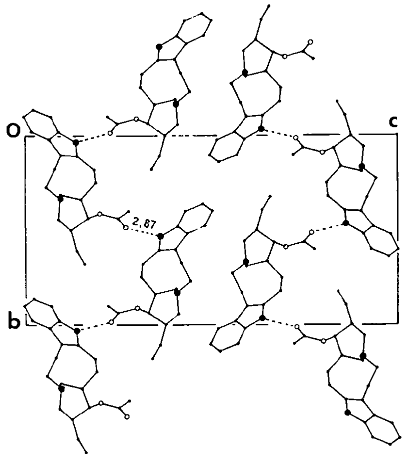

Fig. 5. Projection *Oyz* de la structure, avec la liaison hydrogène (Å).

L'auteur remercie M Henri-Philippe Husson pour son intérêt constant au cours de ce travail.

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An X-ray Powder Diffraction Study of Crystalline α-Methane-d_4

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Abstract

X-ray powder diffraction of methane-d_4 (deuteromethane) has been studied using visual estimation of intensities; these were then compared with those calculated for various models for molecular-orientation arrangement in the lattice. It was found that the tetragonal unit cell of the low-temperature phase of deuteromethane containing 32 molecules has space group $P\bar{4}m2$. The orientational structure of CD_4 as it transforms from the intermediate to the low-temperature phase is also discussed.

Introduction

With regard to the intermolecular-interaction forces and the molecular rotational energy, solid methanes of the type $CH_{4-n}D_n$ ($n = 0,\ldots, 4$) occupy the position in the series of the simplest molecular crystals between hydrogen and carbon. Therefore, in addition to the classical behaviour, quantum effects may be expected in the physical characteristics of methanes. This has stimulated researchers' interest, and in recent years many theoretical and experimental papers have appeared which deal with the physical properties of methanes. However, interpretation of the results and the development of concepts concerning the kinetics of methane phase transitions were severely handicapped by the lack of a reliable knowledge of the crystalline structures of the phases.

Deuteromethane is suitable for an experimental and theoretical investigation of solid methane structures, since the influence of quantum effects on the properties is negligible. A knowledge of the molecular orientation in deuteromethane lattices is expected to facilitate the understanding and definition of the crystalline structures of the lighter methanes.

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Orientational ordering of molecules in solid deuteromethane leads to phase transitions at 22·2 and 27·1 K, attended by marked volume changes (Baer, Fraase, Riehl & Simmons, 1978). The existence of the two phase transitions and the orientational structure of the three phases in deuteromethane were first predicted theoretically by James & Keenan (1959), who suggested that the high-temperature cubic phase of CD_4 is orientationally disordered. In the intermediate 32-molecule cubic unit cell, a quarter of the molecules are also orientationally disordered and have local symmetry 432 (O), while the rest, occupying positions $\bar{4}2m$ (D_{2d}), have their own $\bar{4}$ axes oriented along crystallographic axes. The transition to the low-temperature α-phase is accompanied by ordering of all molecules and lowering of the lattice symmetry to tetragonal $I\bar{4}2m$ with parallel orientation of the CD_4 tetrahedra.

The above-mentioned paper stimulated further theoretical and experimental efforts. Press (1972) used the models of the molecular-orientational packing of the high-temperature and intermediate phases mentioned above to describe experimental results and proposed space groups $Fm3m$ and $Fm3c$, respectively, for the phases. X-ray (Prokhvatilov, Gasan & Erenburg, 1970) and neutron scattering (Arzi & Sandor, 1975) techniques showed that the transition to the low-temperature phase is attended not only by orientational structure changes, but also by substantial tetragonal distortion of the cubic lattice.

Maki, Kataoka & Yamamoto (1978) carried out an analysis of the orientational structure of three deuteromethane phases in the molecular-field approximation by using the potential allowing for high-order multipole interaction terms. In contrast to James & Keenan (1959), who only allowed for the octopole–octopole interaction, Maki *et al.* (1978) also considered octopole–hexadecapole and hexadecapole–hexadecapole interactions. They assumed that carbon atoms in all the three phases of deuteromethane were arranged as a face-centred lattice and that both transitions were of second order. This kind of approach resulted in a model of the α-CD_4 orientational structure having symmetry $P4_2/mbc$ with 16 molecules in the unit cell situated at sites with local symmetries D_2, S_4 and C_s. The structure of the low-temperature deuteromethane phase was studied experimentally on powder crystals by the neutron diffraction method (Arzi & Sandor, 1975). According to the extinction rules obtained, two space groups were proposed: $P4_2bc$ with 16 molecules and $P4_2/nmc$ with 32 molecules per unit cell, the latter being among those which had been suggested earlier (Press & Hüller, 1974). Deuterium-atom coordinates, however, were not determined in the latter two works.

