

## References

- BURNHAM, C. W. (1966). *Amer. Min.* **51**, 159.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962).  
 Oak Ridge National Laboratory Report ORNL-TM-305.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964).  
 Oak Ridge National Laboratory Report ORNL-TM-306.  
 CARON, A. & DONOHUE, J. (1964). *Acta Cryst.* **17**, 544.  
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.  
*International Tables for X-ray Crystallography* (1962). Vol.  
 III, p. 202. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). Oak Ridge National Laboratory  
 Report ORNL-3794.  
 WETTERHOLM, A. (1964). *Nitro Compounds*. Proc. Int.  
 Symp. at the Polish Academy of Sciences, Warsaw, Sep-  
 tember 18–20, 1963, p. 331. Oxford: Pergamon Press.

*Acta Cryst.* (1970). **B26**, 596

## The Crystal Structure of the Anthracene–Tetracyanoethylene Adduct and Complex, $8C_{20}H_{10}N_4 \cdot 2CH_2Cl_2 \cdot C_6N_4$

BY ISABELLA L. KARLE AND A. V. FRATINI\*†

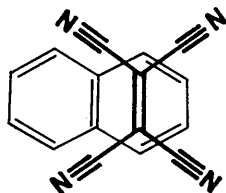
Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20390, U.S.A.

(Received 12 March 1969)

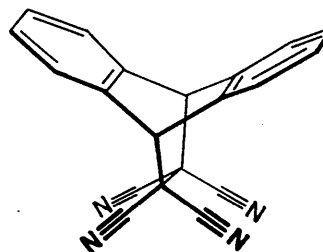
A complex consisting of eight anthracene–tetracyanoethylene adducts, two methylene chloride molecules and one free tetracyanoethylene molecule crystallizes in a triclinic cell, space group  $P\bar{1}$ , with cell dimensions  $a = 13.40$ ,  $b = 17.01$ ,  $c = 20.36$  Å (all  $\pm 0.03$  Å),  $\alpha = 99.8$ ,  $\beta = 94.2$  and  $\gamma = 129.1^\circ$  (all  $\pm 0.3^\circ$ ). The 104 atoms in the asymmetric unit were located using the symbolic addition procedure for phase determination. Short intermolecular approaches, as low as 3.16 Å, exist between the C atom of one  $C\equiv N$  group and the N atom of a  $C\equiv N$  group from another molecule. In addition, intermolecular approaches as short as 3.4 Å exist between the free tetracyanoethylene molecule and the methylene chloride molecules.

### Introduction

The crystal structure of the 1:1 molecular complex naphthalene–tetracyanoethylene (TCNE) which has been reported recently (Williams & Wallwork, 1967) shows that the two planar molecules are oriented in such a way as to facilitate a Diels–Alder reaction,



However, this reaction does not proceed under the conditions of crystallization. By contrast, such a reaction has been observed at room temperature between anthracene and TCNE to form an adduct, 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile,



(Middleton, Heckert, Little & Krespan, 1958). Greenish-yellow crystals of an anthracene–TCNE adduct were grown from a  $CH_2Cl_2$  solution by Dr Craig Eckardt\* at Yale University. The cell parameters of the triclinic cell, along with the measured density, indicated nine molecules of adduct in the unit cell, or  $4\frac{1}{2}$  molecules per asymmetric unit if the space group were  $P\bar{1}$  as indicated by the statistical distribution of intensities. Since the anthracene–TCNE adduct molecule does not have a center of symmetry, it was possible that the space group was  $P1$ , that a partial disorder existed, or that a free TCNE and a free anthracene molecule were present at some of the centers of symmetry. As the structure analysis progressed, it became apparent that these suppositions were not correct, but that the con-

\* National Academy of Sciences–National Research Council Postdoctoral Resident Research Associate.

† Present address: Department of Chemistry, University of Dayton, Dayton, Ohio, 45409, U.S.A.

\* Present address: University of Nebraska.

tents of the unit cell were  $8C_{20}H_{10}N_4 \cdot 2CH_2Cl_2 \cdot C_6N_4$  where the  $CH_2Cl_2$  was a solvent molecule and the  $C_6N_4$  apparently excess TCNE. The symbolic addition procedure for phase determination was used to locate the 104 non-hydrogen atoms in the asymmetric unit.

