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Phase Transition and Crystal Structures of Adamantane

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The −65 °C phase transition in adamantane, $C_{10}H_{16}$, involves a change from the face centered cubic room-temperature structure to a tetragonal structure, space group $P\bar{4}2_1c$, with $a = 6{\cdot}60$, $c = 8{\cdot}81$ Å and $Z = 2$. The low-temperature cell is related to the cubic cell by $a_{\rm tetr} \simeq a_{\rm cubic}/\sqrt{2}$ and $c_{\rm tetr} \simeq a_{\rm cubic}$. A single-crystal X-ray study of the low-temperature phase at −110 °C shows the arrangement of the molecules to be unchanged except for a 9° tilt about the *c* axis. A redetermination of the room-temperature structure using single-crystal data supports a disordered structure, space group $Fm3m$, rather than the previously assumed, ordered, $F\bar{4}3m$ structure.

Introduction

Tricyclo[3, 3, 1, $1^{3,7}$]decane, or adamantane, $C_{10}H_{16}$, is a hydrocarbon whose molecules have a highly symmetrical (T_d) cage-like structure. A solid at room temperature, adamantane has the remarkably high melting point of 270 °C, measured in a sealed tube. The compound sublimes easily even at room temperature.

The crystal structure of adamantane has been studied at room temperature by Nowacki (1945) and by Giacomello & Illuminati (1945) using powder X-ray data. The structure is face centered cubic, and the unit cell contains four molecules. The good agreement obtained with the available X-ray data led these authors to conclude that the structure belongs to the non-centrosymmetric space group $F\bar{4}3m$ (T_d^2). Indeed, the structure proposed by them is the only chemically reasonable one assuming an ordered arrangement of the molecules.

In a recent low temperature heat capacity study Chang & Westrum (1960) discovered that adamantane undergoes a phase transition at 208·62 °K accompanied by an entropy change of 3·87 cal.deg^{-1}. mole^{-1}. The high value of the entropy change suggested the possibility of some previously undetected molecular disorder in the room temperature phase. At about the same time a muclear magnetic resonance study of solid adamantane by McCall & Douglass (1960) indicated that the room temperature structure is disordered.

As part of a series of single-crystal X-ray studies of compounds exhibiting phase transitions we have undertaken a determination of the structure of adamantane below the transition point. In view of the indications of disorder above the transition point we decided to redetermine the room temperature structure also, using single-crystal X-ray data.

Low-temperature structure

Satisfactory crystals of the room-temperature modification were found to have grown on the walls of a storage vial, *i.e.* by slow sublimation in air at room temperature. Owing to the softness of the material some difficulty was encountered in removing the crystals from the wall without distorting them. Touching the outside of the glass wall with the tip of a hot soldering pencil, causing the crystals to fall off, was found to be a satisfactory way of obtaining undistorted specimens 0·3 to 0·5 mm in size. These were mounted in sealed glass capillaries for X-ray examination.

The low-temperature form was obtained by cooling the crystal, mounted on a precession camera, in a stream of cold nitrogen gas. Diffraction patterns taken above and below the transition temperature showed that the direction of the tetragonal c axis of the low temperature form always coincided with one or more of the three a directions of the cubic room temperature form. Typically all three orientations would appear superposed, *i.e.* three orientations of the low-temperature cell would be present. In addition, some general shattering always occurred, causing an angular broadening of the diffraction spots. In a series of about a dozen runs, varying the size of crystal as well as the rate of cooling a few cases occurred in which essentially a single orientation of the low temperature cell was obtained. Precession photographs of these crystals were taken at about −110 °C using Cu $K\alpha$ radiation. Owing to the poor and deteriorating quality of the diffraction patterns nothing would have been gained by using Mo $K\alpha$ radiation. The 53 independent reflections observed in this manner were evaluated visually.

The tetragonal unit cell with the parameters $a = 6{\cdot}60$ and $c = 8{\cdot}81$ Å arises through a distortion of the cubic cell. The relationship between the two cells was observed in the orientation of the tetragonal cell relative to the cubic cell on cooling through the transition, and may be expressed as $a_{\text{tetr}} \simeq a_{\text{cubic}}/\sqrt{2}$ and $c_{\text{tetr}} \simeq a_{\text{cubic}}$. With two molecules per unit cell the low temperature phase has a calculated density of 1·18 g.cm^{-3} compared to 1·08 g.cm^{-3} for the room-temperature form.

