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The Monoclinic Structure of Tetracyanoethylene* (TCNE), C_6N_4, at 5, 150 and 295 K; Powder Diffraction Analysis

BY S. L. CHAPLOT

*Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay-*400085, *India*

A. MIERZEJEWSKI

*I-*4, *Technical University of Wrocław, Wrocław, Poland*

AND G. S. PAWLEY†

*Department of Physics, University of Edingburgh, Kings Buildings, Edinburgh EH*9 3*JZ, Scotland*

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Abstract. $M_r = 128{\cdot}1$, monoclinic, $P2_1/n$, $\lambda = 1{\cdot}909$ Å. At 5 K: $a = 7{\cdot}3313$ (7), $b = 6{\cdot}1108$ (4), $c = 6{\cdot}9315$ (4) Å, $\beta = 97{\cdot}043$ (5)°, $V = 308{\cdot}19$ Å^3, $Z = 2$, $D_x = 1{\cdot}380$ Mg m^{-3}, $R = 7{\cdot}4\%$ for $10 < 2\theta < 154{\cdot}4°$. At 150 K: $a = 7{\cdot}3860$ (12), $b = 6{\cdot}1449$ (9), $c = 6{\cdot}9548$ (9) Å, $\beta = 97{\cdot}138$ (11)°, $V = 313{\cdot}2$ Å^3, $Z = 2$, $D_x = 1{\cdot}358$ Mg m^{-3}, $R = 10{\cdot}0\%$ for $12 < 2\theta < 160°$. At 295 K: $a = 7{\cdot}501$ (6), $b = 6{\cdot}218$ (5), $c = 7{\cdot}004$ (6) Å, $\beta = 97{\cdot}22$ (5)°, $V = 324{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}312$ Mg m^{-3}, $R = 8{\cdot}5\%$ for $12 < 2\theta < 100°$. Structure refinements were made using the *EDINP* program and neutron powder diffraction data obtained on the D1A machine at the Institute Laue–Langevin, Grenoble. The accuracy of the 295 K data is poor, but agrees with X-ray results. The lower-temperature results suggest that the bond lengths in this monoclinic phase do not differ significantly from those in the cubic phase and that the central C=C bond is not anomalously short.

Introduction. The work presented here is part of a research programme to study the intermolecular forces in TCNE by way of lattice-dynamical measurements. Detailed neutron inelastic-scattering results from the monoclinic form of TCNE have already been published by Chaplot, Mierzejewski, Pawley, Lefebvre & Luty (1983), and the success of this experimental work depended in good measure on the quality of the lattice-dynamical calculation which was used both in the planning stage and in the analysis of the experimental results. In the preliminary work at 5 K it was clear that there was a considerable discrepancy between measured phonon inelastic-scattering cross-sections and those calculated with the structure determined at room temperature by Bekoe & Trueblood (1960, 1964). Use of the best-known structure for cross-section calculation is very important, and as the variation of the structure with temperature was not known it was most expedient for us to investigate this behaviour and, in particular, determine the structure at 5 K, the temperature where the phonon measurements are the most resolved. For this work the appropriate quality of result is given by neutron powder diffraction – phonon measurements are never made near Bragg points of very high Miller indices and therefore the highest accuracy obtainable by single-crystal studies is unnecessary here.

In the work which follows measurements were made at 150 and 295 K in addition to the work at 5 K in order to follow the changes in structural parameters with temperature, and to give a check on the accuracy of the powder diffraction method by performing a comparison with the conventional single-crystal X-ray structure determination.

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* Ethylenetetracarbonitrile.

† To whom correspondence should be addressed.

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Experimental. Commercially available TCNE was purified by the method described by Samoć, Zboiński & Mierzejewski (1979). The material was powdered in an atmosphere of dry nitrogen to avoid decomposition which is caused by water vapour. The sample was then sealed in a cylindrical vanadium can.

D1A high-resolution powder diffractometer at the Institut Laue–Langevin (ILL), Grenoble; measurements made at 5, 150 and 295 K, neutron wavelength 1·909 Å, approximate 2θ range 10 to 160°, step size 0·05°.

