

with  $R=0.014$ . These  $B$  values are very significantly different from those in Table 10. These results suggest that identification of low  $R$  factors with the absence of systematic error can be highly misleading.

It is a pleasure to thank Miss B. B. Cetlin for assistance with all the PEXRAD programs, Dr R. D. Burbank for valuable discussions on intensity measurement and Dr W. C. Hamilton and Dr C. L. Mallows for penetrating comment and suggestions on statistical matters.

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## The Crystal and Molecular Structure of 7,7,8,8-Tetracyanoquinodimethane\*

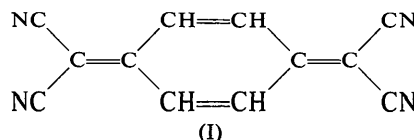
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TCNQ forms orange-red monoclinic crystals belonging to space group  $C2/c$ , with  $a_0 = 8.906$ ,  $b_0 = 7.060$ ,  $c_0 = 16.395$  Å,  $\beta = 98.54^\circ$ , and four centrosymmetric molecules in the unit cell. The structure was solved by conventional Patterson methods and independently by a computer search of possible structures consistent with reasonable molecular packing. It was refined by full-matrix least-squares methods. The molecule, which has essentially  $mmm$  symmetry, librates through a r.m.s. amplitude of about  $5.5^\circ$  about its long axis. The bond distances are in good accord with the predictions of simple molecular orbital theory.

Tetracyanoquinodimethane (I) (TCNQ) is one of a series of novel cyano-olefins prepared in recent years (Cairns *et al.*, 1958; Acker & Hertler, 1962), and is of especial interest not only because it forms unusually stable molecular complexes containing the radical anions  $TCNQ^-$  and  $(TCNQ)_2^-$ , but also because some of these crystalline complexes are semi-conductors and show other unusual solid-state properties (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962).



The present study of the detailed molecular geometry and packing of TCNQ in the pure crystalline state was undertaken partly because of the intrinsic interest of the molecule itself and partly to provide a standard for comparison for proposed studies of some of the complexes containing the aforementioned radical anions.

### Experimental

Orange-red chunky crystals of TCNQ which had been purified by sublimation were supplied to us by R. E.

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Merrifield. Weissenberg photographs with unfiltered Cu  $K\alpha$  radiation confirmed the conclusion by Paul Arthur, Jr. (private communication, 1962), that the crystals belong to space group  $Cc$  or  $C2/c$  (systematic absences:  $hkl$  with  $(h+k)$  odd,  $h0l$  with  $l$  odd). The unit-cell dimensions were measured by comparison with  $hk0$  reflections from a quartz crystal [ $a_0=4.9131 \text{ \AA}$ ,  $\lambda(\text{Cu } K\alpha)=1.5418 \text{ \AA}$ ,  $\lambda(\text{Cu } K\alpha_1)=1.5405 \text{ \AA}$ ] recorded on the same film; the best fit to the experimental observations on the zero level and the third level about  $[110]$  was obtained with unpublished least-squares programs written by R. A. Sparks and P. K. Gantzel. These values, with their e.s.d.'s are:  $a_0=8.906 \pm 0.006 \text{ \AA}$ ,  $b_0=7.060 \pm 0.004 \text{ \AA}$ ,  $c_0=16.395 \pm 0.005 \text{ \AA}$ ,  $\beta=98.54 \pm 0.04^\circ$ . The observed density is  $1.315 \text{ g.cm}^{-3}$  (Arthur, 1962); that calculated for four molecules of TCNQ,  $\text{C}_{12}\text{H}_4\text{N}_4$ , per unit cell is 1.329.

Integrated Weissenberg intensity data were collected with Cu  $K\alpha$  radiation from a crystal mounted about  $[110]$ ; six layers were accessible, permitting 1120 independent values of  $F^2$  to be estimated, including 144 which were too weak to be observed. This corresponds to approximately 91% of the Cu  $K\alpha$  sphere. The data were estimated chiefly with a microdensitometer (Baird Atomic Model CB), although some of the weaker ones were estimated visually. Approximately 2400 measurements of  $F_{\text{obs}}^2$  were made, and they were correlated to obtain the unique values by means of a least-squares program written by R. A. Sparks and based on the method of Rollett & Sparks (1960). Because the full translation range had been recorded for each layer of this monoclinic crystal mounted about  $[110]$ , it was possible to perform this layer correlation without precession photographs or photographs about another axis, inasmuch as symmetry-equivalent reflexions occurred on different layers. The average percentage discrepancy from the mean  $F^2$  for those reflexions measured more than once was about 10%.

