

SHORT COMMUNICATIONS

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The structure of solid acetylene-d₂, C₂D₂, at 4·2 K. A further refinement. By HARRI K. KOSKI, *Department of Physics, University of Helsinki, Siltavuorenpenger 20c, SF-00170 Helsinki 17, Finland*

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The neutron powder diffraction pattern of orthorhombic C₂D₂ at 4·2 K has been re-examined by the Rietveld profile-refinement technique. The final values for R_i were 5·16% and 3·67%, respectively, for least-squares refinements with isotropic and anisotropic thermal parameters.

Introduction

Recently, the crystal structure of the low-temperature phase of solid C₂D₂ has been reported by Koski & Sándor (1975) (K & S). The positional parameters and isotropic B factors were refined with the *ORXFLS3* program of Busing *et al.* (1971). The input data for the refinement on $|F_o^2|$ were obtained by the conventional method of measuring integrated intensities of single reflexions and resolvable multiplets. A considerable amount of information could not be directly used in the analysis. The steeply increasing broadening of the diffraction peaks well above the instrumental focusing angle in the range $0·865 < 2 \sin \theta/\lambda < 0·91$ and several unresolvable multiplets for $2 \sin \theta/\lambda < 0·865$ reduced the number of useful intensity maxima to 24. In the pattern, however, there were about ten reasonably intense diffraction maxima used only as indirect evidence for the structure. Since they were either unresolvable multiplets or strongly overlapping single peaks no reliable intensity distribution could be found. It was considered necessary to reinvestigate the problem by the profile-refinement technique in order to use all the information content of the observed pattern.

Experimental

Details of the experimental procedure are given elsewhere (Koski & Sándor, 1975). The powder pattern observed with the multicounter neutron powder diffractometer PANDA (UKAERE, Didcot, England) was collected by two triple-counter blocks 10° apart in 2θ . The six individual patterns recorded above, at, and below the equatorial diffractometer plane were scaled to the same overall intensity level for the profile analysis. The 2θ scale of the non-equatorial patterns was adjusted in such a way that the centre of the intensity maxima coincided with the centre of the same reflexion at the equatorial level. The combined pattern was found by

Table 1. *The lattice parameters from various refinements*
C₂D₂, orthorhombic, space group *Acam* (No. 64). Unit-cell volume $V = 206·0$ (3) Å³, $Z = 4$, $T = 4·2$ K, $\lambda = 1·848$ (1) Å.

	Isotropic refinement	Anisotropic refinement	K&S (1975)
a	6·188 (3) Å	6·188 (3) Å	6·193 (3) Å
b	6·001 (3)	6·002 (3)	6·005 (3)
c	5·546 (3)	5·547 (3)	5·551 (3)

Table 2. *Structural parameters from various refinements*

The isotropic B parameters (Å²) and the anisotropic thermal parameters (Å²) are multiplied by 10², the positional parameters by 10⁴. The anisotropic temperature factor is of the form $\exp(-\frac{1}{2}\sum_i \sum_j s_{ij})$, with $s_{ij} = B_{ij}h_i h_j a_i^* a_j^*$.

	Isotropic, no constraint	Isotropic + constraint	Anisotropic, no constraint	Anisotropic + constraint	K&S (1975)
x_C	603 (3)	617 (1)	596 (3)	607 (2)	605 (4)
y_C	778 (2)	763 (1)	767 (3)	758 (2)	757 (4)
z_C	0	0	0	0	0
x_D	1728 (3)	1720 (3)	1709 (3)	1701 (3)	1698 (6)
y_D	2103 (2)	2111 (2)	2108 (3)	2115 (3)	2125 (6)
z_D	0	0	0	0	0
B_C	82 (3)	82 (3)			100 (20)
B_D	265 (3)	266 (3)			240 (10)
$B_{11}(C)$			80 (7)	86 (7)	
$B_{22}(C)$			75 (9)	61 (9)	
$B_{33}(C)$			58 (7)	65 (7)	
$B_{12}(C)$			-56 (7)	-51 (7)	
$B_{11}(D)$			288 (13)	317 (12)	
$B_{22}(D)$			224 (12)	200 (10)	
$B_{33}(D)$			222 (8)	217 (8)	
$B_{12}(D)$			-63 (5)	-58 (5)	
R_i (%)	5·16	5·48	3·67	3·83	5·6 on F^2
R_y (%)	8·78	8·73	7·84	7·91	
R_w (%)	9·25	9·19	8·22	8·26	
R_e	5·79	5·79	5·78	5·78	

