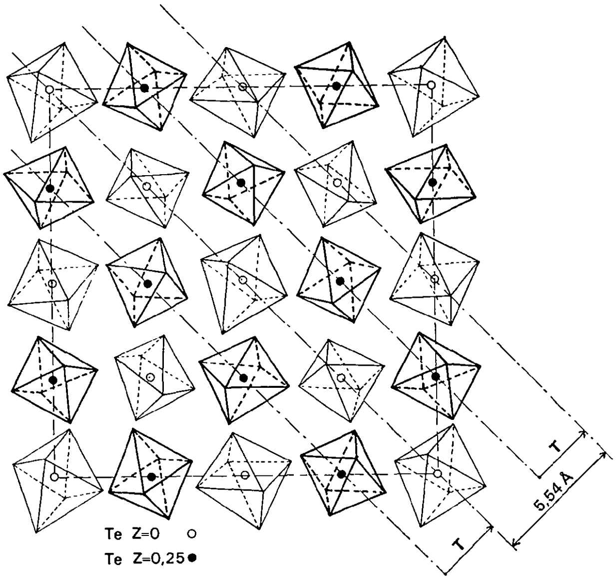

Fig. 7. $Te(OH)_6$ cubique. La translation T montre le déplacement des octaèdres permettant une comparaison avec la structure de H_2TeO_4.

On peut alors proposer un mécanisme formel de transformation de l'acide orthotellurique $Te(OH)_6$ en acide métatellurique H_2TeO_4. Celui-ci consiste en une condensation de deux plans successifs dans les arrangements structuraux de $Te(OH)_6$ aussi bien monoclinique que cubique. Le léger déplacement nécessaire des octaèdres d'une couche par rapport à l'autre, perpendiculairement à la couche, est suivi de la perte de molécules d'eau en engendrant les couches $[Te(VI)O_2(OH)_2]_n$ rencontrées dans H_2TeO_4. Voir Figs. 6, 7 (position des flèches T).

Signalons que la déshydratation ultérieure de H_2TeO_4 conduit à une mise en commun de tous les oxygènes des octaèdres avec élimination d'une molécule d'eau et formation de TeO_3 dont la structure est isotype de PdF_3.

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The Crystal Structure of Tetracyanomethane, $C(CN)_4$

By Doyle Britton

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, *U.S.A.*

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Tetracyanomethane is trigonal with hexagonal axes $a = 9{\cdot}062$ (2) and $c = 11{\cdot}625$ (3) Å; $Z = 6$, space group *R3c*. Least-squares refinement of diffractometer data converged at a conventional R value of 0·046. The molecule has full tetrahedral symmetry within experimental error with average bond lengths: C–C, 1·481 (3), corrected 1·488 Å; C≡N, 1·147 (5), corrected 1·168 Å. The structure is a trigonal distortion of the cubic SiF_4 structure. One nitrogen atoms points directly at the central carbon atom of an adjacent molecule with a N···C (in CN) distance of 3·05 Å. The remaining three (equivalent) nitrogen atoms point approximately at the central carbon atoms of three adjacent molecules with N···C (in CN) distances of 3·00, 3·10, and 3·19 Å. These short distances are regarded as evidence of donor–acceptor interactions.

Introduction

Tetracyanomethane, $C(CN)_4$, has recently been prepared by Mayer (1969). The vibrational spectra (Hester, Lee & Mayer, 1970) show the molecule to have the expected $\bar{4}3m$ (T_d) symmetry. This is confirmed by the electron diffraction measurements on the gaseous molecule (Oberhammer, 1971), which also give the bond lengths: C–C, 1·484 (5); C≡N, 1·161 (3) Å.

The crystal structure of $CH_3C(CN)_3$ (Witt, Britton & Mahon, 1972) shows short intermolecular distances (3·09 and 3·11 Å) between nitrogen atoms on one molecule and the cyanide carbon atoms on the next molecule in such a way that weakly associated trimers can be identified. We have determined the crystal structure of $C(CN)_4$ to see whether similar short intermolecular contacts occur.

