

From Table 3 it can be noted that each atom in the structure has a coordination atmosphere of 14 near neighbors with the coordinated atoms forming nearly regular rhombic dodecahedra with one of the major axes pointing in the $[\bar{1}60]$ direction. The volume contraction associated with phase formation from the solid elemental components has been computed as 3%. The structure shows pronounced layering of the atoms in the (001), (610), ($\bar{8}30$), ($7\bar{1}2$), ($\bar{1}21$), and (614) planes. This layering may well be associated with low activation energies for dislocation glide since it was observed qualitatively that Li_9Al_4 , in contrast to Na_2Tl , could suffer appreciable plastic strain without fracture.

There is a formal relationship between the structure of Li_9Al_4 and the tetragonal MoSi_2 -type structure in the sense that, if one considers only atomic loci and not species, atomic arrays in the two structures are closely comparable. Both structures are formed by alternating atomic layers normal to the c axis in the case of Li_9Al_4 and normal to the a or b axes in the case of MoSi_2 . The relationship can be observed by

comparing Figs. 3 and 4. This relationship between the two structures may simply reflect the fact that geometric constraints govern the efficient filling of space, and both Li_9Al_4 and MoSi_2 are efficiently packed structures.

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The Crystal Structure of Tetracyanocyclobutane

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cis,trans,cis-1,2,3,4-Tetracyanocyclobutane, $\text{C}_8\text{H}_4\text{N}_4$, crystallizes in the monoclinic system; the space group is $P2_1/n$, with $a=8.610$, $b=6.193$, $c=6.983$ Å (all ± 0.005 Å), $\beta=98.4 \pm 0.1^\circ$. There are two molecules per unit cell. The crystal structure has been determined from counter data with use of the symbolic addition phase determining procedure. The cyclobutane ring is planar and rectangular with C-C edges of 1.561 ± 0.003 and 1.547 ± 0.003 Å. Bond lengths in the C-C \equiv N 'legs', corrected for the effects of thermal motion, are C-C, 1.452 ± 0.005 Å and C \equiv N, 1.158 ± 0.008 Å.

Introduction

The configuration of the highly strained cyclobutane ring in organic compounds has long been of considerable interest, but until recently only a few serious efforts had been made to investigate it by the methods of X-ray diffraction. These are summarized in Table 1. It appears that the cyclobutane ring is puckered in some compounds and planar in others. Additional studies are clearly needed to establish the conditions favoring one configuration over the other, as well as to determine bond lengths with maximum precision.

Tetracyanocyclobutane (TCCB) was synthesized by Griffin, Basinsky & Peterson (1962) by the solid state

photodimerization of fumaronitrile. Chemical and physical tests indicated that the product of the reaction was probably the *cis,trans,cis* isomer (Fig. 1).

Both TCCB and fumaronitrile crystallize in the monoclinic system, space group $P2_1/n$, with two mol-

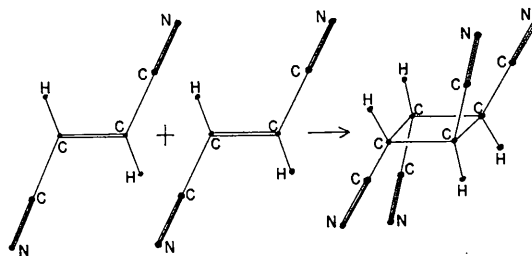


Fig. 1. Dimerization of fumaronitrile to form tetracyanocyclobutane.

* Taken from a thesis submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science.

ecules per unit cell. The crystal structure of fumaronitrile was determined by Orsa (1960). It seemed likely that the analysis of the crystal structure of TCCB would not only establish the configuration of its cyclobutane ring, but might reveal structural relationships between the molecular arrangements in crystals of the monomer and dimer.