### Experimental

The cell dimensions of the triclinic crystal of the anthracene-TCNE adduct were determined from zero and first layer precession photographs. They are listed in Table 1. Intensity data were collected by the multiple-film, equi-inclination Weissenberg technique for  $0kl-9kl$  along the  $[100]$  direction and the zero layer along the  $[110]$  direction. The intensities were estimated visually by comparison with a calibrated intensity strip. Spot size and Lorentz and polarization corrections were applied to the data and normalized structure factors  $|E|$  were derived. The space group, which could have been either  $P1$  or  $P\bar{1}$ , was assigned to be  $P\bar{1}$  from the implication of statistical averages and distribution of the normalized structure factor magnitudes, Table 2.

Table 1. *Physical constants*

Mol. formula	$8C_{20}H_{10}N_4 \cdot 2CH_2Cl_2 \cdot C_6N_4$
M. W.	2748.6
Color	Greenish-yellow
Habit	Prisms (elongated along $a$ )
Space group	$P\bar{1}$
$a$	$13.40 \pm 0.03 \text{ \AA}$
$b$	$17.01 \pm 0.03 \text{ \AA}$
$c$	$20.36 \pm 0.03 \text{ \AA}$
$\alpha$	$99^\circ 47' \pm 20'$
$\beta$	$94^\circ 10' \pm 20'$
$\gamma$	$129^\circ 05' \pm 20'$
Vol.	$3450 \text{ \AA}^3$
$\rho$ X-ray	$1.323 \text{ g.cm}^{-3}$
$\rho$ measured	$1.330 \text{ g.cm}^{-3}$
Radiation	Cu $K\alpha$ ( $1.5418 \text{ \AA}$ )
No. independent reflections	8446 measured 7000 used
Crystal size	$\sim 0.45 \times 0.45 \times 0.45 \text{ mm}$

### Structure analysis

The symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1963, 1966) was used to obtain phases directly from the normalized structure factor magnitudes. In space group  $P\bar{1}$ , the number of interactions for applying the  $\sum_2$  formula is not as extensive as in space groups with more symmetry and therefore more unknown symbols generally need to be assigned. An example of phase determination in  $P\bar{1}$  was described for the jamine structure (Karle & Karle, 1964). In the present investigation, in addition to the origin

specified by  $1\bar{3}16 (+)$ ,  $5\bar{1}2\bar{1}5 (+)$  and  $5\bar{1}5\bar{7} (+)$ , seven other reflections were assigned symbols to facilitate the phase determination. They were  $7\bar{1}5\bar{1} (a)$ ,  $1\bar{4}\bar{4} (b)$ ,  $6\bar{6}\bar{5} (c)$ ,  $2\bar{4}17 (d)$ ,  $5\bar{4}5 (e)$ ,  $3\bar{8}\bar{1}3 (f)$  and  $5\bar{5}5 (g)$ . In the course of applying the  $\sum_2$  formula, it became apparent that  $aef = +$  and  $c = f$ . However, there was not sufficient evidence to assign definitely the signs of the other five symbols. Accordingly, the 150 phases with  $|E| > 2.0$  whose phases were determined as functions of  $+$ ,  $a$ ,  $b$ ,  $d$ ,  $e$ , and  $g$  were used to determine an additional 600 phases with  $|E| > 1.5$  and  $E$  maps were computed. Although with five unknowns, thirty-two possibilities existed, some seemed more probable than others in that there were a few indications as to the probable sign of some symbols and that an approximately equal distribution of plus and minus signs was expected. On the sixth trial with the sign sequence  $--+++$  for  $abdeg$ , a meaningful  $E$  map was obtained which proved to be the correct one.

In the correct  $E$  map, 70 of the peaks were identified as belonging to four of the independent anthracene-TCNE adduct molecules in the asymmetric unit. The remaining peaks which were present in the initial  $E$  map were not identified at this stage, although they were all significant, a fact which became obvious when the complete structure became known. A Fourier synthesis based on phases derived from the 70-atom structure revealed not only the missing atoms in the four anthracene-TCNE adduct molecules but also contained the same additional peaks as the initial  $E$  map. These additional peaks were identified as a free TCNE molecule placed at the center of symmetry at  $0, \frac{1}{2}, \frac{1}{2}$  and a  $CH_2Cl_2$  molecule. The peaks representing the two Cl atoms were quite strong, which indicated the probability of the presence of these atoms. An elemental analysis of the crystals for C, H and N agrees well with the percentages calculated for  $8C_{20}H_{10}N_4 \cdot 2CH_2Cl_2 \cdot C_6N_4$ :

	% (calculated)	% (elemental analysis)*
C	73.41	73.28
N	18.35	18.31
H	3.06	3.15
Cl	5.17	not analyzed

A total of 8446 independent data were collected and processed. However, the capacity of Fourier series and least-squares programs was limited to 7000 data and therefore some of the high index reflections were omitted in these calculations.