Systematic absences of hhl for l odd and $h00$ ($0k0$) for h (k) odd lead to the space group assignment $P\bar{4}2_1c$ (D^4_{2d}). With only two molecules per cell it follows that a $\bar{4}$ axis is demanded in the molecule. The free adamantane molecule has three mutually perpendicular $\bar{4}$ axes; in the room-temperature structure (Nowacki, 1945) these axes coincide with crystallographic $\bar{4}$ axes parallel to the cubic cell edges. In the transition to the tetragonal structure two of these $\bar{4}$ axes are destroyed, while the third, directed along the tetragonal c axis, is preserved. Thus the low-temperature structure must be formed through a tilt of the molecules about the c axis, as shown in Fig. 1(*a*).

A trial model based on the above symmetry considerations was refined by least squares. The final values of the 7 independent carbon atom coordinates and the 12 independent hydrogen coordinates are given in Table 1. A single isotropic thermal parameter B was employed for all atoms; its least-squares value is 3·63 Å^2. Observed and calculated structure amplitudes are listed in Table 2. The R index is 0·080 for the 53 observed reflections.

The three crystallographically independent carbon–carbon bond distances are 1·48, 1·53 and 1·56 Å. The differences among these values undoubtedly arise from experimental inaccuracy. The average value $1{\cdot}52 \pm 0{\cdot}03$ Å agrees with Nowacki's (1945) value $1{\cdot}54_1 \pm 0{\cdot}01_6$ Å. The necessarily inaccurate carbon–

Table 1. *Atomic coordinates in the low-temperature structure*

Atom	Position	x	y	z
Methine C	8(*e*)	−0·028	0·188	0·103
Methylene C	8(*e*)	0·158	0·217	−0·005
Methylene C	4(*c*)	0	0	0·191
Methine H	8(*e*)	−0·07	0·31	0·14
Methylene H(1)	8(*e*)	0·28	0·25	0·10
Methylene H(2)	8(*e*)	0·15	0·38	−0·10
Methylene H(3)	8(*e*)	0·12	0·01	0·34

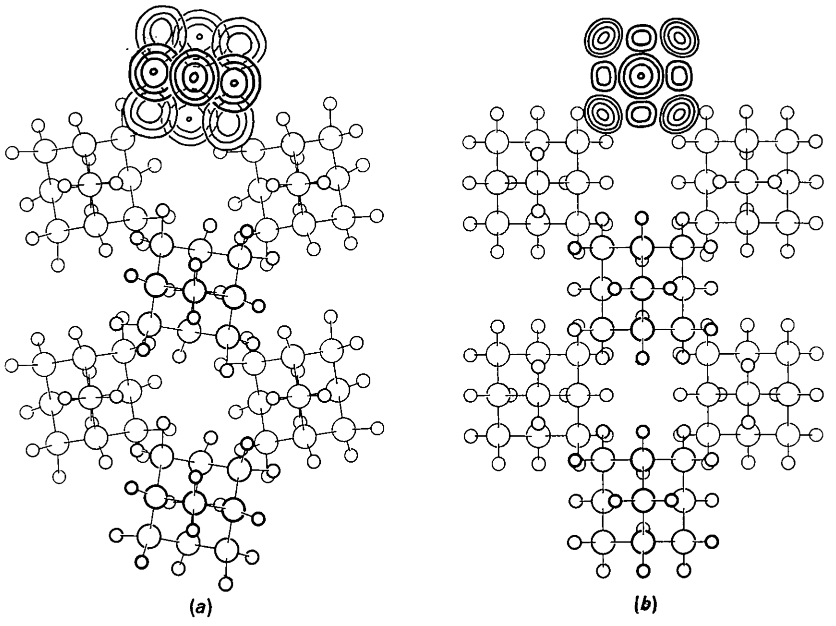
(*a*) (*b*)

Fig. 1. (*a*) The low-temperature structure of adamantane viewed along the tetragonal c axis. The tetragonal a axis is horizontal. Electron density contours are at 1, 2, 3 and 4 e.Å^{-3}. (*b*) The corresponding view of the disordered room-temperature structure. The cubic a axis is diagonal. Contours as in (*a*). Only one of each of the overlapping methine half-carbons is contoured.