Experimental

Single crystals of TCCB suitable for X-ray diffraction analysis were grown by slow evaporation of solutions in benzene and in carbon tetrachloride. Both solvents yielded the same product. A small irregularly shaped crystal ($0.1 \times 0.2 \times 0.3$ mm) was selected for investiga-

Table 1. *Crystallographic studies of compounds containing cyclobutane rings*

	Dihedral angle in ring	C-C bond length(s) in ring	Reference
Tetraphenylcyclobutane	180°	1.555 ± 0.02 Å	Dunitz (1949)
		1.585	
	180	1.566 ± 0.015	Margulis (1965 <i>b</i>)*
Octachlorocyclobutane		1.58	Owen & Hoard (1951)
		1.60	
Photodimer of cyclopentenone	180	1.54	Margulis (1965 <i>a</i>)
		1.60	
<i>cis</i> -1,2-Dibromo-1,2-dimethoxycarbonylcyclobutane	150	1.52	Karle, Karle & Britts (1966)
		1.58 ± 0.027	
		1.58	
		1.55	
<i>trans</i> -1,2-Dibromo-1,2-dimethoxycarbonylcyclobutane	153	1.52	Karle, Karle & Britts (1966)
		1.57 ± 0.027	
		1.58	
Anemonin	152	1.530 ± 0.01	Karle & Karle (1966)
		1.545	
		1.541 ± 0.017	
		1.532	
Octahydroxycyclobutane	180	1.562 average	Bock (1967)
<i>trans</i> -1,3-Cyclobutane-dicarboxylic acid	180	1.552	Margulis & Fisher, M.S. (1967)
		1.567 ± 0.006	
<i>cis, trans, cis</i> -1,2,3,4-Tetracyanocyclobutane	180	1.547 ± 0.003	This study
		1.561	

* Refinement of Dunitz's data.

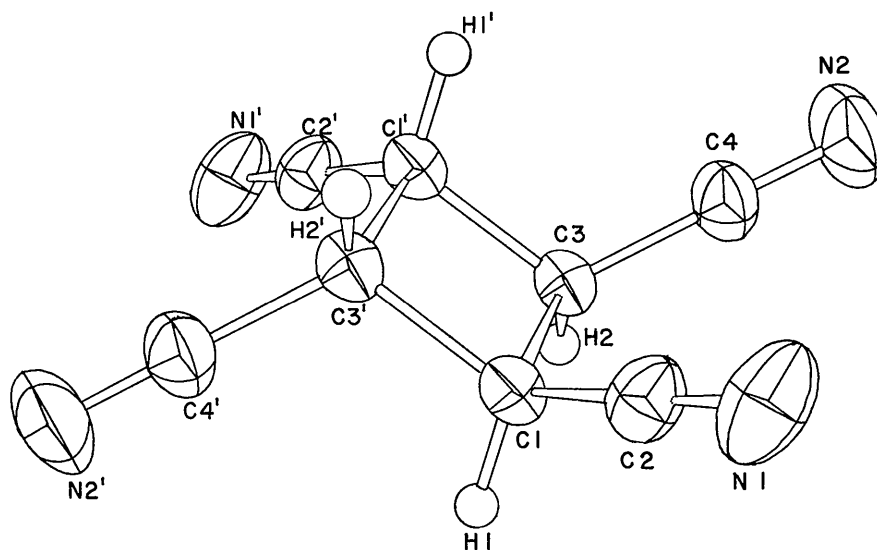


Fig. 2. Thermal motions of atoms in tetracyanocyclobutane.

Table 2. *Crystal data*

Crystal system Space group	TCCB	Fumaronitrile
	Monoclinic $P2_1/n$	Monoclinic $P2_1/n$
<i>a</i>	8.610	3.89 Å
<i>b</i>	6.193	5.60
<i>c</i>	6.983	10.04
β	$98.4 \pm 0.1^\circ$	102.5°
<i>Z</i>	2	2
$\rho_{X\text{-ray}}$	1.408 g.cm ⁻³	1.21 g.cm ⁻³
$\rho_{\text{meas.}}$	1.384	1.196 ± 0.005

tion. Crystal data for TCCB and fumaronitrile are listed in Table 2.

Intensity data were obtained with a single-crystal diffractometer using filtered Cu $K\alpha$ radiation and pulse height analysis to reduce unwanted background. Reflection intensities were measured to $2\theta=150^\circ$ by the stationary-crystal stationary-counter method. Six hundred and fifty-one of a total of 765 reflections accessible to Cu $K\alpha$ radiation were detected and measured. General background was measured as a function of reflection angle and subtracted from each reflection intensity. In addition, forty-seven reflections were remeasured with the use of ' $\theta-2\theta$ ' scans to obtain 'integrated' intensities. The ratios of these intensities to the corresponding 'peak' intensities were plotted as functions of reflection angles to convert 'peak' to 'integrated' intensities. The usual geometrical corrections were then applied to the latter.