Experimental

A sample of $C(CN)_4$ supplied by Dr E. Mayer was resublimed to provide crystals suitable for X-ray diffraction studies. A rotation photograph provided by Dr Mayer and Dr E. Schnell of the University of Innsbruck could be indexed on a hexagonal unit cell with dimensions close to those given below. The picture showed systematic extinctions (hkl, $-h+k+l \neq 3n$; $h\bar{h}l$, $l \neq 2n$), which were later confirmed by the diffractometer data, that indicate the space group to be $R3c$ or $R\bar{3}c$. A test for pyroelectricity [test (*a*), Bunn (1961)] was positive, indicating $R3c$ to be the correct choice; this was confirmed by the eventual solution of the structure. A thick prism, approximately 0·6 × 0·6 × 1·0 mm, elongated along **c**, was mounted in a glass capillary and imbedded in Apiezon L grease to prevent sublimation. Data were collected at room temperature with a four-circle Hilger and Watts automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The cell dimensions, determined from the least-squares mean of eight crystallographically independent planes, are $a = 9{\cdot}062$ (2), $c = 11{\cdot}635$ (3) Å. For six molecules per unit cell the molecular volume is 137·8 (1) Å^3, which is consistent with the molecular volume of $CH_3C(CN)_3$, 150 Å^3; the calculated density is 1·399 (1) g cm^{-3}.

Intensity data were collected for 1598 reflections comprising one hemisphere of reciprocal space out to $\theta = 30°$. A moving-crystal moving-detector scan was used with one hundred 0·01° steps in θ and ω; 1 s step times were used, with 50 s background counts at each end of the scan. The intensities of two check reflections were measured every 25 reflections; there was no trend with time for these check reflections; the estimated standard deviation from the mean was about 1·5%. The equivalent reflections were combined and standard deviations estimated in the following way. Let P_i, B_i, I_i, and $\sigma_1(I_i)$ be the integrated peak count, the background count, the intensity, and the standard deviation of the intensity, respectively, of a single reflection. Then $I_i = P_i - B_i$, and we shall define $\sigma_1(I_i)$ to be given by $\sigma_1^2(I_i) = P_i + B_i + (0{\cdot}04I_i)^2$. Let n, I, $\sigma_1(I)$, and $\sigma_2(I)$ be the number of equivalent reflections being averaged, the average intensity, the standard deviation of the average intensity estimated by combining all the data, and the standard deviation of the average intensity estimated from the variation in the set of equivalent I_i's. Then $I = (\sum I_i)/n$, $\sigma_1^2(I) = (\sum P_i + \sum B_i)/n^2 + (0{\cdot}04I)^2$, and $\sigma_2^2(I) = [\sum (I - I_i)^2]/n(n-1)$.* I, $\sigma_1(I)$, and $\sigma_2(I)$ were calculated for each of the 272 independent reflections included in the original list and the larger of $\sigma_1(I)$ and $\sigma_2(I)$ was assigned as $\sigma(I)$ to be used in the subsequent calculations. The result that $\sigma_1(I) > \sigma_2(I)$ for 170 reflections and $\sigma_1(I) < \sigma_2(I)$ for 102 reflections indicates that the two methods of estimating $\sigma(I)$ were in reasonable agreement. Lorentz and polarization corrections were made. The average value of $\sigma(F)/F$ was 0·039. No reflections were omitted from the subsequent refinement of the structure.

Solution and refinement

The space group requires that the molecule lie on a threefold crystallographic axis; the z coordinate of the central carbon atom was arbitrarily chosen as 0. The approximate coordinates of the other atoms were calculated from the known molecular geometry plus packing considerations. Four cycles of full-matrix least-squares refinement (using program *UMLSTSQ* by L. W. Finger) with isotropic thermal parameters reduced R to 0·074. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$. The numerator of r was the function minimized. The unmodified weights were $1/[\sigma(F^2)]^2$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). No anomalous dispersion corrections were made. Anisotropic thermal parameters were then introduced and refined, with convergence at $r = 0{\cdot}0082$, $R = 0{\cdot}046$. The parameters resulting from this refinement are given in Table 1.†

It has been shown in a number of cases that the positional parameters determined from X-ray diffraction data by least-squares refinement using statistical weights can disagree significantly with the positional parameters determined from neutron-diffraction data since the latter find the nuclear position and the former find the centroid of the electron density for each atom. Recently several methods have been proposed to find the nuclear positions from the X-ray diffraction data. All of these methods utilize the fact that as $(\sin\theta)/\lambda$ increases the relative importance of the inner electrons in the scattering increases. Coppens (1971) has suggested refining the positions of the K and L electron shells separately (the double-atom refine-

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* If the I_i and $\sigma_1(I_i)$ were regarded as independent measurements of the same observable, then the second term in the $\sigma_1^2(I)$ equation should be approximately $(0{\cdot}04I)^2/n$. However, our previous experience has been that this will give a too optimistic estimate of $\sigma^2(I)$. The expression used corresponds to combining all the data as if they were a single measurement and then rescaling by n. n ranged from 1 to 17 but was 6 more often than not.

