms C(1) and C(2) were set to 1; for all other C-atoms they were treated as adjustable parameters. For molecule 3, best results were obtained with all methylene C-atoms half weight; for molecule 4 the weights for C(3) to C(5) and C(3') to C(5') were close to 0.6 and 0.4, respectively (*Table 2*). Then, the H-coordinates were calculated, assuming a local C_{2v} symmetry (C–H = 1.0 Å, H–C–H = 116.0°). A least-squares analysis, including isotropic C- and H-atoms (fixed H-positions for molecules 3 and 4) led to $R = 0.09$. Anisotropic refinements were made in several steps. First, only molecules 1 and 2 were refined, with anisotropic C-atoms and isotropic H-atoms (atomic parameters for molecules 3 and 4 fixed). The C–H bond lengths and H–C–H bond angles were constraint to 1.0 Å (±0.05 Å) and 116.0° (±10°), respectively. Then, the disordered molecules 3 and 4 were refined in turn, including anisotropic C-atoms and isotropic U values of the H-atoms. The H-coordinates for molecules 3 and 4 were recalculated after each refinement as described above. The independent refinements of ordered and disordered molecules were repeated several times, and after many cycles of least-squares, the refinement process converged to $R = 0.04$. The final coordinates (*Table 2*) were obtained after a series of least-squares cycles, including all C-atoms but keeping the H-atoms fixed ($R = 0.038$). The least-squares analysis described here led to reasonable geometries of the C-atom skeletons in molecules 1 and 2, although the number of observations per parameter in the final refinement is only 3.6.

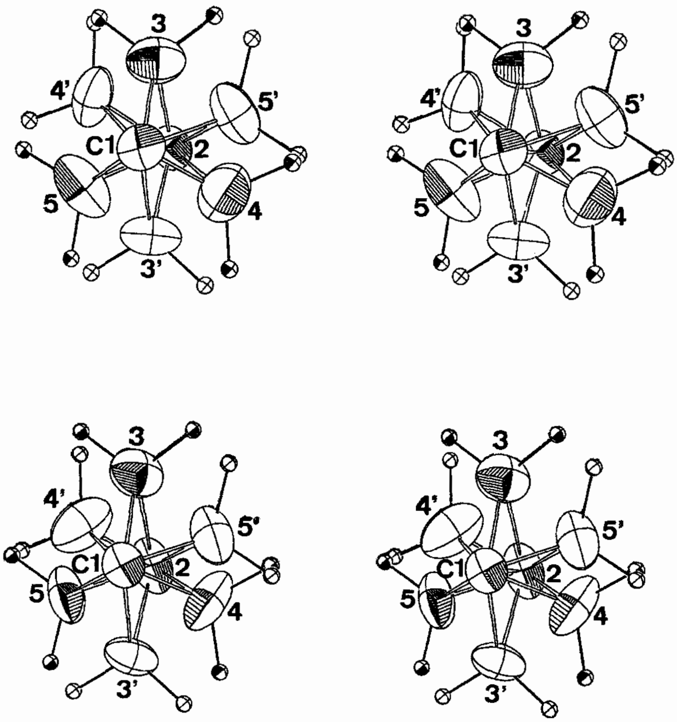


Fig.3. *Stereoscopic view of the disordered molecules 3* (above) *and 4* (below) *at 138 K.* Vibrational ellipsoids for C-atoms are shown at the 30% probability level.

Table 2. *Positional Coordinates and Displacement Parameters* [Å^2](e.s.d. in parentheses) *at 138 K*. For the disordered molecules 3 and 4, the population parameter (*pp*) is also listed. The coordinates of the H-atoms were calculated assuming local C_{2v} symmetry of the methylene groups with C–H = 1.09 (± 0.005) Å, H–C–H = 116.0 ±0.5)°. For the atomic numbering, see *Figs. 2* and *3*.