In the present paper we report the results of an X-ray investigation of the crystalline structure of the low-temperature deuteromethane phase.

Experimental technique

For our experiments we used deuteromethane samples of 99·9% chemical purity containing 98·3% of methane isotopes. They were produced by deuteromethane-gas condensation on to a plane copper substrate precooled to liquid-helium temperature in a cryostat (Prokhvatilov, Gasan & Erenburg, 1970). X-ray powder patterns of 20 samples were obtained with Cu $K\alpha$ radiation in the DRON-0·5 diffractometer at temperatures of 1·5 to 6 K; these were then analysed. The sample temperature was measured by a Ge thermometer to within ±0·1 K. The sample temperature was stabilized during exposure to within ±0·05 K. The experimentally selected conditions of condensation and subsequent annealing at 40 K for two hours very substantially reduced the texture and stress effects on the Bragg-reflection intensities. Because of the very low intensity of reflections representing X-ray scattering from deuterium atoms, a scintillation counter could not detect them.

However, on X-ray patterns, exposed for two or three hours with reflection angles $\theta = 10$–$40°$, many weak lines were always revealed. For each sample, several X-ray patterns were obtained, focused to a variety of reflection angles, which allowed an identification of weak 'superlattice' lines and an estimation of their relative intensities (with the visual intensity scale).

Results and discussion

The experimental data obtained confirm the earlier conclusion (Prokhvatilov, Gasan & Erenburg, 1970) concerning the tetragonal 32-molecule unit cell of the low-temperature deuteromethane phase. Lattice parameters at 6 K refined for all experiments by the least-squares method using 25 to 30 reflections were found to be $a = b = 11{\cdot}537 \pm 0{\cdot}002$ Å, $c = 11{\cdot}723 \pm 0{\cdot}002$ Å. The density at this temperature, $\rho = 0{\cdot}6835$ Mg m^{-3}, is almost equal to that of Baer, Fraase, Riehl & Simmons (1978). For the sample parameters obtained, there is satisfactory agreement between calculated and measured reflection angles (Table 1). In accordance with experimental extinctions for the 32-molecule tetragonal unit cell of deuteromethane, several space symmetry groups proved to be possible: $P\bar{4}m2$, $P\bar{4}2_1m$, $P\bar{4}2m$, $P4_222$ and $P\bar{4}$ (*International Tables for X-ray Crystallography*, 1952). Various models of the molecular orientational packing were developed for each and reflection intensities were also computed by the program *Polycrystal*-3 (Titov, Verkhorobin & Matyushenko, 1972) with an isotropic thermal factor, with $B = 1{\cdot}18$ Å^2. For the construction of the orientational structure model and the atom-coordinate calculation, it was assumed that CD_4 molecules in a crystal are not deformed and that the intra-

Table 1. *Experimental and calculated angles* (θ) *and intensities* (I) *of reflections hkl of* α-CD_4