The crystal used for intensity measurements was a small rectangular parallelepiped, whose minimum thickness was 0.16 mm and maximum thickness 0.28 mm. The absorption coefficient for Cu  $K\alpha$  is about  $6.7 \text{ cm}^{-1}$ ; the corresponding maximum error in relative values of the structure factors because of absorption is about 7%, and of course the average error is considerably smaller than this. No corrections for absorption were made. The atomic scattering factors used were those of McWeeny (1954) for graphite carbon, Hoerni & Ibers (1954) for nitrogen, and the exact quantum mechanical results quoted in *International Tables for X-ray Crystallography* (1962) for hydrogen.

All calculations were made on IBM 7090 and 7094 computers with programs written in this laboratory.

#### Determination and refinement of the structure

Because the molecule was presumed to be planar and centrosymmetric, and because there are just four molecules in the unit cell, it seemed likely that the

space group was the centrosymmetric one,  $C2/c$ , rather than  $Cc$ , and thus that the molecules were centered either at  $(0, 0, 0)$  or at  $(\frac{1}{2}, \frac{1}{2}, 0)$ , these being the two unique centers of symmetry in  $C2/c$ . The bond vectors in a planar TNCQ molecule form a very simple pattern because there are essentially only three bond directions in a given molecule, the  $\text{C}-\text{C}\equiv\text{N}$  directions being nearly parallel to the inclined sides of the quinone ring. A three-dimensional Patterson distribution was calculated, with the use of a variation of the Schomaker & Shoemaker modification function (Lipson & Cochran, 1953) which included an anisotropic 'temperature factor', whose coefficients were adjusted so that at the origin not only the Patterson function but also its second derivatives with respect to  $u$ ,  $v$ ,  $w$ , and the cross-term in  $uw$  vanish (R. A. Sparks, unpublished). Comparison of the region within about  $3 \text{ \AA}$  of the origin in this map rather quickly yielded a plausible fit with a model centered at  $(0, 0, 0)$ ; the corresponding molecular orientation centered at  $(\frac{1}{2}, \frac{1}{2}, 0)$  gave impossibly close intermolecular contacts.

A second and independent approach to solving the structure was made with a computer-search technique to generate possible structures systematically, rejecting those which gave too close packing contacts, and discriminating among those remaining by comparing a selected set of observed and calculated structure factors. This technique was remarkably successful, giving the correct structure in about 12 minutes of 7090 time; it has since also been used successfully in the analysis of the structure of a novel heteroaromatic, dibenzotetraazapentalene (Burke, Sparks & Trueblood, 1963).

The procedure used was the following. A model was assumed for the TCNQ molecule with reasonable bond distances and angles ( $\text{C}=\text{C}$ ,  $1.32 \text{ \AA}$ ;  $\text{C}-\text{C}$ ,  $1.45 \text{ \AA}$ ;  $\text{C}\equiv\text{N}$ ,  $1.15 \text{ \AA}$ ;  $\text{C}-\text{C}\equiv\text{N}$  linear, all other bond angles  $120^\circ$ ) and the entire molecule planar; the hydrogen atoms were ignored. Then a systematic examination of different possible orientations of this model about each of the two unique centers of symmetry was made and all models which gave intermolecular distances smaller than  $3.0 \text{ \AA}$  were rejected. For each origin, it was necessary to consider only two possible sets of structures, those with the major axis of the TCNQ molecule lying in the  $(+++)$  octant, *i.e.*, with all positive values of  $x$ ,  $y$ , and  $z$ , and those with the major axis lying in the  $(-++)$  octant. In each octant the major axis was directed in turn toward each of 325 points in an equilateral triangular grid mapped onto the spherical triangle determined by the octant, and for each of these settings of the major axis, successive rotational positions of the molecule about its major axis in steps of  $3^\circ$  were considered. Because the major axis is a twofold axis for the molecule, it was necessary to step only through  $180^\circ$ .