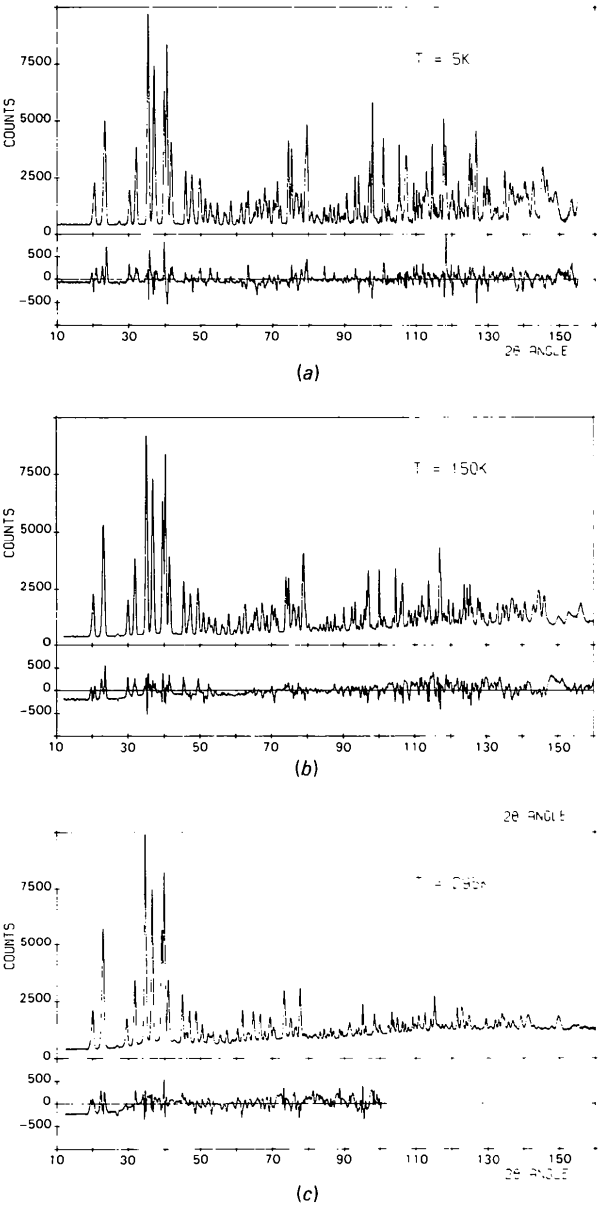

Fig. 1. The observed powder diffraction scans at the three temperatures, and the difference (observed – calculated) plotted on a different scale.

Table 1. *Final results for the three temperatures and a comparison with the results of Bekoe & Trueblood (B & T)*

		5 K	150 K	295 K	B & T
Scale factor		1·58 (3)	1·46 (4)	1·61 (12)	
Flat background		486 (16)	609 (21)	647 (40)	
Scan zero (°)		0·10 (1)	0·10 (1)	0·13 (3)	
Peak-shape parameters	u	0·17 (1)	0·20 (2)	0·90 (60)	
	v	−0·47 (3)	−0·46 (6)	−1·01 (69)	
	w	0·42 (2)	0·41 (3)	0·53 (17)	
Skewness		1·1 (2)	1·1 (2)	0·6 (3)	
Cell constants	a (Å)	7·3313 (7)	7·3860 (12)	7·501 (6)	7·51
	b (Å)	6·1108 (4)	6·1449 (9)	6·218 (5)	6·21
	c (Å)	6·9315 (4)	6·9548 (9)	7·004 (6)	7·00
	β (°)	97·043 (5)	97·138 (11)	97·22 (5)	97·17
C(1)	X	0·083 (13)	0·096 (21)	0·135 (80)	0·0974
	Y	−0·250 (12)	−0·233 (18)	−0·186 (76)	−0·2437
	Z	−0·636 (13)	−0·633 (20)	−0·652 (56)	−0·6017
	B	—	0·3 (3)	—	—
C(2)	X	0·822 (12)	0·823 (19)	0·901 (76)	0·8463
	Y	0·505 (12)	0·532 (22)	0·515 (94)	0·5172
	Z	−1·596 (13)	−1·552 (22)	−1·620 (89)	−1·5836
	B	—	0·6 (4)	—	—
C(3)	X	−0·423 (13)	−0·418 (22)	−0·429 (81)	−0·4378
	Y	−1·527 (13)	−1·528 (20)	−1·507 (82)	−1·5145
	Z	−1·015 (13)	−1·023 (21)	−1·010 (83)	−1·0180
	B	—	0·8 (4)	—	—
N(2)	X	1·393 (10)	1·402 (17)	1·445 (62)	1·4355
	Y	1·111 (9)	1·092 (15)	1·148 (67)	1·1041
	Z	−2·398 (9)	−2·387 (14)	−2·356 (66)	−2·3479
	B	—	0·8 (3)	—	—
N(3)	X	−0·838 (9)	−0·840 (15)	−0·836 (53)	−0·8624
	Y	−2·544 (9)	−2·529 (14)	−2·533 (62)	−2·5098
	Z	−1·337 (8)	−1·337 (13)	−1·280 (60)	−1·3432
	B	—	0·5 (3)	—	—
TO		0·16 (7)	—	—	—
Central C=C (Å)		1·38 (3)	1·36 (4)	1·38 (14)	1·317 (9)
Average C—C (Å)		1·43 (1)	1·42 (2)	1·45 (8)	1·449 (4)
Average C≡N (Å)		1·15 (1)	1·15 (2)	1·12 (7)	1·132 (5)