Table 2. *Observed and calculated structure amplitudes (low-temperature form)*

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*hkl*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	*hkl*	$\lvert F_o\rvert$	$\lvert F_c\rvert$
000	—	152·0	041	1·8	1·9	142	2·3	2·9
002	32·2	34·7	042	3·7	3·5	143	4·4	4·7
004	8·0	4·4	110	35·4	38·2	220	5·7	6·1
011	43·7	42·2	112	10·7	9·4	222	3·4	3·6
012	10·3	9·9	120	5·4	5·5	224	14·4	13·2
013	6·5	6·0	121	9·8	9·7	230	1·4	1·6
015	2·2	2·2	122	15·0	15·0	231	2·1	2·6
020	4·6	4·5	123	13·7	13·5	232	4·1	4·8
021	15·0	15·9	124	7·1	6·8	233	4·8	4·6
022	31·4	28·5	125	4·1	4·5	234	6·5	7·2
023	19·3	17·6	130	1·1	1·1	235	18·2	16·7
024	9·5	10·8	131	5·8	5·8	240	3·5	3·9
025	1·9	1·6	132	14·4	13·8	241	2·9	2·5
031	12·0	12·2	133	14·0	11·8	242	2·9	3·0
032	18·5	19·5	134	3·2	1·8	243	3·0	4·0
033	20·5	20·3	135	7·9	7·4	244	5·3	4·2
034	10·9	6·7	140	6·7	6·3	330	2·1	2·4
040	13·1	12·7	141	5·5	5·9	332	3·4	3·4

hydrogen distances calculated from the least-squares parameters range from 0·9 to 1·5 Å.

The molecules are cocked at angles of 9° relative to the *a* or *b* axes, as shown in Fig. 1(*a*). The molecules are significantly squashed in the *c* direction, *i.e.* their 'diameter', taken as the distance between two opposite methylene carbons, is 3·37 Å along the $\bar{4}$ axis compared to 3·54 Å perpendicular to it. There is no readily apparent interpretation of this effect in terms of close intermolecular contacts in the *c* direction.

Room-temperature structure

Weissenberg photographs taken with Cu $K\alpha$ radiation and precession photographs using Mo $K\alpha$ yielded visual intensity values for 39 independent reflections from crystals of the room temperature modification. The unit-cell parameter evaluated from these photographs was $a=9{\cdot}45$ Å, giving $Z=4$. This *a* value is in reasonable agreement with the previously reported values 9·426 ± 0·008 Å (Nowacki, 1945) and 9·54 Å (Giacomello & Illuminati, 1945) considering the presumably very large effect of thermal expansion in this material.

The diffraction symmetry is *m*3*m* and the only systematic absences those of a face centered lattice. These observations are consistent with the space groups *F*433, $F\bar{4}3m$ and *Fm*3*m*, of which the first can be disregarded here.

It was at once evident that Nowacki's (1945) ordered model based on the non-centrosymmetric space group $F\bar{4}3m$ satisfied our data very well. However, at least equally good agreement was obtained with a disordered model, in which the four methine carbons in the molecule are distributed over eight sites at the corners of a cube. This corresponds to a random distribution of the molecules among two distinct orientations, which are related to each other by a 90° rotation about a line joining two opposite methylene groups. The nature of this disorder is indicated in Fig. (1*b*). The disordered model belongs to the centrosymmetric space group *Fm*3*m*.

In order to reach a choice between $F\bar{4}3m$ and *Fm*3*m* both models were subjected to least-squares refinement with the use of two different forms of the temperature factor.

In the first approach individual isotropic temperature factors for the two independent carbon atoms were employed. The positional and two thermal parameters of the carbon atoms were refined with constant, assumed values of the positional and thermal parameters of the hydrogen atoms. The resulting *R* values were 0·197 for the ordered and 0·131 for the disordered model. Corresponding values of $R_2=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ were 0·244 and 0·209. Thus the result seemed to favor the disordered structure, although not very convincingly.