Structure determination

Although the structure was clearly a simple one, we experienced considerable difficulty in interpreting 'sharpened' and 'unsharpened' Patterson maps computed from the three-dimensional data. The causes of these difficulties became apparent when the structure

determination was completed and will be discussed below.

At this point we decided to use the symbolic addition procedure of Karle & Karle (1963) to determine the signs of the structure factors. Using a program described by Bednowitz (1966), *E* factors were computed from the experimental intensities. Six reflections with large *E* factors and many interactions were selected to initiate the phase determining procedure. Three of the six were assigned positive signs to fix the origin of the unit cell; the three others were given symbolic signs *A*, *B* and *C* (Table 3).

Table 3. *Phase assignments for the symbolic addition procedure*

<i>h, k, l</i>	$ E $	Signs	Number of interactions
10,0, $\bar{4}$	3.34	<i>B</i>	41
4,3,4	3.11	+	44
3,2, $\bar{4}$	3.01	+	51
1,2,0	2.96	<i>A</i>	58
4,3, $\bar{6}$	2.80	<i>C</i>	45
2,2,3	2.44	+	43

Symbolic signs of approximately 270 reflections with $|E| > 0.90$ were calculated, including 29 *h0l* terms. With the use of these 29 terms, eight projections of electron density onto the *ac* plane were computed with the von Eller (1955) photosommateur. These projections were based on the eight phase combinations of the three symbolic signs, A reasonable peak arrangement was detected in one of the projections and the values of the symbolic signs based on that arrangement were used to compute (*hk0*) and (*0kl*) electron density maps. These confirmed that the correct choice had been made.

Coordinates obtained from these electron density maps served as the starting positions for least-squares

Table 4. *Atomic position and thermal parameters*

Estimated standard deviations $\times 10^4$ in parentheses.

A. Position parameters

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.0362 (2)	0.0853 (3)	-0.1245 (3)
C(2)	0.1499 (3)	0.2579 (3)	-0.1217 (3)
C(3)	0.0921 (2)	-0.1211 (3)	-0.0059 (3)
C(4)	0.2504 (2)	-0.1151 (4)	0.0952 (3)
N(1)	0.2421 (3)	0.3884 (3)	-0.1150 (4)
N(2)	0.3733 (2)	-0.1055 (4)	0.1753 (3)
H(1)	-0.0069 (20)	0.0435 (36)	-0.2528 (29)
H(2)	0.0758 (22)	-0.2541 (34)	-0.0830 (28)

B. Thermal parameters ($\times 10^4$)

(based on $b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl$)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	79 (3)	155 (6)	118 (4)	8 (3)	5 (3)	8 (3)
C(2)	99 (3)	177 (6)	170 (5)	15 (3)	40 (3)	25 (3)
C(3)	69 (3)	137 (5)	135 (4)	4 (3)	4 (3)	-5 (3)
C(4)	77 (3)	230 (6)	181 (5)	12 (3)	8 (3)	53 (4)
N(1)	145 (4)	206 (6)	334 (6)	-23 (3)	105 (4)	18 (4)
N(2)	92 (3)	508 (10)	270 (5)	2 (4)	-34 (3)	132 (6)
H(1)	$B=1.0$ (0.4)					
H(2)	$B=0.5$ (0.4)					