Calculation of intermolecular contacts for these 78,000 possible trial structures required ten minutes of 7090 time; only 57 acceptable structures were found, and these fell into only six different classes, that is,

most differed only by one rotational step or one grid point from another acceptable solution. About two additional minutes of computer time was required to evaluate all of these structures; the criterion used was the discrepancy index,  $R$ , calculated for the 278 observed and unobserved reflexions with  $\sin \theta/\lambda$  less than 0.4. The scale factor was normalized for each structure so that the sums of the observed and calculated structure factors were identical. The average of  $R$  for the 57 acceptable structures was 0.71, not far below the value 0.83 expected for a random centrosymmetric structure (Wilson, 1950), and of course this average includes several structures close to the correct one.

Six of the acceptable structures gave  $R$  values below 0.50, but actually all of these six represented minor variations on just one solution. The structure with the lowest  $R$  (0.33) was essentially the same as that found by examination of the Patterson distribution, the average discrepancy in atomic position parameters being about 0.2 Å. Preliminary least-squares refinement of these two structures was carried out separately as an experiment to check that they would indeed converge to the same point; as with all of the other least-squares calculations here, this was done with a modified version of ACA program 317 (Gantzel, Sparks & Trueblood, unpublished), which minimizes  $\sum w(|F_o| - k|F_c|)^2$ . Only the 278 low-order reflections were used, and the scale factor and temperature factor were kept constant, the latter at 3.32 Å<sup>2</sup>; the unobserved reflections were evaluated at  $F_{\min}/\sqrt{3}$  (Hamilton, 1955). After five cycles of refinement,  $R$  for each structure was 0.17, and the average discrepancy in atomic positions was now only 0.03 Å, with a maximum discrepancy of 0.07 Å. It seemed clear that the refinements were converging to a common solution.

Refinement was now continued with the complete set of data; variation in an overall scale factor and individual anisotropic temperature factors was permitted. The Hughes (1941) weighting scheme was used. After four cycles,  $R$  had decreased to 0.102; the average shift in a positional parameter was 0.02 Å. At this juncture a three-dimensional difference Fourier synthesis was calculated. The unique portion of this map showed two, and only two, distinct maxima, of heights 0.57 and 0.68 e.Å<sup>-3</sup>, within 0.1 Å of the positions expected for the two unique hydrogen atoms in the molecule. The next highest peak in the map was 0.24 e.Å<sup>-3</sup>, and the lowest minimum was -0.30 e.Å<sup>-3</sup>; these fluctuations are not considered significant.

A final set of least-squares calculations was now done, with a total of 81 parameters, nine for each of the eight 'heavy' atoms, four (including an isotropic temperature factor) for each of the two hydrogen atoms, and an overall scale factor. The seven strongest reflections, which apparently suffered from extinction, were omitted. Three different weighting schemes were tried: first, that of Hughes (1941), with  $1/w=0.8$  for  $F_o \leq 4.0$ , and  $1/w=3.2/F_o$  for  $F_o > 4.0$ ; second, a scheme which gave less weight to the weakest reflections,  $1/w=$

$0.4 \sqrt{F_o}$  for  $1/F_o \leq 4.0$ , and  $1/w=3.2/F_o$  for  $F_o > 4.0$ ; and third, individual weights,  $1/w=1/\sigma(F_o)$ , where  $\sigma(F_o)$  is the e.s.d. of  $F_o$  calculated by the scaling program. The shifts in the last cycles of each series were negligible with respect to the e.s.d.'s. The value of  $[\sum w(\Delta F)^2/(m-n)]^{1/2}$  for the last cycle of least squares for the third weighting scheme was 2.21; thus on the average  $\sigma(F_o)$  estimated by the scaling program appeared low by a factor of two. The resulting sets of parameters for the three weighting schemes were compared using the  $\chi^2$  test and for all comparisons the significance level was greater than 0.998; thus there was no significant difference in the results of these refinements and those from the first weighting scheme were used thereafter. The final structure factors are listed in Table 1. The final value of  $R$  was 0.086 including all reflections, 0.081 including observed reflections only, and 0.071 if the seven strongest (marked E in Table 1) are also omitted. The value of  $F_o$  listed for the unobserved reflections (marked U in Table 1) is  $F_{\min}/\sqrt{3}$ , which is the value that was used in the least-squares refinement.