\* Galbraith Laboratories, Inc., Knoxville, Tennessee, U.S.A.

Table 2. *Averages and distribution of  $|E|$  values*

	$\langle  E  \rangle$	$\langle  E^2 - 1  \rangle$	$ E  > 3$	$ E  > 2$	$ E  > 1$
Experimental	0.739	1.012	0.5%	4.2%	28.7%
Theoretical: Centrosymmetric	0.798	0.968	0.3	5.0	32.0
Noncentrosymmetric	0.886	0.736	0.01	1.8	37.0



Table 3 (cont.)

A large table of numerical data with multiple columns and rows, containing various numerical values and some text labels like 'L', 'R', 'S', 'T', 'U', 'V', 'W', 'X', 'Y', 'Z' interspersed throughout the data.

Table 3 (cont.)

Table with multiple columns of numerical data and labels (e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100). Includes various numerical values and alphanumeric labels.

Table 3 (cont.)

Table with multiple columns of numerical data, organized into groups by row and column headers. The data includes various numerical values, some with superscripts and subscripts, and some with letters indicating specific categories or units. The table is dense and spans the entire page.

Table 3 (cont.)

Table with multiple columns of numerical data, organized into sections labeled with letters (e.g., 'e', 'f', 'g') and numbers. Each section contains a list of values, possibly representing bond lengths or angles, with some values in bold. The table is dense and covers the entire page.

A full-matrix least-squares analysis was performed on the 104 atoms of the asymmetric unit. A maximum of 243 parameters could be varied in any one cycle, so that two cycles were required to vary each parameter once for refinement with isotropic thermal parameters. An anisotropic refinement was not feasible. The function minimized was  $\sum w(F_o - F_c)^2$  where  $w = 0.25$  for  $F_o = 0$ ,  $w = 1$  for  $|F_o| < 30$ , and  $w = 30/|F_o|$  for  $|F_o| > 30$ . Isotropic refinement lowered the  $R$  value to 14.4%. Observed and calculated structure factors are listed in Table 3. Fractional coordinates and thermal parameters are listed in Table 4.

Table 4 (cont.)

Table 4. Fractional coordinates and isotropic thermal parameters

Atom	$x$	$y$	$z$	$B$	$\text{\AA}^2$
1A	0.3101	0.0971	0.5529	1.4	2.6
2A	0.2773	0.1410	0.5123	2.6	2.8
3A	0.1607	0.0747	0.4612	2.8	2.6
4A	0.0735	-0.0359	0.4508	2.6	2.2
5A	0.1046	-0.0795	0.4929	2.2	1.5
6A	0.2224	-0.0126	0.5435	1.5	1.2
7A	0.2687	-0.0451	0.5950	1.2	1.3
8A	0.4051	0.0008	0.5937	1.3	1.7
9A	0.4547	-0.0530	0.5886	1.7	2.7
10A	0.5848	0.0014	0.5906	2.7	3.1
11A	0.6748	0.1115	0.5997	3.1	2.0
12A	0.6284	0.1660	0.6041	2.0	1.3
13A	0.4945	0.1102	0.6019	1.3	1.4
14A	0.4298	0.1567	0.6094	1.4	1.0
15A	0.3809	0.1379	0.6784	1.0	0.8
16A	0.2765	0.0112	0.6682	0.8	1.2
17A	0.3165	-0.0185	0.7210	1.2	1.5
18A	0.1453	-0.0247	0.6714	1.5	1.6
19A	0.4929	0.1914	0.7353	1.6	2.0
20A	0.3198	0.1837	0.6900	2.0	2.6
N(1A)	0.3452	-0.0467	0.7604	2.6	3.1
N(2A)	0.0433	-0.0552	0.6745	3.1	2.9
N(3A)	0.5870	0.2338	0.7780	2.9	3.6
N(4A)	0.2661	0.2184	0.6964	3.6	1.2
1B	0.5338	0.2125	0.0635	1.2	1.9
2B	0.5475	0.1584	0.1010	1.9	3.1
3B	0.6614	0.2170	0.1553	3.1	3.1
4B	0.7549	0.3268	0.1714	3.1	2.0
5B	0.7392	0.3790	0.1318	2.0	1.1
6B	0.6284	0.3218	0.0787	1.1	1.0
7B	0.5940	0.3671	0.0315	1.0	0.8
8B	0.4591	0.3272	0.0321	0.8	1.8
9B	0.4212	0.3892	0.0469	1.8	2.2
10B	0.2942	0.3400	0.0489	2.2	3.0
11B	0.1944	0.2297	0.0333	3.0	2.1
12B	0.2314	0.1671	0.0182	2.1	1.1
13B	0.3602	0.2178	0.0169	1.1	1.3
14B	0.4193	0.1640	0.0042	1.3	0.8
15B	0.4759	0.1910	-0.0612	0.8	0.8
16B	0.5917	0.3182	-0.0429	0.8	1.5
17B	0.5666	0.3604	-0.0923	1.5	1.8
18B	0.7206	0.3487	-0.0454	1.8	1.1
19B	0.3733	0.1511	-0.1197	1.1	1.7
20B	0.5330	0.1409	-0.0758	1.7	2.8
N(1B)	0.5498	0.3949	-0.1319	2.8	4.2
N(2B)	0.8183	0.3706	-0.0493	4.2	2.8
N(3B)	0.2891	0.1153	-0.1663	2.8	3.5
N(4B)	0.5783	0.1024	-0.0870	3.5	2.3
1C	0.1835	0.4139	0.1977	2.3	3.1
2C	0.1453	0.4544	0.1590	3.1	4.2
3C	0.0255	0.3850	0.1110	4.2	4.9
4C	-0.0616	0.2763	0.1038	4.9	