Table 5. Observed and calculated structure factors $\times 10$

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	
0	0	2	133	131	4	5	35	38	7	-1	11	11	2	-8	32	31	4	-3	111	109	2	3	27	27	
0	0	4	240	245	4	6	36	35	7	0	10	15	2	-7	27	29	4	-1	83	95	2	4	64	65	
0	0	6	19	20	4	7	35	34	7	1	16	15	2	-6	18	18	4	1	42	41	3	-5	45	41	
0	0	8	77	76	5	-5	37	37	7	3	22	20	2	-5	30	32	4	5	33	31	3	-4	17	18	
1	1	1	294	344	5	-3	29	30	3	0	29	30	2	3	83	82	4	5	44	41	3	-3	35	34	
1	2	1	455	502	5	-2	113	118	3	0	-7	26	29	2	-3	56	57	4	5	70	70	3	-2	54	57
1	3	5	1	50	5	-1	92	95	0	-3	175	173	2	-2	52	47	5	-5	14	15	3	0	31	34	
1	4	7	8	8	5	0	66	68	0	-1	33	31	2	-1	54	61	5	-3	29	28	3	1	113	112	
1	5	30	31	5	1	17	14	0	1	18	21	2	0	118	109	5	-2	9	11	3	2	17	20		
1	6	94	94	5	2	27	21	0	3	30	27	2	1	41	43	5	2	52	48	4	-4	27	27		
1	7	33	34	5	3	33	33	0	7	39	38	2	2	68	69	5	2	38	36	4	-3	14	8		
1	8	18	17	5	4	15	13	1	0	29	30	2	3	138	137	5	3	22	22	4	-2	14	13		
2	0	7	17	5	5	9	8	1	-6	61	62	2	4	66	66	5	4	60	57	4	-1	65	73		
2	1	197	189	5	6	19	17	1	-5	63	66	2	5	86	87	6	-4	26	25	4	0	54	59		
2	2	46	45	6	-5	16	18	1	-4	157	163	2	6	36	36	5	-3	19	19	4	1	33	33		
2	3	35	29	6	-4	15	15	1	-3	91	89	2	7	32	31	6	-2	18	17	4	2	10	7		
2	4	41	33	6	-2	27	32	1	-2	269	275	3	-7	28	27	6	0	43	51	4	3	28	30		
2	5	44	46	6	-1	22	23	1	-1	82	80	3	-6	102	102	6	2	25	26	5	-4	39	38		
2	7	20	21	6	0	82	82	1	0	230	217	3	-5	27	27	6	0	16	15	5	-4	34	32		
3	1	87	85	6	1	75	71	1	1	97	87	3	-4	17	18	6	3	18	16	5	-3	35	32		
3	2	226	219	6	2	32	28	1	2	98	88	3	-2	134	135	6	2	25	26	5	-2	81	80		
3	3	46	45	6	4	5	7	1	4	18	17	3	-1	52	51	6	0	-6	32	33	5	-1	12	16	
3	4	16	8	6	5	43	40	1	5	75	73	3	0	44	41	6	0	-4	46	45	5	1	26	27	
3	5	32	30	7	-2	22	23	1	6	38	37	3	1	23	25	6	0	-2	95	98	5	2	58	57	
3	6	34	34	7	-1	24	20	1	7	36	38	3	2	160	160	6	0	131	130	5	1	34	33		
3	7	14	14	7	1	13	13	2	-8	8	8	3	3	15	14	6	0	103	105	8	0	-6	15	27	
3	8	19	17	7	2	9	8	2	-7	24	24	3	3	141	140	6	0	4	15	35	6	-4	56	56	
4	0	234	234	7	3	5	4	2	-6	124	123	3	5	32	29	6	0	6	33	34	0	0	73	69	
4	1	80	76	7	3	5	4	2	-5	37	35	3	6	42	39	6	0	3	23	20	0	0	123	120	
4	2	76	75	2	0	-8	12	12	2	-4	213	221	4	-6	36	37	1	-5	17	19	0	2	41	40	
4	3	20	19	0	-6	101	107	2	-3	78	77	4	-5	30	27	1	-3	90	93	0	4	48	44		
4	4	14	11	0	-4	173	181	2	-2	140	141	4	-4	126	128	1	-2	20	18	1	-5	45	37		
4	5	28	29	0	-2	394	422	2	-1	131	133	4	-3	8	11	1	-1	15	15	1	-4	9	9		
4	6	21	22	0	0	191	183	2	0	107	104	4	-2	33	35	1	0	27	26	1	-3	39	38		
4	7	21	21	0	2	342	329	2	1	68	64	4	-1	19	20	1	1	16	70	1	-2	108	106		
5	1	91	91	0	4	42	39	2	2	157	148	4	0	92	87	1	2	36	39	1	-1	19	19		