As a check, a three-dimensional difference Fourier synthesis was calculated with all atoms removed. The highest peak was 0.26 e.Å<sup>-3</sup>, and the lowest minimum was -0.29 e.Å<sup>-3</sup>; these fluctuations are not considered significant, since the e.s.d. of the electron density is 0.12 e.Å<sup>-3</sup>.

The anisotropic thermal parameters of the 16 'heavy' atoms of the molecule (Table 2) were used in an analysis of the rigid-body translational and librational motion (Cruickshank, 1956, 1961), with the results shown in Table 3. The fit is fairly good, although as expected from the analysis of tetracyanoethylene (Bekoe & Trueblood, 1960) the fit for the cyano groups is not as good as for the other atoms because they are, presumably, undergoing appreciable 'wagging' motion. Even when these atoms are included, the r.m.s. value of the percentage discrepancy between the observed and derived  $U_{ii}$  (Table 3) is only 5.8; however, when only the eight atoms of the hydrocarbon skeleton are considered, it is about 3%. The overall translational motion indicated by this analysis is not markedly anisotropic. However, the r.m.s. librational amplitude of the molecule about one principal axis, which very nearly coincides (within 3°) with the long axis of the molecule, axis  $A$  of Table 7, is more than twice that about the other two principal axes. These other two axes each lie within about 10° of the natural molecular axes of Table 7. Because of the anisotropy of this librational motion, the corrections for librational motion are much smaller for bonds parallel to the long axis of the molecule, e.g., C(1)-C(2') and C(3)-C(4), than for the others, but the largest such correction indicated by this analysis is 0.006 Å. Because of the presumed wagging motion of the cyano groups, it seems likely that corrections of at least 0.01 Å, and probably more, should be applied to the C-N bonds, as in tetracyanoethylene (Bekoe & Trueblood, 1960). The uncorrected values of the individual atomic positional

Table 1. Observed and calculated structure factors

Table with multiple columns containing numerical data for observed and calculated structure factors. The table is organized into several sections, each with a header indicating the type of structure factor (e.g., H, K, L, M, N, O, P, Q, R, S, T, U, V, W, X, Y, Z) and the corresponding values. The data is presented in a grid-like format with varying column widths.

The running index is I. F\_0 values marked with E are suspected of having been diminished by secondary extinction. Those marked with U were below the minimum observable intensity; the F\_0 listed is 0.58 F\_min.

parameters which resulted from the least-squares refinement, and the values corrected for libration, together with the standard deviations estimated from the inverse of the matrix of the normal equations, are given in Table 4. Since the corrections for apparent motion resulting from libration are themselves subject to significant uncertainty, the listed e.s.d.'s which are postulated upon the existence of only random and not systematic errors, are somewhat underestimated. We have arbitrarily assumed in estimating the precision of the bond distances and angles that the librational corrections may be in error by as much as 50%; since these corrections were in fact small, amounting to no more than 0.006 Å, and to less than 0.2°, the increases in the e.s.d.'s as a result of this allowance were small.

### The molecular structure

The intramolecular bond distances and angles in the TCNQ molecule are illustrated in Fig. 1 and summarized in Table 5, along with their e.s.d.'s. The molecule has essentially *mmm* symmetry, although the only symmetry required by the space group is  $\bar{1}$ . The  $\chi^2$  test indicates that there is no significant difference in the bond lengths and angles which are chemically equivalent but not crystallographically equivalent.