Atom	$x$	$y$	$z$	$B$
5C	-0.0218	0.2360	0.1443	3.2
6C	0.0989	0.3052	0.1912	1.7
7C	0.1607	0.2772	0.2381	1.7
8C	0.2981	0.3249	0.2267	1.1
9C	0.3437	0.2720	0.2148	1.7
10C	0.4782	0.3282	0.2107	2.6
11C	0.5609	0.4388	0.2198	2.3
12C	0.5100	0.4914	0.2310	2.0
13C	0.3800	0.4330	0.2345	1.4
14C	0.3131	0.4779	0.2493	1.3
15C	0.2804	0.4610	0.3219	1.1
16C	0.1865	0.3362	0.3150	1.2
17C	0.2499	0.3143	0.3607	1.6
18C	0.0604	0.2971	0.3318	1.9
19C	0.4013	0.5207	0.3726	1.9
20C	0.2149	0.5017	0.3412	1.9
N(1C)	0.2982	0.2954	0.3950	2.6
N(2C)	-0.0355	0.2662	0.3465	3.7
N(3C)	0.5023	0.5706	0.4121	3.7
N(4C)	0.1691	0.5390	0.3576	3.6
1D	0.0156	0.7728	0.2562	1.2
2D	-0.0684	0.7113	0.2963	2.2
3D	-0.0625	0.6326	0.3055	3.0
4D	0.0104	0.6135	0.2735	2.7
5D	0.0909	0.6747	0.2304	2.3
6D	0.0832	0.7549	0.2239	1.6
7D	0.1655	0.8275	0.1785	1.0
8D	0.2493	0.9407	0.2248	1.2
9D	0.3853	1.0183	0.2310	1.8
10D	0.4445	1.1195	0.2761	2.2
11D	0.3703	1.1364	0.3079	1.5
12D	0.2334	1.0586	0.2990	1.3
13D	0.1736	0.9584	0.2569	0.9
14D	0.0275	0.8646	0.2428	1.2
15D	-0.0223	0.8344	0.1621	1.1
16D	0.0574	0.8090	0.1232	0.9
17D	0.1263	0.8804	0.0788	1.4
18D	-0.0331	0.6991	0.0795	1.2
19D	-0.0054	0.9237	0.1459	1.8
20D	-0.1656	0.7422	0.1426	2.0
N(1D)	0.1829	0.9317	0.0439	3.4
N(2D)	-0.0982	0.6151	0.0480	2.7
N(3D)	0.0155	0.9976	0.1370	3.5
N(4D)	-0.2749	0.6664	0.1302	3.4
N(5)	0.1224	0.7135	0.4836	3.7
N(6)	-0.1713	0.3961	0.3576	4.5
21	-0.0007	0.5190	0.4795	8.2
22	0.0742	0.6333	0.4903	3.8
23	-0.1040	0.4358	0.4103	2.8
24	0.3876	0.5787	0.5552	7.2
Cl(1)	0.2324	0.4449	0.5164	7.7
Cl(2)	0.3813	0.6655	0.5245	6.4