In the second approach the thermal motion amplitude of each atom was assumed to correspond to a uniaxial, flat ellipsoid with its axis directed along the radius vector from the center of the molecule. The parameters of these ellipsoids were constrained so as to leave only two independent thermal parameters, representing, respectively, isotropic translational and rotational vibrations of the molecule as a whole. Least-squares refinement of these two thermal parameters and the two independent carbon atom coordinates was again carried out for the two models, with constant, assumed hydrogen coordinates. *R* and R_2 values of 0·140 and 0·168 for the ordered model, and 0·069 and 0·097 for the disordered model show a distinctly improved agreement and a clearer preference for the disordered structure. The final carbon atom coordinates for the disordered and the ordered structures were not significantly different. They are listed in Table 3, with the assumed hydrogen coordinates. The corresponding structure factors are given in Table 4.

Table 3. *Atomic coordinates in the room-temperature structure*

Group	Atom and position $F\bar{4}3m$	 *Fm*3*m*	*x*	*y*	*z*
Methylene	C 24(*f*)	C 24(*e*)	0·182	0	0
Methine	C 16(*e*)	C/2 32(*f*)	0·095	(0·095)	(0·095)
Methylene	H 48(*h*)	H/2 96(*k*)	0·066	(0·066)	0·252
Methine	H 16(*e*)	H/2 32(*f*)	0·159	(0·159)	(0·159)

The structure factor *F*(*hkl*) calculated for space group *Fm*3*m* using the model of Table 3 is identical with the real part *A*(*hkl*) of the structure factor for $F\bar{4}3m$. The imaginary part *B*(*hkl*) of the $F\bar{4}3$m structure factor is made up of contributions from the four methine carbons and the hydrogens only, the six methylene carbons being in a centrosymmetric arrangement and thus contributing only to *A*(*hkl*). Consequently, the *B*'s tend to be much smaller in magnitude than the *A*'s, making the differences between $|F_c|_{\text{noncentro}}=(A^2+B^2)^{\frac{1}{2}}$ and $|F_c|_{\text{centro}}=|A|$ very small,

Table 4. *Structure factors, room-temperature form**

hkℓ	$\lvert F_o\rvert$	F_c (Fm3m)	$\lvert F_c\rvert$ ($F\bar{4}3m$)	cos α	hkℓ	$\lvert F_o\rvert$	F_c (Fm3m)	$\lvert F_c\rvert$ ($F\bar{4}3m$)	cos α
000	--	304.00	304.00	1.000	139	0.66	-0.73	0.83	-0.821
002	18.29	17.68	17.32	1.000	155	5.18	4.99	4.73	0.998
004	0.49	1.14	0.86	1.000	157	1.38	1.17	1.07	0.961
006	0.80	1.11	0.96	1.000	159	<0.82	-0.52	0.53	-0.999
008	<0.65	-0.41	0.54	-1.000	177	<0.56	-0.13	0.31	-0.531
0.0.10	1.55	1.48	1.38	1.000	222	11.96	-12.52	15.80	-0.779
022	3.16	-3.01	3.19	-1.000	224	5.40	-4.87	6.16	-0.751
024	1.50	-1.35	1.40	-1.000	226	<0.60	-0.02	1.11	0.114
026	0.65	1.13	1.13	1.000	228	1.54	-1.59	1.99	-0.745
028	0.81	-0.98	0.98	-1.000	244	0.63	-0.68	1.93	-0.274
0.2.10	0.70	0.71	0.69	1.000	246	1.30	1.29	1.61	0.794
044	3.99	3.63	3.52	1.000	248	1.08	-1.13	1.32	-0.804
046	3.99	3.99	3.79	1.000	266	1.13	1.18	1.07	0.986
048	<0.93	-0.51	0.54	-1.000	268	0.66	-0.50	0.57	-0.846
066	3.35	3.03	2.73	1.000	288	0.51	-0.44	0.55	-0.671
068	<0.61	-0.29	0.34	-1.000	333	8.37	-8.03	9.98	-0.761
088	0.55	-0.57	0.52	-1.000	335	0.91	-0.90	0.79	-0.915
111	22.58	23.23	23.28	0.988	337	1.34	-1.27	1.91	-0.598
113	4.62	-4.17	5.60	-0.773	339	0.87	-0.92	1.01	-0.813
115	0.58	0.90	0.85	0.994	355	0.89	0.65	0.84	0.706
117	<0.60	-0.48	0.81	-0.627	377	0.58	-0.40	0.64	-0.559
119	<0.65	0.03	0.34	-0.032	444	0.87	-1.22	1.21	-0.940
1.1.11	0.83	1.05	0.99	0.999	446	<0.62	-0.36	0.83	-0.465
133	6.12	-6.07	7.52	-0.790	448	0.83	-0.90	0.89	-0.942
135	1.66	1.78	1.84	0.985	555	<0.64	-0.12	0.33	-0.731
137	<0.63	-0.15	1.00	-0.103	577	<0.45	0.05	0.27	0.261