A comparison of the bond lengths with those predicted by Hückel molecular orbital calculations is given in Table 6. The values used for the resonance integrals

Table 2. *Final thermal parameters and their estimated standard deviations\**

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	1063 25	1898 40	276 7	148 44	313 19	-77 24
C(2)	928 23	1874 39	298 7	365 43	325 19	9 24
C(3)	1016 25	1578 36	278 7	103 41	260 19	46 22
C(4)	1071 25	1717 38	289 7	64 43	198 19	105 23
C(5)	1197 27	2126 46	301 7	-91 51	111 20	-97 27
C(6)	1026 26	2151 45	329 8	-64 47	83 20	35 26
N(1)	1853 36	3149 58	376 8	-71 63	193 25	-513 32
N(2)	1089 26	3654 63	486 10	-74 58	213 23	-53 36
	Atom		$B$			
	H(1)		3.3			
			0.6			
	H(2)		2.4			
			0.5			

\* Anisotropic values  $\times 10^5$ ; isotropic in Å<sup>2</sup>. The number below each parameter is its e.s.d.

Table 3. *Rigid-body thermal parameters*

(For the molecule centered at the origin)

$$T\ddagger = \begin{pmatrix} 363 & 31 & 58 \\ & 360 & 22 \\ & & 353 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$$

$$\omega\ddagger = \begin{pmatrix} 138 & 48 & 129 \\ & 56 & 33 \\ & & 170 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

$$\sigma(T) = \begin{pmatrix} 7 & 7 & 6 \\ & 9 & 7 \\ & & 7 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$$

$$\sigma(\omega) = \begin{pmatrix} 6 & 5 & 9 \\ & 3 & 4 \\ & & 7 \end{pmatrix} \times 10^{-1} (^\circ)^2$$

Principal axes: Eigenvalue	Direction cosines ( $\times 10^4$ ) relative to			Eigenvalue	Direction cosines ( $\times 10^4$ ) relative to		
	a	b	c*		a	b	c*
T 0.0435 Å <sup>2</sup>	-6679	-4521	-5913	$\omega$ 29.7 (°) <sup>2</sup>	6539	2270	7218
0.0342	-2659	8869	-3778	5.0	2111	8612	-4623
0.0299	-6952	0951	7125	1.6	7266	-4546	-5152

$U_{ij}(\text{Å}^2) \times 10^4 \ddagger$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	401	479	367	27	59	-22
	11	0	-10	-17	-4	4
C(2)	346	473	396	58	59	3
	-19	-16	3	17	-2	16
C(3)	388	399	371	14	39	13
	8	25	7	-8	-6	-12
C(4)	417	433	385	6	15	30
	-11	20	-9	9	5	-3
C(5)	478	537	400	-10	-20	-28
	-68	-1	-6	-6	-11	7
C(6)	413	543	438	-12	-35	10
	-1	-44	-54	4	-16	-23
N(1)	735	795	501	11	-5	-149
	54	-3	51	-1	13	10
N(2)	429	923	647	-9	-19	-15
	25	19	17	2	21	1

† Referred to the directions of the orthogonal axes a, b, c\*.

‡ Numbers below  $U_{ij}$  are differences ( $\times 10^4$ ) of  $U_{ij}$  derived from  $B_{ij}$  and those calculated from rigid-body parameters. The r.m.s. difference is 0.0021 Å<sup>2</sup>.

Table 4. Final position parameters and their estimated standard deviations\*

Atom	From final least squares*			After correction for libration		
	x	y	z	x	y	z
C(1)	-0341 2	0778 3	0741 1	-0344	0781	0743
C(2)	1497 2	-0253 3	-0162 1	1502	-0255	-0164
C(3)	1214 2	0550 2	0611 1	1215	0550	0612
C(4)	2393 2	1077 3	1204 1	2396	1079	1205
C(5)	2148 2	1877 3	1979 1	2146	1882	1982
C(6)	3950 2	0840 3	1091 1	3957	0839	1090
N(1)	1960 2	2524 4	2592 1	1957	2529	2596
N(2)	5179 2	0648 3	0996 1	5188	0646	0994
H(1)	-0577 34	1312 45	1216 20	-0581	1315	1218
H(2)	2447 31	-0295 37	-0253 16	2452	-0296	-0255

\*  $\times 10^4$ . The number below each parameter is its e.s.d.

are given in the table; the Coulomb integral,  $\alpha$ , for the nitrogens was assumed to be  $0.5\beta_0$  greater than that for the carbons, all of which were assumed to be equal. The bond lengths were obtained from the bond orders by using the empirical curve of Cruickshank & Sparks (1960); the agreement is remarkably good, certainly better than the approximations of Hückel molecular-orbital theory and the empirical bond order-length curve would lead one to expect.