X, *Y*, *Z* are in orthogonal Å coordinates; *X* and *Y* are parallel to the crystal *x* and *y* axes respectively, and *Z* is parallel to z^*. *B* denotes individual isotropic temperature parameters (Å^2) and TO the overall isotropic temperature factor (Å^2). For 295 K, anisotropic temperature factors were refined but were not physically meaningful. The peak-shape parameters and skewness are defined by Rietveld (1969).

Results

The diffraction pattern obtained at 5 K shows a large number of well defined peaks above a flat background over the full range of the scan (see Fig. 1*a*), suggesting that thermal motion could be treated with an overall isotropic temperature factor in the refinement. This was not so clear in the case for the higher-temperature scans where the background variation and the loss of Bragg intensity is evident.

Structure refinements were made with the program *EDINP* (Pawley, 1980), using the structure parameters of Bekoe & Trueblood (1960) as initial values. No structural constraints were applied in any of the refinements so that in the cases where anisotropic temperature parameters were varied as many as 56 independent parameters were fitted to the data at the same time. Nevertheless, in most cases convergence was very fast and a stable *R* factor was achieved after only a few cycles. The *R* factors (see *Abstract*) are the percentage unweighted residuals calculated from all

Table 2. *Values from Hamilton's F distribution*

				Probability levels					Experimental *R* ratio
	NOBS	NPC	NP	0·25	0·10	0·05	0·01	0·001	
5 K TO/*B* (isotropic)	145	27	31	1·0228	1·0329	1·0401	1·0560	1·0784	1·003
5 K TO/*B* (anisotropic)	145	27	56	1·1800	1·2117	1·2326	1·2762	1·3323	1·152
150 K *B* (isotropic)/*B* (anisotropic)	148	31	56	1·1530	1·1817	1·2006	1·2402	1·2914	1·179

points in the scan, including those regions of pure background.

The experimental data used in the refinements have been deposited along with the calculated values obtained by using the parameters of Table 1.* Although the measurements had been taken at 0·05° intervals of 2θ it was found that this spacing was unnecessarily small and the data for refinements (and thus those deposited) were at 0·10° intervals only, there being no evident loss in final accuracy. The errors estimated by *EDINP* for the refined parameters are given in Table 1. These have been calculated using as the number of observations (NOBS) the total scan angle divided by the mean peak full width at half height. This is the value used in the *F*-distribution *R*-factor-ratio test suggested by Hamilton (1964), appropriate values of which are presented in Table 2 and have been calculated by the method of Pawley (1970).

The first test we performed was to find out whether the introduction of individual isotropic temperature factors gave a significant improvement over the refinement with an overall temperature factor for the 5 K data. The number of parameters in these two refinements was NP=31 and NPC=27 respectively, as the overall temperature factor refinement involves the constraint of the five temperature factors to one value. The *R*-factor ratio found was 1·003 and the values of Table 2 show the improvement on using the individual temperature parameters to be insignificant even at the 25% level. A similar test of a refinement with anisotropic temperature parameters showed no significant improvement, as the numbers in Table 2 show. The results presented in Table 1 are therefore calculated with the overall temperature parameter.

For the data at 150 K it was found that the isotropic temperature parameters gave a significant improvement, but the numbers in Table 2 show that the improvement on introducing anisotropic temperature parameters is significant only at the 25% level. Results for the isotropic refinement are therefore presented.

For the data at 295 K the anisotropic result was significantly the best, but as the parameter values were of dubious physical meaning they have not been recorded here. Furthermore, refinement using the full range of the scan proved unstable, and the range was therefore restricted to 10 to 100°. As a result the quality of the refined parameters is not high, giving much larger estimated errors for these parameters than are obtained for the lower-temperature refinements.

A comparison of our results at 295 K and those of Bekoe & Trueblood shows that although our results are poorer as expected at this temperature, the results agree within the estimated errors. We take this as support for our error-analysis procedure, giving credence to the errors quoted for the more accurate lower-temperature analyses. If the calculation of the errors had been based on a value of NOBS equal to the number of points in the scan, then our error estimates would have been much smaller and there would have been a serious discrepancy with Bekoe & Trueblood.