Atom	*x*/*a*	*y*/*b*	*z*/*b*	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Molecule 1									
C(1)	0.2160(3)	0.0235	0.2690(5)	0.063(2)	0.066(2)	0.078(2)	0.003(2)	0.053(2)	–0.001(2)
C(2)	0.2331(3)	–0.0802(6)	0.1888(5)	0.072(2)	0.062(2)	0.076(2)	0.008(2)	0.054(2)	0.004(2)
C(3)	0.1355(3)	–0.0370(6)	0.1197(5)	0.073(2)	0.093(3)	0.080(2)	0.010(2)	0.042(2)	0.012(2)
C(4)	0.2694(4)	0.0481(6)	0.2104(7)	0.113(2)	0.086(3)	0.156(3)	–0.022(2)	0.108(2)	–0.025(2)
C(5)	0.2580(4)	–0.0983(6)	0.3445(6)	0.093(2)	0.094(3)	0.074(2)	0.039(2)	0.043(2)	0.017(2)
H(31)	0.0924	–0.0998	0.1277						
H(32)	0.1004	0.0199	0.0175						
H(41)	0.3450	0.0615	0.2962						
H(42)	0.2353	0.1057	0.1076						
H(51)	0.3325	–0.0996	0.4424						
H(52)	0.2143	–0.1624	0.3508						
Molecule 2									
C(1)	–0.0530(3)	0.2084(5)	0.1809(5)	0.053(2)	0.067(2)	0.048(2)	–0.008(2)	0.022(2)	–0.011(2)
C(2)	0.0408(3)	0.2423(6)	0.3384(5)	0.053(2)	0.069(2)	0.059(2)	–0.005(2)	0.024(2)	–0.013(2)
C(3)	–0.0476(3)	0.3022(6)	0.2865(6)	0.072(2)	0.066(2)	0.095(2)	0.002(2)	0.051(2)	–0.005(2)
C(4)	0.0053(4)	0.1135(6)	0.3030(5)	0.088(2)	0.071(2)	0.074(2)	0.000(2)	0.048(2)	–0.003(2)
C(5)	0.0273(4)	0.2614(6)	0.1937(7)	0.101(2)	0.083(2)	0.125(2)	–0.014(2)	0.087(2)	–0.010(2)
H(31)	–0.0781	0.2738	0.3409						
H(32)	–0.0591	0.3977	0.2482						
H(41)	–0.0220	0.0779	0.3600						
H(42)	0.0413	0.0468	0.2826						
H(51)	0.0638	0.1989	0.1699						
H(52)	0.0193	0.3562	0.1539						

Table 2 (cont.)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*	*pp*
Molecule 3					
C(1)	0.1985(3)	0.4931(6)	0.2034(5)	0.067(2)	1.0
C(2)	0.3003(3)	0.4509(6)	0.2820(5)	0.066(2)	1.0
C(3)	0.2737(8)	0.546(1)	0.346(1)	0.099(3)	0.5
C(4)	0.2238(9)	0.368(1)	0.244(2)	0.119(3)	0.5
C(5)	0.2444(7)	0.515(1)	0.129(1)	0.113(3)	0.5
H(31)	0.2975	0.6382	0.3473		0.5
H(32)	0.2856	0.5158	0.4504		0.5
H(41)	0.2335	0.3314	0.3443		0.5
H(42)	0.2025	0.3011	0.1540		0.5
H(51)	0.2631	0.6102	0.1282		0.5
H(52)	0.2190	0.4593	0.0293		0.5
Molecule 3'					
C(3')	0.2215(7)	0.404(1)	0.129(1)	0.091(3)	0.5
C(4')	0.2745(8)	0.581(1)	0.251(1)	0.100(3)	0.5
C(5')	0.2564(7)	0.422(1)	0.353(1)	0.098(3)	0.5
H(31')	0.1996	0.3080	0.1201		0.5
H(32')	0.2145	0.4374	0.0291		0.5
H(41')	0.2981	0.6405	0.3484		0.5
H(42')	0.2701	0.6249	0.1584		0.5
H(51')	0.2328	0.3280	0.3438		0.5
H(52')	0.2773	0.4749	0.4523		0.5
Molecule 4					
C(1)	0.0270(3)	0.7632(6)	0.2492(6)	0.063(2)	1.0
C(2)	–0.0158(4)	0.6556(6)	0.2760(7)	0.084(2)	1.0
C(3)	–0.0032(6)	0.657(1)	0.141(1)	0.098(3)	0.6
C(4)	0.0777(7)	0.688(1)	0.3870(9)	0.109(3)	0.6
C(5)	–0.0642(7)	0.774(1)	0.218(1)	0.099(3)	0.6
H(31)	–0.0717	0.6550	0.0267		0.6
H(32)	0.0455	0.5849	0.1620		0.6
H(41)	0.0979	0.7369	0.4894		0.6
H(42)	0.1316	0.6297	0.4018		0.6
H(51)	–0.1253	0.7784	0.0980		0.6
H(52)	–0.0647	0.8316	0.2977		0.6
Molecule 4'					
C(3')	0.0140(8)	0.778(1)	0.375(1)	0.079(3)	0.4
C(4')	–0.064(1)	0.711(2)	0.141(1)	0.125(3)	0.4
C(5')	0.074(1)	0.645(1)	0.306(2)	0.099(3)	0.4
H(31')	0.0758	0.7712	0.4944		0.4
H(32')	–0.0428	0.8360	0.3487		0.4
H(41')	–0.0712	0.6670	0.0458		0.4
H(42')	–0.1188	0.7768	0.1089		0.4
H(51')	0.0756	0.5874	0.2269		0.4
H(52')	0.1363	0.6401	0.4263		0.4