5	2	25	25	0	6	18	17	2	3	72	67	4	1	16	17	1	3	9	10	1	0	88	84		
5	4	13	12	0	8	37	34	2	4	124	118	4	2	42	43	1	4	28	28	1	1	46	46		
5	6	24	21	-8	20	24	2	5	34	36	4	3	54	42	1	5	16	16	1	2	34	33			
6	0	125	124	1	-7	30	30	2	6	61	59	4	4	91	86	2	-7	28	25	1	3	9	7		
6	1	16	5	1	-5	12	14	3	-8	7	10	4	5	68	69	2	-6	47	43	1	4	9	10		
6	3	14	14	1	-4	207	208	3	-7	49	50	5	-6	25	25	2	-5	36	35	2	-6	10	16		
6	4	7	7	1	-3	66	66	3	-6	8	9	5	-5	17	19	2	-4	30	30	2	-5	21	17		
6	7	14	13	1	-2	512	523	3	-4	62	68	5	-4	10	8	2	-3	37	36	2	-4	15	13		
7	2	86	80	1	-1	12	12	3	-3	46	48	5	-3	30	30	2	-2	68	66	2	-2	14	15		
-7	3	36	33	1	0	214	207	3	-2	76	73	5	-2	24	25	2	-1	34	38	2	-1	91	98		
				1	1	309	300	3	-1	77	74	5	-1	45	49	2	0	41	45	2	1	36	35		
				1	2	21	21	5	0	31	25	5	0	8	9	2	0	41	45	2	2	18	17		
1	0	-7	87	91	1	4	100	96	5	1	194	196	5	0	8	9	2	4	37	36	3	-4	39	37	
0	-5	19	18	1	4	100	96	3	2	49	46	5	4	34	33	2	5	21	20	3	-2	68	67		
0	-3	61	63	1	5	38	35	3	3	75	74	5	5	54	50	2	6	27	30	3	0	21	23		
0	-1	273	313	1	6	14	15	3	4	13	8	6	-4	18	18	3	-6	44	40	3	1	12	12		
0	1	365	369	1	7	53	53	3	5	23	23	6	-3	27	23	3	-5	23	22	3	2	17	13		
0	3	174	166	1	8	11	9	4	-7	19	20	6	-1	40	42	3	-4	88	87	3	3	13	12		
0	5	84	81	1	8	13	13	4	-6	26	25	6	0	10	8	3	-4	30	32	4	-4	22	23		
0	7	38	36	2	-7	37	37	4	-5	63	66	6	1	14	14	3	-2	59	63	4	-3	31	28		
1	-8	27	27	2	-6	32	32	6	2	8	11	6	2	8	11	3	-1	23	27	4	-2	25	23		
1	-7	21	24	2	-5	86	91	4	-3	71	73	6	3	28	28	3	0	61	67	4	-1	30	33		
1	-6	13	15	2	-3	131	131	4	-2	54	54	7	-1	7	7	3	1	60	57	4	0	39	45		
1	-5	97	102	2	-2	52	52	4	-1	84	89	7	0	21	23	3	2	104	111	4	1	20	19		
1	-4	9	9	2	0	66	61	4	0	46	48	7	1	37	35	3	3	33	34	4	2	9	8		
1	-3	19	20	2	0	86	75	4	1	20	24	4	1	20	20	3	4	23	22	5	-2	38	28		
1	-2	372	418	2	2	149	137	4	3	54	50	5	0	-7	28	29	4	-5	20	19	5	-1	17	22	
1	1	56	59	2	2	84	75	4	4	36	35	0	-5	10	10	4	-4	24	22	9	0	-5	67	60	
1	0	177	176	2	3	211	202	5	-6	41	40	0	-3	140	139	4	-3	16	5	0	-3	19	16		
1	1	52	54	2	4	46	47	5	-5	21	23	0	-1	105	102	4	-2	88	91	0	-3	19	16		
1	2	154	144	2	5	23	23	5	-4	64	68	0	3	141	152	4	-1	29	31	0	1	13	11		
1	3	149	143	2	6	31	33	5	-3	24	27	0	5	69	71	4	2	28	29	0	3	62	59		
1	5	33	33	2	8	14	17	5	-2	106	107	1	-8	30	30	4	4	25	25	1	-4	50	44		
1	6	21	25	3	-7	8	9	5	-1	30	31	1	-6	21	23	4	5	22	22	1	-3	16	15		
1	7	54	53	3	-5	23	21	5	0	39	40	1	-5	15	11	5	-5	19	18	1	-2	49	51		
1	8	70	63	3	-6	25	25	5	2	62	63	1	-4	13	13	5	-3	50	50	1	-1	13	15		
2	-8	19	23	3	-5	23	21	5	3	20	19	1	-3	11	13	5	-2	46	45	1	0	23	24		
2	-6	42	45	3	-4	60	65	6	-5	21	20	1	-2	78	72	5	1	20							