	Calculation for space group $P\bar{4}m2$			Experiment		Calculation with the model of Maki, Kataoka & Yamamoto (1978), space group $P4_2/mbc$		
$h\ k\ l$	θ_{calc}	I_{calc}	θ_{exp}	I_{exp}	n*	$h\ k\ l$	θ_{calc}	I_{calc}
1	2	3	4	5	6	7	8	9
1 3 0	12·20°	1·33	12·18°	weak	1	–	–	–
1 1 3	12·64	0·24	12·75	weak	1	1 2 1	12·69°	6·33
1 3 1	12·73	2·22						
2 2 2	13·31	1000·00	13·31	very strong	1	0 2 2	13·26	1000·00
0 2 3	13·79	0·54	13·83	weak	0·7	–	–	–
0 3 2	13·87	0·23						
1 3 2	14·41	1·68	14·41	weak	0·95	1 2 2	14·35	0·16
0 0 4	15·25	140·10	15·28	medium	1	0 0 4	15·36	334·00
0 4 0	15·50	267·10	15·49	strong	1	2 2 0		
0 1 4	15·75	0·56	15·82	very weak	0·15	0 2 3	15·85	1·78
2 2 3	15·85	0·10						
2 3 2	15·93	0·14	16·07	very weak	0·50	–	–	–
0 4 1	15·97	0·26						
1 1 4	16·23	0·11	16·30	extremely weak	0·55	–	–	–
–	–	–	–	–	–	1 2 3	16·78	0·16
3 3 1	16·92	0·61	16·88	very weak	0·9	–	–	–
0 4 2	17·33	0·30	17·30	extremely weak	0·3	114, 222, 130	17·23	0·12
1 2 4	17·60	0·53	17·49	very weak	0·15	1 3 1	17·67	3·80
2 4 1	17·81	0·26	17·85	extremely weak	0·25	–	–	–
–	–	–	–	–	–	024, 132	18·93	0·43
0 3 4	19·31	0·24	19·36	extremely weak	0·30	–	–	–
0 5 0	19·52	0·13	19·48	extremely weak	0·25	–	–	–
1 3 4	19·72	0·71	19·75	very weak	0·60	124, 230	19·73	0·74
1 1 5	20·00	0·27	20·24	very weak	0·50	–	–	–
3 3 3	20·20	0·39						
1 5 1	20·30	0·30						
0 2 5	20·79	1·22	20·83	very weak	0·25	1 3 3	20·89	9·08
2 3 4	20·89	0·42						
2 4 3	20·98	1·26	21·01	very weak	0·30	–	–	–
3 4 2	21·04	0·17						
2 5 0	21·09	0·59						
–	–	–	–	–	–	2 3 2	21·27	0·10
1 5 2	21·42	0·32	21·50	extremely weak	0·50	–	–	–
0 4 4	22·02	92·27	22·03	medium	1	224, 040	22·00	107·69
4 4 0	22·21	40·74	22·17	medium	1			
2 5 2	22·52	0·33	22·48	extremely weak	0·15	025, 041	22·36	5·26
–	–	–	–	–	–	1 4 0	22·72	1·38
–	–	–	–	–	–	125, 233, 141	23·07	5·49
3 5 1	23·27	0·63	23·40 wide	very weak	0·90	006, 134, 042, 330	23·41	1·54
2 4 4	23·46	0·15						
0 6 1	23·97	0·32	23·82	extremely weak	0·05	–	–	–
1 6 0	23·98	0·11						
–	–	–	–	–	–	1 4 2	23·10	0·75
3 5 2	24·28	0·49	24·29	extremely weak	0·40	–	–	–
–	–	–	–	–	–	332, 240	24·76	0·65
3 4 4	25·16	0·16	24·96	extremely weak	0·20	043, 241	25·09	0·24
1 5 4	25·49	1·79	25·50	very weak	0·50	–	–	–
3 5 3	25·89	0·13	25·95	medium	0·95	026, 242	26·06	72·86
2 2 6	25·94	41·28						
0 3 6	26·26	0·15	26·23	medium	1	–	–	–
2 6 2	26·27	79·25						
–	–	–	–	–	–	1 3 5	26·38	3·61
0 6 3	26·54	0·20	26·60	extremely weak	0·25	–	–	–
1 3 6	26·58	0·20						
4 4 4	27·42	28·94	27·44	medium	0·95	0 4 4	27·31	25·69
2 3 6	27·53	0·17						
–	–	–	–	–	–	2 4 3	27·62	0·12
–	–	–	–	–	–	144, 340	27·92	0·71
5 5 1	28·49	0·14	28·40	extremely weak	0·15	226, 334, 150	28·53	0·14
1 7 1	28·49	0·53						
0 2 7	28·64	0·55						
–	–	–	–	–	–	1 5 1	28·83	0·35
–	–	–	–	–	–	3 4 2	29·12	0·12
–	–	–	–	–	–	0 4 5	30·00	0·31
–	–	–	–	–	–	127, 343, 251	30·58	0·51
–	–	–	–	–	–	1 5 3	31·15	1·85
–	–	–	–	–	–	2 5 2	31·43	0·39
0 0 8	31·74	4·25	31·70	very weak	0·10	008, 440	31·99	4·67
0 8 0	32·31	9·43	32·30	weak	0·50			
–	–	–	–	–	–	4 4 2	33·10	0·16
–	–	–	–	–	–	1 3 7	33·38	0·31
–	–	–	–	–	–	1 4 6	33·65	0·24
–	–	–	–	–	–	0 2 8	34·19	0·46
–	–	–	–	–	–	2 3 7	35·00	0·17
2 6 6	35·32	22·48	35·38	weak	0·65	246, 062	35·26	25·60
6 6 2	35·59	9·82	35·62	weak	0·30			
–	–	–	–	–	–	1 5 5	35·53	0·78
–	–	–	–	–	–	1 6 2	35·85	0·36
0 4 8	36·16	10·74	36·16	very weak	0·15	228, 444, 260	36·32	18·65
0 8 4	36·56	10·56	36·55	very weak	0·10			
4 8 0	36·70	9·96	36·69	extremely weak	0·05			

molecular distances and angles remain the same as those in a free molecule (Krasnov, Timoshin, Danilova & Khandozhko, 1968): D—D = 1·788, C—D = 1·095 Å, D—C—D = 109° 26′.