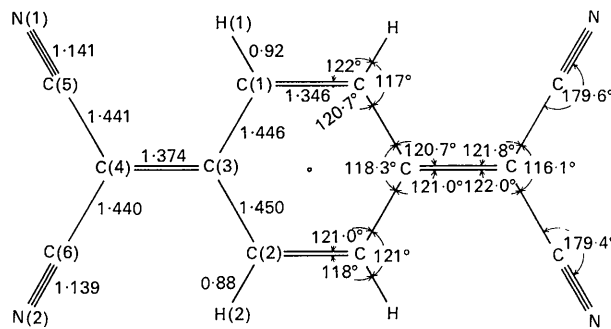


Fig. 1. Molecular dimensions (corrected for libration).

Table 5. Intramolecular distances and angles and their e.s.d.'s

Distance*	e.s.d.†	Angle*	e.s.d.
C(1)–C(2')	1.346 Å (1.344)	C(1)–C(3)–C(2)	118.3° (118.1)
C(1)–C(3)	1.446 (1.440)	C(2)–C(3)–C(4)	120.7 (120.8)
C(2)–C(3)	1.450 (1.445)	C(1)–C(3)–C(4)	121.0 (121.1)
C(3)–C(4)	1.374 (1.373)	C(3)–C(1)–C(2')	121.0 (121.1)
C(4)–C(5)	1.441 (1.436)	C(3)–C(1)–H(1)	121 (121)
C(4)–C(6)	1.440 (1.435)	H(1)–C(1)–C(2')	118 (118)
C(5)–N(1)	1.141‡ (1.139)	C(3)–C(2)–C(1')	120.7 (120.8)
C(6)–N(2)	1.139‡ (1.137)	C(3)–C(2)–H(2)	117 (117)
C(1)–H(1)	0.92 (0.92)	H(2)–C(2)–C(1')	122 (122)
C(2)–H(2)	0.88 (0.88)	C(5)–C(4)–C(6)	116.1 (115.9)
C(5)···H(1)	2.593 (2.591)	C(5)–C(4)–C(3)	122.0 (122.1)
C(6)···H(2)	2.534 (2.532)	C(6)–C(4)–C(3)	121.8 (121.9)
C(5)···C(6)	2.446 (2.434)	C(4)–C(5)–N(1)	179.4 (179.4)
N(1)···N(2)	4.381 (4.364)	C(4)–C(6)–N(2)	179.6 (179.6)
N(1)···N(2')	8.310 (8.303)	N(1)···N(2)···N(1')	90.26 (90.26)
N(1)···N(1')	9.411 (9.397)	N(2)···N(1)···N(2')	89.74 (89.74)
N(2)···N(2')	9.376 (9.362)		
C(3)···C(3')	2.832 (2.829)		
C(1)···C(1')	2.824 (2.813)		
C(2)···C(2')	2.829 (2.818)		

\* Numbers in parentheses are before correction for libration.

† Includes estimated error in libration corrections.

‡ The librational corrections to the C–N distances are based on the rigid body model and are undoubtedly low. They should probably be nearer 0.01 Å.