† A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30404 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England or from the author.

ment). Dunitz & Seiler (1973) have suggested using a weighting scheme similar to that used to produce sharpened Patterson and Fourier maps and then refining in the usual way. Most simply, perhaps, several authors have suggested using only the high-angle data for refinement. Little, Pautler & Coppens (1971) showed for tetracyanoethylene that the refinement of only the high-angle data gave the same intramolecular distances, within experimental error, as the double-atom refinement. In order to compare our results with the results of the gas-phase electron-diffraction experiments, we have refined our data in alternative ways. The Dunitz & Seiler scheme replaces the statistical weight, w, by $w\exp(2B'\sin^2\theta/\lambda^2)$.* We have carried out the refinement using B' values of 5, 10, and 15, as well as using only the 142 reflections with $(\sin\theta)/\lambda > 0{\cdot}55$ with $B'=0$.

Results

The intramolecular distances and angles determined in the various refinements are given in Table 2. The special weights all have the effect of decreasing the C–C distances, and increasing the C≡N distances. The angles are not significantly different from those for a regular tetrahedral molecule in any of the refinements. Within experimental error the refinements with B' equal to 10 and 15 and the refinement of the high-angle data alone give the same final parameters. The result of all three is to give C–C distances that agree with the electron-diffraction results but C≡N distances that are shorter by about 0·015 Å. A model with the cyanide nitrogen atoms riding on the cyanide carbon atoms seems reasonable and corrections were made on this basis for two of the sets of data (Busing & Levy, 1964). All of the corrected distances are longer than the corresponding electron diffraction values although not by a significant amount. Becker, Coppens & Ross (1973) have found that in cubic tetracyanoethylene the C≡N bond length determined from core refinement is greater than that determined from neutron diffraction in the solid or electron diffraction in the gas.

The packing and the intermolecular distances (from the first refinement in Table 2) are shown in Fig. 1. The structure is clearly related to that of SiF_4, which has SiF_4 molecules at the corners and body center of a cubic cell so that each Si–F bond points directly toward the silicon atom in an adjacent molecule (Natta, 1930; Atoji & Lipscomb, 1954). If the $C(CN)_4$ molecules were rotated around the crystallographic threefold axis by about 20° so that the three cyanide groups pointed directly at the central carbon atoms that are 3·26 Å away (see Fig. 1), and all of the central-carbon-atom to central-carbon-atom distances were made equal to 5·812 Å ($=c/2$), then the structure would become cubic and exactly correspond to that of SiF_4.

Table 1. *Positional and thermal parameters*

Anisotropic temperature factors are of the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots)]$. Estimated standard deviations for the final significant figures are given in parentheses. The positional parameters are multiplied by 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(0)	0	0	0	2·15 (5)	2·15 (5)	2·17 (10)	1·07 (3)	0	0
C(1)	0	0	1275 (4)	2·54 (6)	2·54 (6)	2·71 (14)	1·27 (3)	0	0
N(1)	0	0	2250 (4)	4·65 (10)	4·65 (10)	2·59 (15)	2·33 (5)	0	0
C(2)	1660 (2)	1412 (2)	−425 (3)	2·46 (6)	2·52 (6)	2·71 (6)	1·27 (5)	0·15 (5)	−0·20 (5)
N(2)	2927 (2)	2481 (3)	−738 (3)	2·98 (7)	3·29 (7)	4·55 (10)	1·18 (6)	0·91 (7)	0·15 (7)

Table 2. *Intramolecular distances and angles*

Estimated standard deviations are in parentheses.

	Crystal data							Gas phase*
$\sin\theta/\lambda$	0·00–0·70						0·55–0·70	
B'†	0		5	10	15		0	
Correction‡	no	yes	no	no	no	yes	no	
C(0)–C(1)	1·482 (4) Å	1·485 Å	1·483 (4) Å	1·482 (4) Å	1·482 (4) Å	1·489 Å	1·478 (5) Å	1·484 (5) Å
C(0)–C(2)	1·490 (2)	1·495	1·485 (2)	1·481 (2)	1·480 (2)	1·488	1·482 (3)	
C(1)–N(1)	1·134 (6)	1·158	1·140 (6)	1·143 (7)	1·144 (7)	1·168	1·142 (7)	1·161 (3)
C(2)–N(2)	1·130 (3)	1·149	1·141 (4)	1·146 (4)	1·148 (4)	1·168	1·147 (4)	
C(1)–C(0)–C(2)	109·4 (2)°		109·4 (2)°	109·4 (2)°	109·3 (3)°		109·5 (3)°	(109·47°)
C(2)–C(0)–C(2′)	109·6 (2)		109·6 (2)	109·6 (2)	109·6 (3)		109·5 (3)	
C(0)–C(1)–N(1)	180		180	180	180		180	(180)
C(0)–C(2)–N(2)	174·9 (3)		179·2 (3)	179·1 (3)	178·9 (4)		179·1 (4)	
r	0·0082		0·0080	0·0073	0·0067		0·0057	
R	0·0459		0·0493	0·0521	0·0550		0·0555	

* Oberhammer (1971).