We have also tried to improve geometry and orientation of the individual propellane skeletons, by constraining structurally equivalent interatomic distances to nearly equal values (within ±0.002 Å). In a first refinement (a), only the disordered molecules 3 and 4 were subjected to constraints. For each of these molecules, two variables were introduced to constrain the lengths of the side bonds as well as distances between methylene C-atoms. In a second refinement (b), the constraints were extended to all molecules. In a third refinement (c), the (idealized) geometry of the propellane C-atom skeleton determined in C (81 K [7]) was imposed to all molecules, by fixing central and side bond lengths to 1.585 Å (± 0.001 Å) and 1.527 Å (± 0.001 Å), respectively; bond angles formed by two side bonds were kept at 62.5° (± 0.1°).

The main results of the different refinements can be summarized as follows: the *R*-values increased successively from 0.038 (unconstrained refinement) to 0.056 in (a), 0.061 in (b) and 0.083 in (c). Bond lengths and angles of molecules 1 and 2, derived from (a) were somewhat less regular than those listed in *Table 3*. The displacement parameters of C-atoms subjected to constraints became more anisotropic. The increase of anisotropy was marked in molecules 3 and 4, in which the C-atom skeletons are highly distorted. The different refinements (with and without constraints) produce very similar orientations of the individual molecules. The central and (mean) side bond lengths obtained from the unconstrained refinement agree well with those obtained from (a) and (b) (within 0.01 Å for molecules 1, 2 and 3, and within 0.025 Å for molecule 4). Additional experimental details are summarized in *Table 1*.

Table 3. *Bond Lengths* [Å] *and Bond Angles* [°] *from the X-Ray Analysis at 138 K.* Values in Parentheses are corrected for librational motion. E.s.d.'s are *ca.* 0.008 Å for the bond lengths and *ca.* 0.5° for the bond angles.

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C(1)–C(2)	1.581(1.605)	1.549(1.593)	C(1)–C(2)–C(3)	58.8	59.7
C(1)–C(3)	1.519(1.555)	1.509(1.539)	C(1)–C(2)–C(4)	58.1	59.0
C(1)–C(4)	1.494(1.528)	1.495(1.532)	C(1)–C(2)–C(5)	57.9	59.0
C(1)–C(5)	1.494(1.530)	1.493(1.532)	C(2)–C(1)–C(3)	58.2	57.9
C(2)–C(3)	1.509(1.551)	1.481(1.518)	C(2)–C(1)–C(4)	58.0	58.4
C(2)–C(4)	1.493(1.525)	1.485(1.512)	C(2)–C(1)–C(5)	58.4	58.3
C(2)–C(5)	1.503(1.538)	1.482(1.522)	C(1)–C(3)–C(2)	63.0	62.4
Side C–C (mean)	1.502(1.538)	1.491(1.526)	C(1)–C(4)–C(2)	63.9	62.6
			C(1)–C(5)–C(2)	63.7	62.8
			C(3)–C(1)–C(4)	92.9	95.3
			C(3)–C(1)–C(5)	92.4	94.6
			C(4)–C(1)–C(5)	99.0	94.4
			C(3)–C(2)–C(5)	92.4	96.3
			C(3)–C(2)–C(4)	93.3	96.9
			C(4)–C(2)–C(5)	98.6	95.3

Molecular Geometry. – Stereoviews and atomic numbering of the individual molecules are shown in *Figs. 2* and *3*. Bond lengths and bond angles in *Table 3* are only listed for the ordered molecules 1 and 2.