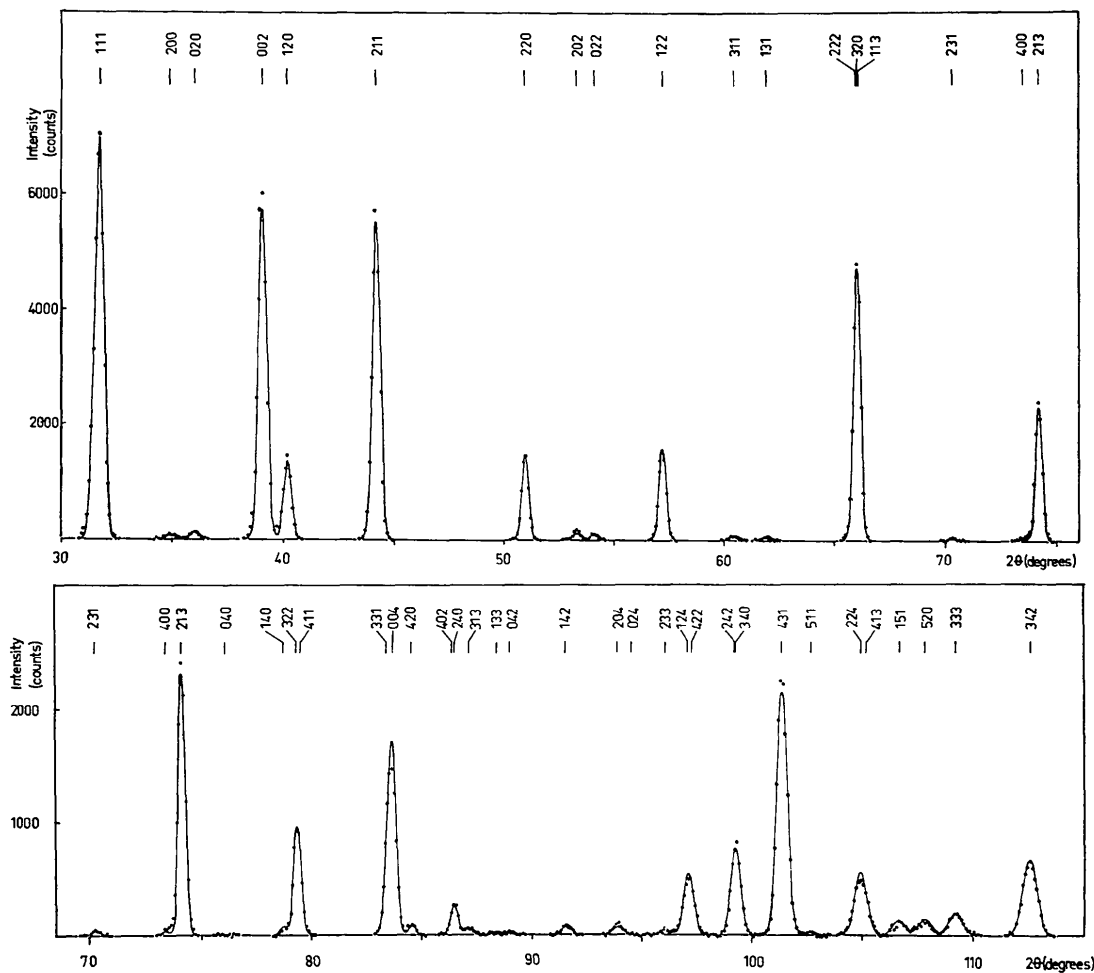


Fig. 1. The comparison of the observed (●) and calculated (solid line) diffraction patterns. The theoretical pattern was obtained with anisotropic thermal parameters; no constraint was applied.

averaging the corrected individual subpatterns. The refined lattice parameters are given in Table 1.