† See text and Dunitz & Seiler (1973).

‡ Distances corrected for riding motion. See text and Busing & Levy (1964).

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* This expression differs from that of Dunitz & Seiler by a factor of 2 in the exponent since we are refining on F^2 and they are refining on F.

However, this would increase the molecular volume by 9·7% and the average linear dimensions by 3·1%.

The SiF_4 structure at first glance seems unlikely. Indeed, Wyckoff (1948) has said of the results of Natta (1930), 'A cubic structure ... has been suggested for solid SiF_4 at -170°C. This and the atomic arrangement proposed for it are most certainly wrong.' However, Atoji & Lipscomb (1954) verified the results of Natta (1930), and Bent (1968) suggested that the explanation lay in the occurrence of donor–acceptor F···Si bonds between adjacent molecules.

Tetracyanomethane occurs in essentially the same structure for essentially the same reason, except that the acid site is not localized on the central atom but involves the three adjacent cyanide carbon atoms as well. The distortion away from cubic symmetry makes the interaction of the nitrogen atom (at three of the four nitrogen atoms) with the four carbon atoms less symmetric, but not especially weaker; the three N···C distances of 3·05 Å that occur in the interaction parallel to the *c* axis become 3·00, 3·10, and 3·19 Å at the three remaining nitrogen atoms. The distortion presumably arises from the generally improved van der Waals interactions that are possible in the more compact trigonal structure. In particular, it does not appear that the symmetry of the molecular orbitals involved in the donor–acceptor bonding requires a lowering of the local symmetry from tetrahedral to trigonal. The N···C distances in this crystal structure should be compared with the distances of 3·09 and 3·11 Å in $CH_3C(CN)_3$ (Witt, Britton & Mahon, 1972).

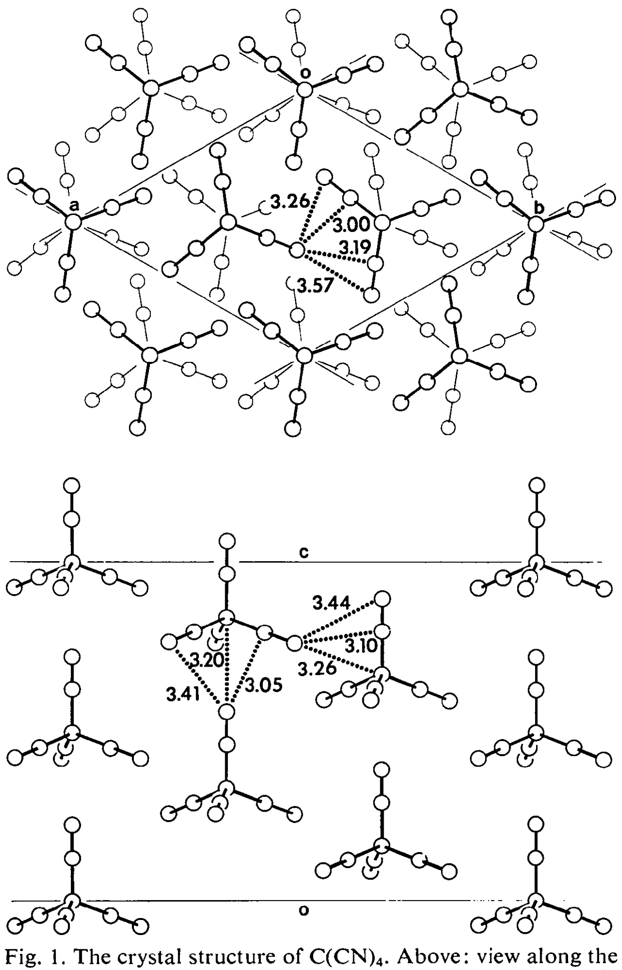

Fig. 1. The crystal structure of $C(CN)_4$. Above: view along the *c* axis. Below: view perpendicular to the (110) plane. Only the central row of molecules in the top figure is shown in the bottom figure. Interatomic distances are given in Å.

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