The resolution of our X-ray experiment is too low to yield accurate atomic parameters. Thus, a detailed comparison with the accurate X-ray analyses of the two [1.1.1]propellane derivatives **B** and **C** at 81 K [7] is not very meaningful. For molecules 1 and 2, the estimated standard deviations of the C–C bond lengths, obtained from the unconstrained refinement are *ca.* 0.008 Å. However, molecular vibration introduces a systematic shortening of the C-C bond lengths between 0.024 and 0.045 Å, as shown by the corrections in parenthesis (*Table 3*). The atomic displacement parameters, judged by their e.s.d.'s (*Table 2*) and the rigid-bond test [11] (details not given here) are not accurate either. So, the librational corrections, calculated with the program THMA11 [12], are only a rough estimate.

The bridgehead–bridgehead distances for molecules 1 and 2 are 1.581(1.605) Å and 1.549 (1.593) Å, respectively. The side bonds range from 1.494 (1.525) to 1.519 (1.555) Å for molecule 1 (mean 1.538 Å) and from 1.481 (1.512) to 1.509 (1.539) Å (mean 1.526 Å) for molecule 2. The C–C bond lengths in molecule 1 appear to be 0.012 Å longer on average than in molecule 2. These differences, also present in the constrained refinements (a) and (b), show that the quality of our X-ray data is insufficient. The mean, corrected lengths of central and side bonds determined from both molecules are 1.599 and 1.532 Å, respectively, and so 0.013 and 0.006 Å longer than the corresponding values found in **B** and **C**. It seems that the librational corrections for **A** are somewhat overestimated. The mean C–C bond lengths reported here also agree within 0.025 Å with theoretical [1][4] and experimental [4][5] values summarized in *Table 4* of *Seiler et al.* [7].

The six C–C–C bond angles formed by the central and the individual side bonds range from 57.9 to 58.8° for molecule 1 and from 57.9 to 59.7° for molecule 2; the three C–C–C angles formed by the two side bonds are close to 63.5° and 62.6°, respectively. The symmetry of the C-atom skeletons, especially for molecule 2, is close to D_{3h}.

The propellane skeletons of the disordered molecules 3 and 4 are distorted (*Fig. 3*). The uncorrected distances between bridgehead atoms are 1.549 and 1.531 Å, respectively. The 12 side bond lengths in molecule 3 range from 1.406 to 1.513 Å (mean 1.474 Å). Molecule 4 is even less regular with side bond lengths ranging from 1.318 to 1.650 Å (mean 1.478 Å).

As mentioned in *Experimental*, the lengths of the central bonds as well as the (mean) lengths of the side bonds derived from the constraint refinements (a) and (b) are close to those listed in *Table 3* (within 0.01 Å for molecules 1, 2, and 3, and within 0.025 Å for molecule 4). The bond lengths of molecules 1 and 2 derived from (b) were also corrected for librational motion. The lengths of the central bonds are 1.574 (1.606) Å and 1.539 (1.582) Å, those of the side bonds 1.501 (1.545) and 1.492 (1.529) Å, respectively.

Crystal Packing. – With two ordered and two disordered molecules in the asymmetric unit (labeled 1–4, see *Fig. 4*), a detailed description of the crystal packing is problematic. First, we do not know the details of the disorder detected in molecules 3 and 4. For example, we do not know, if the individual (half-molecules) at a given site jump from one orientation to the other during the X-ray experiment, or if they vibrate about different equilibrium positions at (formally) symmetry-equivalent sites within a unit cell. Also, the disorder is probably not uniform from one unit cell to another, and the assumed space group symmetry *C*2 is at best statistical in nature. Second, the propellane skeletons of the disordered molecules are distorted and their orientations inaccurate. The intermolecular distances listed in this analysis are based on the atomic coordinates of the constraint refinement (c), in which an idealized propellane C-atom skeleton was imposed on all molecules, as well as on the coordinates listed in *Table 2* (values in parenthesis). The H-positions are based on stereochemical considerations (C–H = 1.09 Å, H–C–H = 116.0°). Hence, even the C···H and H···H distances between ordered molecules are uncertain. In spite of these uncertainties and approximations, there are some interesting aspects.