Discussion. The average mean bond lengths from this analysis are given in Table 1. Bekoe & Trueblood (1960) were concerned by the shortness of the central C=C double bond, but later work on the cubic form by Little, Pautler & Coppens (1971) suggests a value of 1·353 (3) Å when calculated using the higher-order reflections only, this being the appropriate calculation to compare with neutron scattering results. This is consistent with the mean over the 5 K and 150 K results of 1·37 (2) Å, suggesting that the Bekoe & Trueblood result is systematically too small. If this is so their C–C bond is likely to be too long, and again our result of 1·425 (9) Å is in good agreement with the high-angle cubic result of 1·432 (2) Å. The final comparison we make with the results of Little *et al.* is of the mean C≡N bond, where our 1·150 (9) Å compares with their 1·166 (2) Å. These comparisons suggest that there is no appreciable difference in the bond lengths between the two phases, but our results are not quite accurate enough to be able to determine the changes in bond angles due to the different strains within the structures of the two phases.

Although the results of this analysis are not as accurate as a single-crystal study would be they do give a reliable result at low temperatures. As the knowledge of the latter is essential for the phonon-dispersion

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* The numerical data corresponding to Fig. 1 and the calculated values have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39101 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

measurements, these results provide a basis for the calculations needed in this work.

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Inclusion Behavior of 2-Hydroxy-3,5-dinitro-*N'*-(5-nitrofurfurylidene)benzohydrazide, $C_{12}H_7N_5O_9$. Crystal Structures with Acetonitrile and Acetic Acid

By Israel Goldberg* and Zafra Stein

Department of Chemistry, Tel-Aviv University, 69978 *Ramat Aviv, Israel*

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Abstract. Acetonitrile (1:1) complex: $M_r = 406{\cdot}3$, monoclinic, $P2_1/c$, $a = 12{\cdot}977$ (2), $b = 8{\cdot}021$ (4), $c = 16{\cdot}830$ (3) Å, $\beta = 106{\cdot}95$ (1)°, $V = 1675{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}610$ g cm^{-3}, $F(000) = 832$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo } K\alpha) = 1{\cdot}5$ cm^{-1}, room temperature. Acetic acid (1:1) complex: $M_r = 425{\cdot}3$, triclinic, $P\bar{1}$, $a = 8{\cdot}665$ (1), $b = 8{\cdot}696$ (7), $c = 12{\cdot}077$ (2) Å, $\alpha = 90{\cdot}82$ (3), $\beta = 99{\cdot}82$ (1), $\gamma = 105{\cdot}15$ (3) Å, $V = 863{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}635$ g cm^{-3}, $F(000) = 436$, $\mu(\text{Mo } K\alpha) = 1{\cdot}6$ cm^{-1}, room temperature. The two structures were determined by a combination of direct and Fourier methods and refined to R values of respectively 0·048 and 0·052 for 2062 and 1690 observed reflections $[F_o^2 \geq 3\sigma(F_o^2)]$. The observed dense packing arrangements are dominated by characteristic dipole–dipole interactions between molecular entities located across crystallographic centers of symmetry. The solvent guest species are included in pseudo-channels formed between layers of the hydrazide molecules. Structural differences between the two compounds are mainly due to the different functionality of the solvent environments as revealed by observed hydrogen-bonding patterns. They reflect a considerable influence of the solvation forces on the host conformation, as a result of which polymorphic crystal-structure types are formed.

Introduction. Organic compounds containing polar surfaces frequently exhibit interesting inclusion properties upon crystallization from various environments, which are associated with the appearance of channels or cages within the crystal lattice (*e.g.* MacNicol, McKendrick & Wilson, 1978). Such phenomena of co-crystallization with other species into a multicomponent system, which can be directly related to the energetics of intermolecular interactions, are even more pronounced when the polar substituents act also as good donors or acceptors of hydrogen bonds. The crystal packing of dipolar species is usually stabilized by a combination of attractive and repulsive forces. However, an optimized accommodation of all interactions in the solid structure may not always be consistent with an efficient packing of the molecular entities (particularly those characterized by an irregular shape), inducing in such case voids within the host lattice. To achieve a thermally stable crystal this space must be filled by another (guest) component with complementary geometric and functional properties, requirements often giving rise to selective molecular complexations (*e.g.* Iwamoto, 1979). In inclusion structures with imperfect geometric relationships and lacking specific bindings between the complex constituents the guest species are either disordered or thermally smeared within the rigid host lattice (Allcock, Allen, Bissell, Smeltz & Teeter, 1976; Goldberg, 1982). Solvation

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* To whom correspondence should be addressed.

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