* The $|F_o|$'s are scaled for best fit to the *Fm3m* model.

and the assignment of model by comparison of the $|F_o|$ with the two alternative $|F_c|$ very difficult.

Nevertheless, a convincing space group assignment can be made by considering the dependence of the ratio of observed to calculated structure amplitudes on the calculated phase angle. Since $|\cos\alpha| = A/(A^2+B^2)^{\frac{1}{2}} = |F_c|_{\text{centro}}/|F_c|_{\text{noncentro}}$ it follows that the ratios $|F_o|/|F_c|_{\text{noncentro}}$ can be expected to approximate $|\cos\alpha|$ if the structure is centrosymmetric. If the structure is non-centrosymmetric the structure factor ratios will be approximately unity, and show no trend with $|\cos\alpha|$.

Fig. 2 shows a plot of the ratio $\Sigma|F_o|/\Sigma|F_c|_{\text{noncentro}}$ *versus* $|\cos\alpha|$ for the observed reflections. The structure factor sums are evaluated over four 0·2 unit intervals in $|\cos\alpha|$, and for $|\cos\alpha| = 1$, using the final least-squares $|F_c|$ values for the $F\bar{4}3m$ model. The plot shows a clear upward trend with $|\cos\alpha|$. The fact that it exceeds unity near $|\cos\alpha| = 1$ merely reflects the fact that least-squares scaling of the data in effect demands that $\Sigma|F_o|/\Sigma|F_c| = 1$ for all reflections. The corresponding ratios $\Sigma|F_o|/\Sigma|F_c|_{\text{centro}}$ for the reflections in each interval are shown for comparison. They show no significant trend with $|\cos\alpha|$. It can be concluded that the structure corresponds to the disordered model, and that the correct space group is *Fm*3*m*.

The least-squares values of the two rigid-body thermal parameters used in the refinement correspond to a root-mean-square translational vibration amplitude of 0·06 Å and a root-mean-square rocking amplitude of about 8°. Including appropriate corrections for the effect of the rocking motion on the apparent molecular parameters the carbon–carbon bond distance is 1·54 Å and the C···C distance between two opposite methylene groups is 3·51 Å. The latter value compares reasonably with the corresponding distances 3·54, 3·54 and 3·37 Å in the molecule of the low-temperature phase.

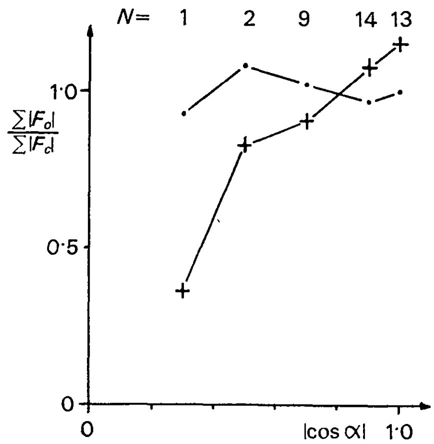

Fig. 2. Scale factors $\Sigma|F_o|/\Sigma|F_c|$ for the non-centrosymmetric (+) and centrosymmetric (·) models as functions of $|\cos\alpha|$ for the non-centrosymmetric model. N is the number of reflections in each 0·2 unit range of $|\cos\alpha|$, or the number with $|\cos\alpha| = 1$.

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