The agreement of the dimensions of the dicyanomethylene group with those found by us in our reinvestigation of tetracyanoethylene (Bekoe & Trueblood, 1964) is excellent, the bond distances being the same within a few 0.001 Å, only a fraction of their respective e.s.d.'s. On the other hand the double bond in tetracyanoethylene is about 0.03 Å shorter than the value predicted from the order-length curve, a discrepancy about twice that of the double bond adjacent to the dicyanomethylene group in the present molecule. It is

Table 6. Results of molecular-orbital calculations

Bond	Distance (Corrected for libration) (Å)	Distance predicted from bond order (Å)	Bond order	Assumed resonance integral (units, $\beta_0$ )
C(1)–C(2')	1.346	1.35	0.82	1.05
C(1)–C(3)	1.446	1.45	0.45	0.90
C(2)–C(3)	1.450			
C(3)–C(4)	1.374	1.39	0.65	1.05
C(4)–C(5)	1.441	1.46	0.41	0.95
C(4)–C(6)	1.440			
C(5)–N(1)	1.141	—	0.88*	1.25
C(6)–N(2)	1.139			
		Atom	Effective	
		charge	charge	
		C(1) and C(2)	+0.02	
		C(3)	+0.07	
		C(4)	+0.01	
		C(5) and C(6)	+0.16	
		N(1) and N(2)	–0.22	

\* The C–N bond has, of course, another  $\pi$ -bond orthogonal to this one.

tempting to speculate that the cyano groups decrease the trigonal-carbon bond radius by 0.01–0.02 Å because of their electron-withdrawing effect; this sort of phenomenon was discussed at length by Bekoe & Trueblood (1960) in the earlier paper on tetracyanoethylene. The formal single bonds to this carbon are also short in both molecules, by amounts consistent with this suggestion. However, it can only be considered very tentative because of all the approximations involved in deriving the relevant data.

The approximate molecular axes (of the molecule centered at the origin) are given in Table 7; axis *B* is the normal to the least-squares plane of the entire molecule. The deviations from the least-squares plane are listed in Table 8. Several atoms deviate from this plane by more than twice the e.s.d. of their positions which ranges from about 0.002 to 0.004 Å when the uncertainty of the librational corrections is included. A  $\chi^2$  test suggests that the deviation from planarity is significant.

Table 7. Molecular axes

Axis	Direction cosines ( $\times 10^4$ ) relative to			Description
	a	b	e*	
<i>A</i>	6595	2708	7012	The long axis of the molecule, i.e., parallel to C(3)–C(4)
<i>B</i>	0508	9146	–4011	Normal to the least-squares plane of the molecule
<i>C</i>	7500	–3001	–5895	Approximately parallel to C(1)···C(2)

The shortest intermolecular contacts (Table 9) are between nitrogen and hydrogen atoms, with two independent distances of 2.6 (2.59) Å, just the sum of the van der Waals radii. The shortest intermolecular C···N distance is 3.18 Å, which is close to the sum expected for this pair, about 1.7 plus 1.4–1.5 Å. The molecular packing is illustrated in Figs. 2 and 3. One of the N···H contacts is evident in the *b*-axis projection (Fig. 2), involving a pair of molecules related by the twofold axis at  $(0, \frac{1}{2})$ ; the other is between molecules related by translation along *a*. The typical herring-bone packing pattern of many planar organic

Table 8. Deviations from the least-squares plane\*

C(1)	+0.004 Å	N(1)	–0.002 Å
C(2)	–0.012	N(2)	+0.007
C(3)	–0.005		
C(4)	–0.007	H(1)	–0.02
C(5)	+0.001	H(2)	–0.09
C(6)	+0.001		

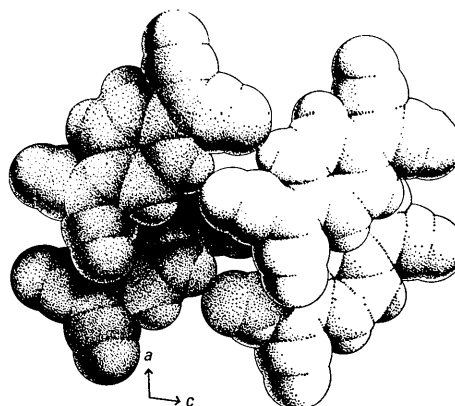
\* Plane calculated for the 16 heavy atoms of the molecule, and thus constrained to pass through the origin. The normal is axis *B* of Table 7.