Standard deviation				
C, N	0.0012	0.0007	0.0004	0.2
Cl	0.0006	0.0004	0.0002	0.2
C(21) }	0.0024	0.0015	0.0009	0.5
C(24) }				

### Discussion

The contents of the unit cell are illustrated in Figs. 1, 2 and 3. Six molecules of the adduct labelled  $A$ ,  $B$ ,  $C$ ,  $A'$ ,  $B'$  and  $C'$  lie with their short direction, *i.e.* the direction defined by atoms C(7) and C(14), perpendicular to the  $a$  axis, while molecules  $D$  and  $D'$  lie approximately perpendicular to the other six. Near the middle



of the cell, at  $y \sim \frac{1}{2}$ , lie the two  $\text{CH}_2\text{Cl}_2$  and the TCNE molecules. One ring of molecule *B*, atoms C(8)–C(13), lies parallel to one ring of molecule *C*. Similarly one ring of molecule *A*, atoms C(8)–C(13), lies parallel to one ring of molecule *A'*, related by a center of symmetry. The nearest approach between these parallel rings is 3.6 Å, a normal intermolecular approach.

The nearest intermolecular approaches are between

the C atom of one  $-\text{C}=\text{N}$  group and the N atom of a  $-\text{C}=\text{N}$  group of another molecule. Some of the shortest of these distances are listed in Table 5. Atom N(3*B*) is nearly equidistant from atoms C(17*A*), C(18*A*), C(19*A*) and C(20*A*), for example, at distances of 3.16–3.30 Å. Similarly short  $\text{C} \cdots \text{N}$  approaches have been found in tetracyanocyclobutane (Greenberg & Post, 1968).

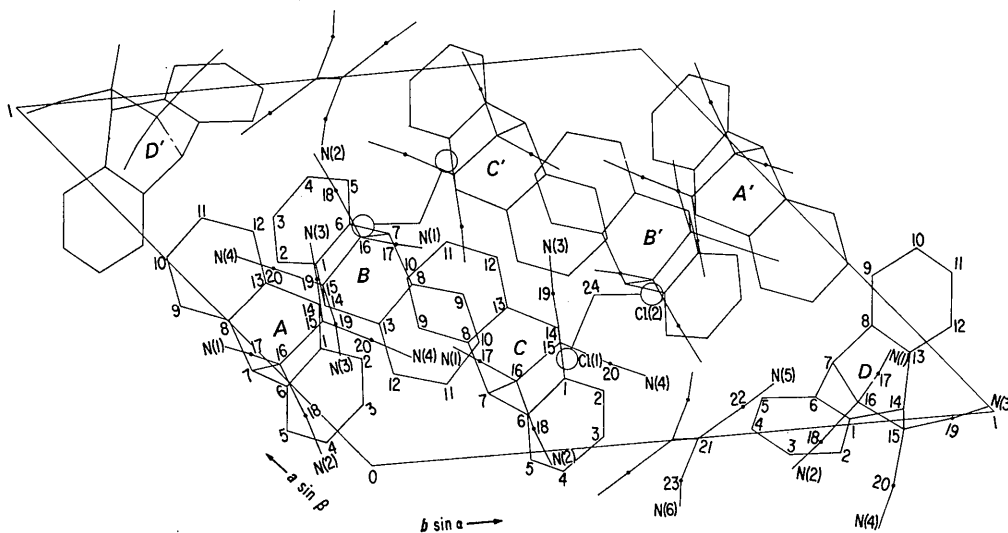


Fig. 1. Contents of the unit cell.

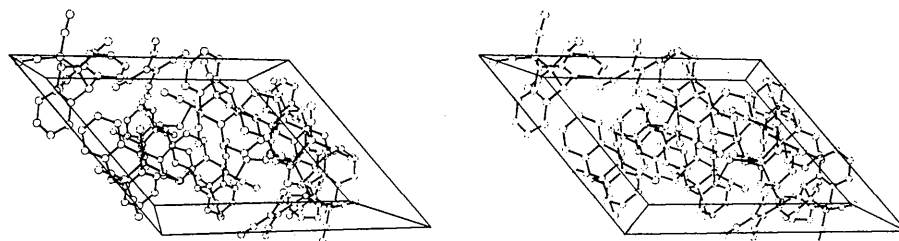


Fig. 2. Stereodiagram of the unit cell. The axes are  $b \rightarrow$ ,  $a \nearrow$  and  $c$  is directed out of the paper. (This Figure was drawn by a computer using a program written by Johnson, 1965.)