refinements of the structure. The BNL* version of the Busing-Levy, full-matrix least-squares program was used. This minimizes:

$$\sum_{hkl} W_{hkl} [(F_{\text{obs}})_{hkl} - (F_{\text{calc}})_{hkl}]^2.$$

Initially 109 reflections, recorded at relatively low Bragg angles, were used to refine the positions of the carbon and nitrogen atoms. After a few cycles

$$R = \sum_{hkl} \left[\frac{|(F_{\text{obs}})_{hkl} - [\text{scalefactor}] (F_{\text{calc}})_{hkl}|}{|(F_{\text{obs}})_{hkl}|} \right]$$

decreased to 0.18. All the experimental data were then included in the least-squares calculations. Anisotropic temperature factors were computed for the carbon and nitrogen atoms. The positions and isotropic temperature factors of the hydrogen atoms, which were initially located on the basis of geometrical considerations, were also refined.

Late in the refinement process, it became clear that the measured intensities of ten reflections were grossly in error and the corresponding reflections were discarded. The final value of R for the remaining 641 reflections was 0.054.

In the final refinement cycle the changes of atomic parameters, excluding those of hydrogen atoms, were less than two per cent of their estimated standard deviations. A difference electron density map was then computed which confirmed the locations of the hydrogen atoms. The largest background peaks were less than one third the height of the hydrogen peaks on the difference maps. The final atomic positions and thermal parameters are listed in Table 4. Observed and calculated structure factors are shown in Table 5.

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Three weighting schemes were used in the final stage of the least-squares refinement process, *i.e.* $\sigma = \text{constant}$; $\sigma \propto F$, and a more elaborate scheme in which σ was evaluated by taking explicit account of statistical counting errors in peak intensities, background, and errors made in relating peak heights to integrated intensities. Bond lengths and angles obtained from all three weighting schemes were within two estimated standard deviations of one another. Results reported in Table 6 are based on the third of the schemes mentioned above.

Discussion

The cyclobutane ring in TCCB is planar and rectangular with bonds of 1.561 Å between *cis* C–C≡N 'legs' and 1.547 Å between *trans* C–C≡N 'legs' (each ± 0.003 Å).

The difference between the two bond lengths equals five estimated standard deviations and is therefore statistically significant. These results agree well with previous studies involving compounds with planar cyclobutane rings (Table 1). Our efforts to establish the C≡N bond lengths with high accuracy were relatively unsuccessful. The values obtained from the least squares analysis (1.123 and 1.129 Å) were unexpectedly low, apparently owing to the large anisotropic thermal motions of these atoms (Fig. 2).

To correct these bond lengths for the effects of thermal motion, individual atoms were assumed to 'ride' on their neighbors (Busing & Levy, 1964). This led to calculated increases of 0.007 Å in the average C–C bond (from 1.445 to 1.452 Å) and 0.032 Å in the average C≡N bond (from 1.125 to 1.158 Å). The latter value is close to the expected one and it is tempting to view this as a confirmation of the assumed model

Table 6. Bond lengths and angles in tetracyanocyclobutane

C(1)–C(3)	1.561 Å	C(3)'–C(1)–C(3)	89.8°
C(1)–C(3)'	1.547	C(1)'–C(3)–C(1)	90.2
C(1)–C(2)	1.448	C(1)–C(2)–N(1)	177.6
C(3)–C(4)	1.441	C(3)–C(4)–N(2)	178.3
C(1)–C(2)*	1.453	C(3)–C(1)–C(2)	116.2
C(3)–C(4)*	1.451	C(3)'–C(1)–C(2)	115.2
C(2)–N(1)	1.129	C(1)–C(3)–C(4)	115.8
C(4)–N(2)	1.123	C(1)'–C(3)–C(4)	114.4
C(2)–N(1)*	1.155	C(3)–C(1)–H(1)	108.9 ± 1.3
C(4)–N(2)*	1.162	C(3)'–C(1)–H(1)	112.3 ± 1.0
C(1)–H(1)	0.95 ± 0.02	C(1)–C(3)–H(2)	112.8 ± 1.1
C(3)–H(2)	0.98 ± 0.02	C(1)'–C(3)–H(2)	112.7 ± 1.1
		C(2)–C(1)–H(1)	112.4 ± 1.2
		C(4)–C(3)–H(2)	109.9 ± 1.1
		Other intramolecular distances	
C(1)–C(1)'	2.201 Å	C(2)–C(4)	2.828 Å
C(3)–C(3)'	2.194	N(1)–N(2)	3.751

* Corrected for thermal motion.