A comparison of experimental intensities with those calculated for all the above-mentioned space groups showed that the structure of the low-temperature phase of deuteromethane has symmetry $P\bar{4}m2$ with molecular orientations as represented in Fig. 1. Table 1, together with experimental intensities and angular positions of α-CD_4 Bragg reflections, lists results calculated for the orientational structure of Fig. 1 for space group $P\bar{4}m2$ and a model proposed in the theory of Maki, Kataoka & Yamamoto (1978). Reflections with calculated relative intensities less than 0·1 and which are unobservable experimentally are not included in the table. The experimental reflection reproducibility is characterized by the coefficient n^*, specifying the relative number of particular reflection observations from 20 experiments. It follows from Table 1 that the model of the α-CD_4 orientational structure in Fig. 1 is realistic, unlike that suggested by Maki *et al.* (1978), which is unable to describe many of the observable reflections.

Table 2 presents coordinates, Wyckoff positions, position multiplicities and point symmetries (*International Tables for X-ray Crystallography*, 1952) of the independent atoms in a unit cell. It lists C atom coordinates for each independent molecule and, in the following rows, coordinates of independent deuterium atoms corresponding to the same molecule. To rule out overlapping of van der Waals radii of neighbouring molecules, interatomic separations in the first coordination sphere were calculated. The minimum interatomic separations, D—D = 2·406 and C—D = 3·040 Å, for this orientational structure were slightly higher than the sum of the appropriate van der Waals radii, $2r_D = 2{\cdot}34$ and $r_{C-D} = 2{\cdot}97$ Å (Kitaigorodskii, 1971).

As is suggested by our results, the transition to the low-temperature phase is attended by orientational ordering of molecules, which were, in the intermediate phase, completely disordered with point symmetry O (432) (Fig. 2). During this transition, the symmetry of the surrounding field of the molecule in the low-temperature phase is lowered to C_1 (1). Moreover, at the phase transition, the point symmetry of the sites of previously ordered molecules is also lowered. Two thirds of the molecules, which in the intermediate phase were situated at sites of the lattice with symmetry D_{2d} ($\bar{4}2m$) (Press, 1972), after the transition occupy sites with point symmetry C_s (m), and the rest occupy sites with point symmetry C_{2v} ($mm2$) (see Fig. 1 and Table 2). Molecules at sites C_{2v} have the same orientation as in the intermediate phase, and the molecules which were oriented along **a** and **b** in the field of symmetry C_s assume an orientation such that their $\bar{4}$ axes, while remaining as before in planes m parallel to the unit-cell faces, tend to adopt an orientation close to **c**. One half of these molecules are rotated by 90° around their own $\bar{4}$ axis (see Figs. 1 and 2). As calculations show, molecules at sites C_1 occupy more than one orientation, as the $\bar{4}$ axis departs from plane (001) by ±15°, without appreciable change in the reflection intensities.

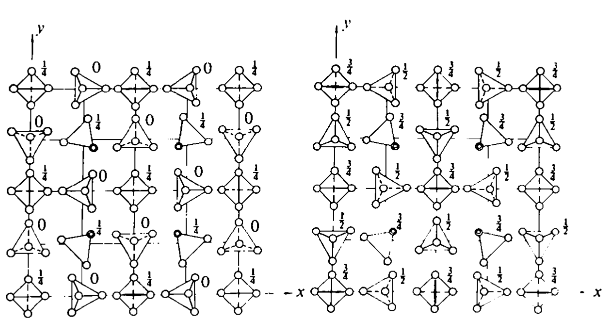

Fig. 1. Orientational structure of the tetragonal 32-molecule unit cell of the low-temperature phase of CD_4 (space group $P\bar{4}m2$). The projection is on the plane (001); the values indicate the z coordinates of the C atoms. On the left, molecules are shown located in planes with $z = 0$ and $z = \frac{1}{4}$, and on the right with $z = \frac{1}{2}$, $z = \frac{3}{4}$.