Structure refinement

The combined neutron diffraction pattern was analysed by the profile-fitting method of Rietveld (1967), modified by Hewat (1974) for anisotropic thermal vibrations. The observed pattern is treated as the sum of Gaussian reflexion maxima. Each count forms an observation along the scanned range. The coherent neutron scattering lengths used were $b_C = 0.665$ and $b_D = 0.667$ (Bacon, 1972; in units $\text{cm} \times 10^{-12}$). The initial values for the positional parameters and the isotropic Debye-Waller B -factors were taken from K & S. For anisotropic refinement of the thermal parameters the β -restrictions reported by Peterse & Palm (1966) were applied. The residuals are $R_I = \sum |I_o - I_c| / \sum I_o$, $R_y = \sum |y_o - y_c| / \sum |y_o|$, $R_w = [\sum w(y_o - y_c)^2 / \sum w(y_o)^2]^{1/2}$; I_o , I_c = the observed and calculated, scaled integrated intensities; y_o , y_c = the observed and scaled calculated count values; the weight applied to an observation $w = y_o^{-1}$. A statistical residual is given as $R_e = [\text{NDF} / \sum w(y_o)^2]^{1/2}$, NDF = number of degrees of freedom. The parameters used as variables in the refine-

ments were: the scale factor, the positional parameters $x(\text{Å})$ and $y(\text{Å})$, the thermal parameters $B(\text{Å}^2)$ or $B_{ij}(\text{Å}^2)$, the lattice parameters, the profile zero-point and the peak half-width parameters; A = carbon or deuterium. In order to eliminate a possible asymmetry of the diffraction maxima at low 2θ the asymmetry parameter was included in the variables. Tentatively, several refinements were carried out with a linear approximation for the C_2D_2 molecule. The equation $x_C y_D = y_C x_D$ was applied for a quadratic constraint function. The refined structural parameters are in Table 2 with the estimated standard deviations in parentheses in units of the last significant digit. The fit between the observed and the calculated neutron powder pattern profiles is good (Fig. 1).

Discussion

The average molecular and bond lengths were determined separately for the isotropic and anisotropic refinements. The values derived for $r(\text{DC}\equiv\text{CD})$, $r(\text{C}\equiv\text{C})$ and $r(\text{C}-\text{D})$ (in Å) are: 3.309 (6), 1.194 (5) and 1.058 (4) for the isotropic, 3.301 (7), 1.180 (6) and 1.061 (5) for the anisotropic analysis. It can be seen from Table 2 that though no major differences were found in the positional parameters of this work and

the ones reported earlier (K & S), a reasonable reduction in the standard deviations of the variables is gained and also a smaller R_p . The use of the retrieved information content of the powder pattern has led to a further improvement in the form of the anisotropic thermal parameters obtained.

The author is indebted to Dr M. Ahtee for access to the Rietveld profile refinement program submitted to her by Dr A. W. Hewat, Institute Max von Laue–Paul Langevin, Grenoble, France. The calculations were carried out on the Burroughs B6700 computer at the Computing Centre of the University of Helsinki. The financial support by the Finnish Academy, the Royal Society and the Finnish Academy of Sciences is acknowledged.

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Crystallization effects on the space group of (+)- α -naphthylphenylmethoxy-(–)-menthoxysilane, $C_{27}H_{34}O_2Si$.