Table 9. Shortest intermolecular distances\*†

From atom X at position <i>A</i>	To atom Y at position	Distance
H(2)	N(2) <i>B</i> (100)	2.59 Å
N(1)	H(1) <i>C</i>	2.59
N(2)	H(1) <i>E</i> (0 $\bar{1}$ 0)	3.17
N(1)	C(4) <i>G</i>	3.18
N(1)	C(5) <i>G</i>	3.22
N(2)	N(2) <i>B</i> (100)	3.35
N(1)	C(6) <i>G</i>	3.36
N(2)	C(2) <i>B</i> (100)	3.44
N(2)	N(1) <i>C</i> (100)	3.44
N(2)	C(5) <i>E</i> (0 $\bar{1}$ 0)	3.45
N(1)	N(1) <i>C</i>	3.45
C(2)	C(6) <i>F</i>	3.46
N(2)	C(1) <i>E</i> (0 $\bar{1}$ 0)	3.48
C(1)	N(1) <i>C</i>	3.49

\* Position *A* is (*x*, *y*, *z*); *B* is (–*x*, –*y*, –*z*); *C* is (–*x*, *y*,  $\frac{1}{2}$ –*z*); *E* is ( $\frac{1}{2}$ +*x*,  $\frac{1}{2}$ +*y*, *z*); *F* is ( $\frac{1}{2}$ –*x*,  $\frac{1}{2}$ –*y*, –*z*); *G* is ( $\frac{1}{2}$ –*x*,  $\frac{1}{2}$ +*y*,  $\frac{1}{2}$ –*z*). Positions equivalent by translation are identified by the numbers in parentheses. Corrected for libration.

† All N···H and C···H less than 3.2 Å and all N···N, N···C and C···C less than 3.6 Å are listed. There are no close H···H contacts.

Fig. 2. A view of the structure along *b*.

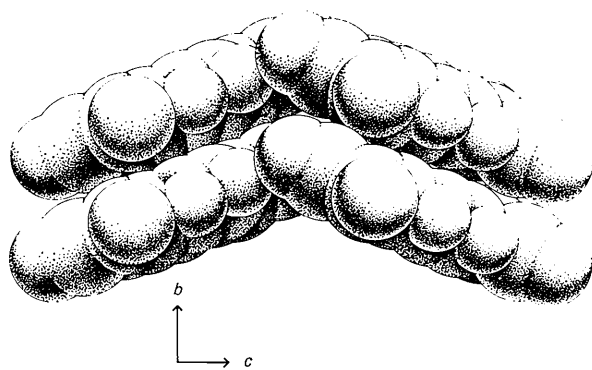


Fig. 3. A view of the structure along  $a^*$ .

molecules is evident in Fig. 3 which is a view along  $a^*$ ; the angle between the planes of molecules in adjacent stacks, related by the twofold axis, is  $48^\circ$ . The perpendicular distance between the planes of adjacent molecules within a given stack is  $3.45 \text{ \AA}$ , only about  $0.1 \text{ \AA}$  more than that in graphite.

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### Crystallographic Studies of Metal–Peptide Complexes. III. Disodium Glycylglycylglycylglycino Cuprate(II) Decahydrate

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The structure of the pink complex disodium glycylglycylglycylglycino cuprate(II) decahydrate has been determined by X-ray diffraction methods from three-dimensional intensity data recorded on Weissenberg films and estimated visually. The structure (without hydrogen atoms) has been refined by full-matrix least-squares with anisotropic temperature factors to an  $R$  index of 0.092. The environment of the copper(II) atom is approximately square-planar, the copper being coordinated by the four nitrogen atoms of one peptide molecule. The discrete glycylglycylglycylglycino cuprate(II) ions are extensively hydrogen bonded to water molecules. Both sodium ions exhibit distorted octahedral coordination, the octahedra sharing a face of three water molecules.

#### Introduction

This is the third in a series of papers describing a crystallographic study of complexes between metals and small peptides (Freeman, Robinson & Schoone, 1964;

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Freeman, Schoone & Sime, 1965). From the study of a number of these complexes it is hoped to establish possible stereochemical relationships for metal–protein interaction. Disodium glycylglycylglycylglycino cuprate(II) decahydrate is the first complex to be studied in this series where there exists the possibility of fourfold coordination of a metal ion by nitrogen atoms of the same peptide molecule. Koltun, Roth & Gurd (1963)

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