Table 2. *Coordinates and point symmetry of independent atoms in the low-temperature deuteromethane unit cell (space group $P\bar{4}m2$)*

Serial number	Atom	Position and multiplicity	Point symmetry	x	y	z
1	C	2(*e*)	*mm*2	0	0	0·2500
2	D	4(*j*)	*m*	0·0775	0	0·3039
3	C	2(*g*)	*mm*2	0	0·5000	0·2500
4	D	4(*k*)	*m*	0·0775	0·5000	0·1961
5	D	8(*l*)	1	0	0·5775	0·3039
6	C	2(*g*)	*mm*2	0	0·5000	−0·2500
7	D	4(*k*)	*m*	0·0775	0·5000	−0·3039
8	D	8(*l*)	1	0	0·5775	−0·1961
9	C	2(*f*)	*mm*2	0·5000	0·5000	0·2500
10	D	4(*k*)	*m*	0·5775	0·5000	0·3039
11	C	4(*k*)	*m*	0·2500	0·5000	0
12	D	4(*k*)	*m*	0·2578	0·5000	0·0931
13	D	4(*k*)	*m*	0·1582	0·5000	−0·0237
14	D	8(*l*)	1	0·2920	0·5775	−0·0352
15	C	4(*k*)	*m*	0·2500	0·5000	0·5000
16	D	4(*k*)	*m*	0·2422	0·5000	0·4069
17	D	4(*k*)	*m*	0·3418	0·5000	0·5237
18	D	8(*l*)	1	0·2080	0·5775	0·5352
19	C	4(*j*)	*m*	0·2500	0	0
20	D	4(*j*)	*m*	0·2422	0	0·0931
21	D	4(*j*)	*m*	0·3418	0	−0·0237
22	D	8(*l*)	1	0·2080	0·0775	−0·0352
23	C	4(*j*)	*m*	0·2500	0	0·5000
24	D	4(*j*)	*m*	0·2578	0	0·4069
25	D	4(*j*)	*m*	0·1582	0	0·5237
26	D	8(*l*)	1	0·2920	0·0775	0·5352
27	C	8(*l*)	1	0·2500	0·2500	0·2500
28	D	8(*l*)	1	0·2887	0·2887	0·3263
29	D	8(*l*)	1	0·2887	0·2887	0·1737
30	D	8(*l*)	1	0·2660	0·1565	0·2500
31	D	8(*l*)	1	0·1565	0·2660	0·2500

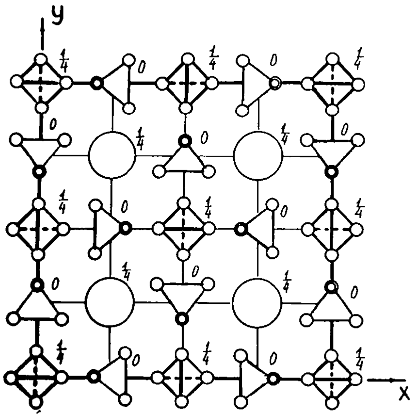

Fig. 2. Orientational structure of the cubic 32-molecule intermediate phase of deuteromethane (space group $Fm3c$). The projection is of two layers on the plane (001).

Tetragonal lattice distortion along z resulting from the transition of the cubic intermediate phase into the low-temperature phase seems to be due to a preferred molecular orientation in planes parallel to the c axis and containing molecules with point symmetry C_1.

Thus, in the low-temperature phase of deuteromethane, molecules reside at three types of sites which essentially differ in their lattice-field symmetry; however, contrary to the results of Maki, Kataoka & Yamamoto (1978), our experiments provide evidence for lower point symmetry. It should be noted that some recent work (Medina & Daniels, 1978; Kobashi, 1978) on Raman and IR spectra in the intermediate and low-temperature phases of methane under pressure at 4·2 K also revealed three types of molecular point symmetries in α-CH_4 which have very different molecular fields.

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The Structures of Two Forms of Tetraphenyldithiapyranylidene* Polyiodide, One-Dimensional Organic Conductors

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Abstract

The crystal structures of two forms of the ion–radical salt of tetraphenyldithiapyranylidene (φ_4DTP) and iodine have been determined from X-ray diffractometer data. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares. One form (DTPI1) is orthorhombic, $Fddd$, with $a = 30{\cdot}99$ (3), $b = 54{\cdot}83$ (7), $c = 3{\cdot}700$ (4) Å and $Z = 8$. The second form (DTPI2) is tetragonal, $P\bar{4}b2$, with $a = 19{\cdot}74$ (2), $c = 3{\cdot}721$ (5) Å and $Z = 2$. In addition to the Bragg reflections, diffuse streaks on precession photographs indicate disordered lattices incommensurate along c with a repeat of $c' = 9{\cdot}39$ Å

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* 3,3′,5,5′-Tetraphenyl-4,4′-dithia-1,1′-bi-2,5-cyclohexadienylidene.

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