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Studies made by Vidal, Galigné & Falgueirettes [*C. R. Acad. Sci. Paris* (1970). **270**, 690–691] and Kanters & van Veen [*Cryst. Struct. Commun.* (1973). **2**, 261–267] on crystals given by Lanneau (Thèse de spécialité, Poitiers, 1969) have shown that there are two different space groups depending on the crystallization conditions.

Introduction

(+)- α -Naphthylphenylmethoxy-(–)-menthoxysilane is isolated by fractional crystallization from two diastereomers (+– and ––). The former diastereomer (+–), I_a melts at 103°C and has a specific rotation of -58.8° . The latter (––), I_b has a specific rotation of -76.4° and a melting point of 79°C. Under certain crystallization conditions a compound, I, with well defined physical properties can be obtained; its melting temperature is 74°C, and its specific rotation -68.6° .

These compounds have been synthesized by Lanneau (1969). Chemical properties and a number of reactions have been described by Corriu, Lanneau & Royo (1972).

Results

Vidal, Galigné & Falgueirettes (1970) made a crystallographic study of the compounds I_a , I_b and I and showed that the compound I is a quasi-racemate of the diastereomers I_a and I_b . Use of Weissenberg and Buerger precession cameras enabled us to obtain approximate values for the parameters and to determine the space group.

The parameter values were refined by least-squares calculations, using the Bragg angles measured with precision on a semi-automatic Enraf–Nonius CAD-3 diffractometer. The radiation used was Cu $K\alpha$.

Crystal I_a : $a = 18.402$ (6), $b = 16.260$ (7), $c = 8.362$ (5) Å, $V_{\text{cell}} = 2500$ Å³, space group $P2_12_12_1$, $Z = 4$, $D_{\text{calc}} = 1.11$, $D_{\text{obs}} = 1.11$ g cm⁻³.

Crystal I_b : $a = 19.260$ (7), $b = 17.636$ (5), $c = 7.177$ (5) Å, $V_{\text{cell}} = 2483$ Å³, space group $P2_12_12_1$, $Z = 4$, $D_{\text{calc}} = 1.13$, $D_{\text{obs}} = 1.11$ g cm⁻³.

Crystal I: $a = 18.566$ (6), $b = 16.000$ (7), $c = 16.553$ (4) Å, $V_{\text{cell}} = 4917$ Å³, space group $P2_12_12_1$, $Z = 8$, $D_{\text{calc}} = 1.13$, $D_{\text{obs}} = 1.11$ g cm⁻³.

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Recently, Kanters *et al.* (1973) determined the absolute configuration of the compound I_a and obtained the following data.

Crystal I_a : (single-crystal Enraf–Nonius CAD-3 diffractometer with Cu $K\alpha$ radiation), $a = 9.774$, $b = 9.520$, $c = 8.447$ Å, $\alpha = 90.1$, $\beta = 114.4$, $\gamma = 117.5^\circ$, $V_{\text{cell}} = 617$ Å³, space group $P1$, $Z = 1$, $D_{\text{calc}} = 1.09$, $D_{\text{obs}} = 1.11$ g cm⁻³.

Discussion

In both the studies, samples of I_a were provided by Lanneau. For our study (Vidal *et al.*, 1970), it was very difficult to obtain good crystals, as these compounds are inclined to give either syrupy solutions or solid agglomerates. Different neutral solvents and different crystallization conditions were tried. The best results were obtained for the compound I_a with anhydrous heptane.

In the other study (Kanters *et al.*, 1973), the crystals of I_a were recrystallized from ethanol.

Lanneau had remarked that if the compound I_a was subjected to a quick crystallization (for example by using a warming plate gently), there was emission of very perceptible sparks with very audible sputterings. I think that if the crystallization conditions are poor space group $P1$ is obtained, but if the crystallization proceeds normally the higher-symmetry space group $P2_12_12_1$ is obtained.

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