A stereopicture, of the unit cell viewed along a direction slightly tilted to c^* is shown in *Fig.4*. The molecules extend in layers approximately parallel to the (100), (001), (110), and ($\bar{1}10$) planes. Each molecule is effectively in close packing, *i.e.*, in contact with 12 nearest neighboring molecules with H···H distances <2.95 Å. A complete set of nearest neighbors, consisting of molecules of type 1, type 2 and type 4 (four each), is only shown for molecule 3. Molecule 1 is surrounded by molecules of type 2, type 3, and type 4 (four each); molecule 2 by type 1 and type 3 (four each), and by type 2 and type 4 (two each); molecule 4 by type 1 and type 3 (four each), and type 2 and type 4 (two each). In spite of the close packing, the calculated density of 1.02 g/cm^3 at 138 K is lower than in the propellane derivatives **B** (1.05 g/cm^3) and **C** (1.17 g/cm^3). With regard to the approximations made in this analysis, only three critical regions in the unit cell were analyzed in more detail. Two short intermolecular H···H distances of *ca.* 2.35 (2.28) Å occur roughly parallel to *c* (indicated in *Fig. 4*), between neighboring molecules of type 4'. For comparison, the shortest H···H distances between molecules of type 4, and type 4 to type 4', also approximately parallel to *c* (not indicated), are <2.42 (2.52) Å. In addition, there are also two short H···H distances of *ca.* 2.32 (2.33) Å approximately parallel to *b*, between molecules of type 1 and type 3, and type 1 and type 3' (indicated in *Fig. 4*). Apart from these two critical regions, there are *ca.* 25 (20) relatively short H···H distances between 2.42 and 2.70 Å. The shortest intermolecular C···H distance of *ca.* 2.52 (2.62) Å (indicated in *Fig. 4*) occurs between the inverted C-atom C(1) of molecule 3 and H(51') of molecule 4' (C(1)···H(51')-C(5') angle *ca.* 140 (139)°. Moreover, there are 7 (5) relatively short C···H distances (2.64 to 2.75 Å) between inverted C-atoms and H-atoms of neighboring molecules. In the crystal packings of **B** and **C**, all short C···H distances were of the same type [7].

The structure analysis clearly shows that a free rotation of molecules 3 and 4 in the crystal can be excluded, at least at 138 K, since all methylene C-atoms, including the disordered ones, could be located in the first E map and refined successfully in the least-squares analysis. The population parameters of the methylene C-atoms (*Table 2*) indicate that molecules of type 3 and type 3' occur with about equal probability within the crystal, whereas molecules of type 4 and type 4' occur with a probability of *ca.* 3/2, respectively. The pattern of short intermolecular distances shown in *Fig. 4* suggest that the two orientations found for molecules 3 and 4 are distributed over (at least) two sites in the unit cell. Molecule 2, which is not involved in short intermolecular distances, exhibits somewhat smaller and more isotropic displacement parameters than molecule 1 and also a slightly more regular C-atom skeleton (see, *e.g.*, the list of bond angles in *Table 3*, obtained from the unconstrained refinement). According to this analysis, molecule 4' should be influenced most strongly by the crystal packing, as it is involved in three short intermolecular distances. Indeed, the methylene C-atoms of its highly distorted propellane skeleton exhibit not only large anisotropic displacement parameters but also the lowest population parameters.

The distortions found in the propellane skeletons, especially in the individual half-molecules, could be a hint that the C-centring is only an approximation, or that the real unit cell is effectively larger as mentioned in the *Experimental*. If this were the case, the independent molecules in our assumed asymmetric unit would have to be regarded as an average superposition of two or more molecules, slightly displaced from the position and orientations reported here.