The estimated standard deviations of bonds, involving non-hydrogen atoms only, equal ± 0.003 Å; the corresponding *e.s.d.* of angles involving these atoms equal $\pm 0.2^\circ$.

of the thermal motion, but this can only be unambiguously established on the basis of low temperature work.

Both C-C≡N angles in TCCB are approximately 178°. A similar non-linearity of the C-C≡N 'legs' has been noted in tetracyanoquinodimethane by Hanson (1965) and *cis*-1,2,3-tricyanocyclopropane by Hartman

& Hirshfeld (1966). Hartman & Hirshfeld (1966) and Dunitz & Ibers (1967) have discussed possible causes of this effect.

The closest intermolecular approaches are listed in Table 7 and are illustrated in Fig. 3. All involve at least one nitrogen atom. N1(1), for example is less than

Table 7. Closest intermolecular approaches in TCCB (Å)

For H...X less than 3.0 Å and for X...X' less than 3.5 Å, where X is C or N. The second number in the atom symbol designates:

	(1)	x	y	z			
	(2)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	N(2)(1)...	C(1)(5)	
	(3)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	C(3)(1)...	N(1)(4)	
	(4)	x	$y-1$	z	C(4)(1)...	N(1)(4)	
	(5)	$\frac{1}{2}+x$	$-\frac{1}{2}-y$	$\frac{1}{2}+z$	N(2)(1)...	C(2)(2)	
	(6)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-\frac{1}{2}-z$	N(1)(1)...	C(4)(6)	
N(1)(1)...	H(2)(6)	2.94 ± 0.02			N(2)(1)...	C(1)(5)	3.490 ± 0.003
N(2)(1)...	H(1)(5)	2.92 ± 0.03			C(3)(1)...	N(1)(4)	3.430 ± 0.003
N(1)(1)...	H(1)(6)	2.75 ± 0.02			C(4)(1)...	N(1)(4)	3.404 ± 0.003
H(2)(1)...	N(1)(4)	2.66 ± 0.03			N(2)(1)...	C(2)(2)	3.366 ± 0.003
N(2)(1)...	H(2)(5)	2.41 ± 0.02			N(1)(1)...	C(4)(6)	3.363 ± 0.003
N(1)(1)...	N(2)(3)		3.363 ± 0.003				
C(2)(1)...	N(2)(3)		3.264 ± 0.003				
N(1)(1)...	C(3)(6)		3.186 ± 0.003				
N(2)(1)...	C(3)(5)		3.185 ± 0.003				
N(1)(1)...	C(2)(6)		3.159 ± 0.003				
N(1)(1)...	C(1)(6)		3.074 ± 0.003				