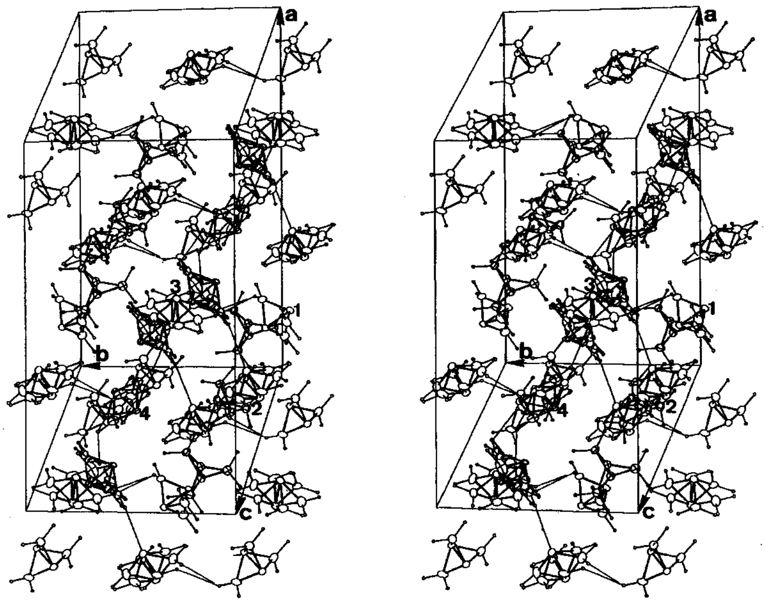


Fig.4. *Stereoscopic view of the high-temperature unit cell of [1.1.1]propellane at 138 K.* The reference molecules 1 to 4 whose coordinates are listed in *Table 2* are marked. Vibrational ellipsoids for C-atoms are shown at the 10% probability level.

Results of the Low-Temperature Modification. – On cooling, the crystals of **A** undergo a phase transition. The transition temperature, in the range of 100 to 132 K, varied from one crystal specimen to an other and depends on the growing process, the purity of the sample and other factors. For a fresh crystal specimen, the transition temperature was reproducible within a few K. All crystals obtained of the low-temperature phase were highly twinned. Typical reflection profiles from crystals of the low-temperature phase were 2 to 6°, *ca.* 6 times larger than those of corresponding reflections of the high-temperature phase. On rewarming the crystal specimens above the transition point, the original crystal quality was almost restored. *Fig. 1* shows the cell parameters as a function of temperature, obtained with the crystal specimen used for data collection. Below *ca.* 123 K, the a-axis increases by *ca.* 0.4 Å, b stays almost the same, c decreases by *ca.* 0.35 Å; β

increases by *ca.* 0.7°, α, and γ stay close to 90° (not shown here). The accuracy of the measurements below the phase transition was poor, partly due to splitting of the reflection peaks and a large mosaic spread, and partly because the reflection intensities dropped to *ca.* 1/3 of their values measured at 138 K. *Fig.1* also shows that *b* and *c* are nearly equal in lengths below the phase transition. This could suggest that the symmetry of the low-temperature modification is higher than monoclinic, as observed in an other phase transition study [13]. Various transformations of the unit cell and a comparison of integrated intensities of several low-order reflections with corresponding values of the high-temperature data set suggest that the symmetry of the low-temperature phase is probably also monoclinic, and the packing not very different from the high-temperature phase. With the present data, it was just not possible to identify the space group.

An interesting observation was made with the crystal specimen used for data collection: the transition temperature dropped from 123 K to *ca.* 100 K after a two-week exposure time (see *Fig. 1*). We provisionally assume that this change is connected with radiation damage, which leads to a slight increase of lattice dimensions during data collection. Below 100 K, the crystal specimen transformed into a powder.

The main obstacle in obtaining an accurate crystal structure of [1.1.1]propellane is that the low-temperature crystals, produced by cooling through the transition point, form twinned intergrowths. An accurate low-temperature structure could not only provide information about the nature of the central bond but possibly also on the origin of the phase transition. In principle, the twinning problem could be avoided by growing a single crystal below the transition temperature [13b]. Unfortunately, crystallization at very low temperatures is problematic and time-consuming. We have made several attempts to produce a single crystal of **A** below 100 K, but so far our efforts have been without success.

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