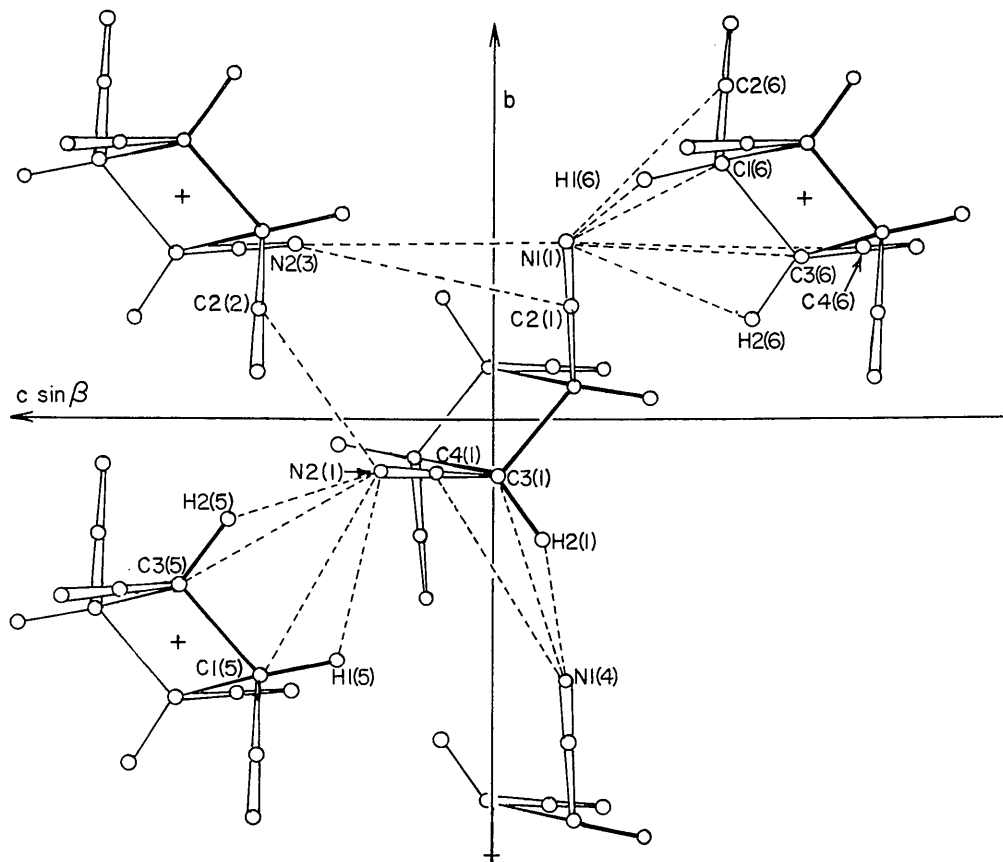


Fig. 3. The crystal structure of tetracyanocyclobutane as viewed along the *a* axis.

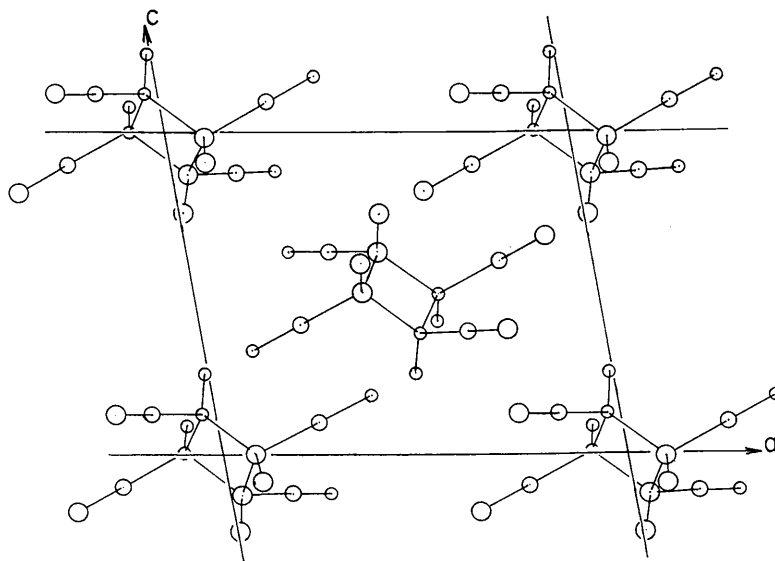


Fig. 4. The crystal structure of tetracyanocyclobutane as viewed along the b axis.

3.5 Å from ten adjacent atoms and N2(1) is less than 3.5 Å from seven atoms. The molecular packing is also shown in Fig. 4. It can be seen that the molecules are most closely packed in layers approximately parallel to the (101) and (10 $\bar{1}$) planes, leaving large open channels along $\frac{1}{2}, y, 0$ and $0, y, \frac{1}{2}$.

We have mentioned that TCCB was synthesized by the solid state photodimerization of fumaronitrile. Griffin *et al.* (1962) have pointed out that . . . 'the orientation (of fumaronitrile molecules in one crystal) is completely consistent with the formation of a dimer having the structure of tetracyanocyclobutane providing bond formation takes place between nearest neighbor molecules and no major shifts in relative positions of the atoms take place during the reaction' . . .

Our analysis of the two crystal structures indicates, in agreement with Griffin, that the arrangement of molecules in fumaronitrile, in parallel layers 3.16 Å apart, does indeed favor the formation of molecules of the dimer (TCCB) from pairs of nearest molecular neighbors. We are unable, however, to detect any significant influence of the crystal structure of fumaronitrile on the crystal structure of TCCB.

Analysis of the completed structure revealed some of the causes of our difficulty in interpreting the Patterson maps. A large number of peaks, unrelated by symmetry, are separated by $y = \frac{1}{2}$. This factor, plus the

large anisotropic thermal motions of the atoms in the C-C \equiv N 'legs', made interpretation of the Patterson maps difficult. By contrast the symbolic addition method proceeded smoothly and rapidly.

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