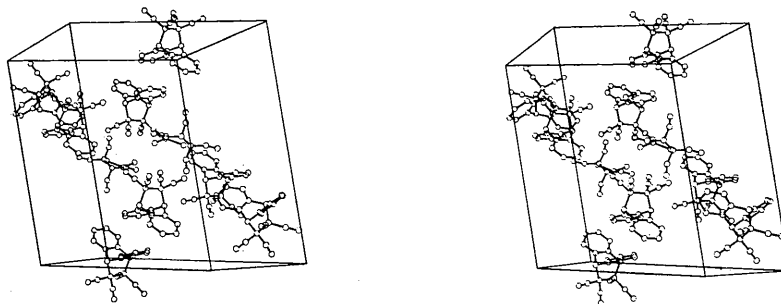


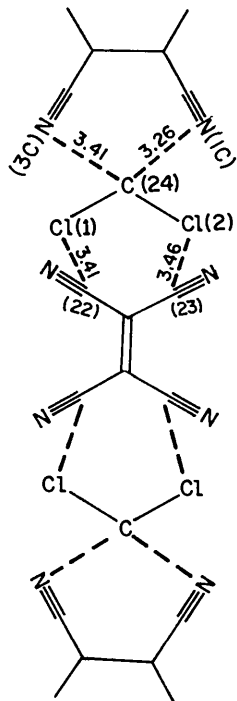
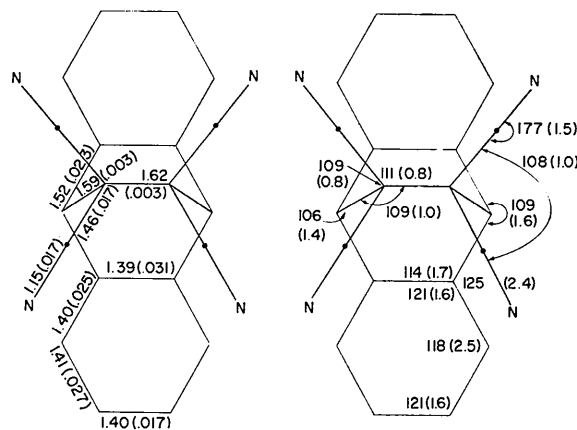
Fig. 3. Another view of the unit cell. The axes are  $b \rightarrow$ ,  $c \uparrow$  and  $a$  is directed into the paper.

Table 5. Some of the nearest intermolecular approaches

	Distance
C(17A)···N(3B)	3.16 Å
C(18A)···N(3B)	3.30
C(19A)···N(3B)	3.22
C(20A)···N(3B)	3.29
C(17A)···N(3A)	3.25
C(17A)···N(2C)	3.33
C(18A)···N(2C)	3.31
C(9D)···N(1A)	3.31
C(23)···N(4C)	3.28
C(24)···N(1C)	3.26
C(24)···N(3C)	3.41
N(1B)···N(4D)	3.14
C(22)···Cl(1)	3.41
C(23)···Cl(2)	3.46

Near  $y \sim \frac{1}{2}$ , there are close intermolecular approaches between C···N and approaches between C···Cl which are  $\sim 0.4$  Å shorter than the van der Waals distance of 3.8 Å. Fig. 4 shows the disposition of these short approaches between the three different species of molecules in the crystal.

The TCNE-anthracene adduct molecule has approximate symmetry described by two perpendicular mirror planes. The four independent molecules in the cell are quite similar to each other. Bond distances and angles are listed in Table 6. Since the least-squares refinement was not performed with anisotropic thermal factors, the bond distances and angles have fairly large standard deviations. Based on the least-squares fit alone, they are  $\sim 0.02$  Å for C–C and C–N bonds and  $\sim 1.1^\circ$  for the angles. If *mm* molecular symmetry is assumed, sixteen (or eight) independent values can be averaged

Fig. 4. Close approaches between molecules near  $y \sim \frac{1}{2}$ .Fig. 5. Average bond lengths and angles from the four independent molecules of the TCNE-anthracene adduct assuming *mm* symmetry for each molecule. The figures in parentheses are the r.m.s. deviations.

for the bond lengths and angles. Fig. 5 shows these averages along with the root-mean-square deviations. These r.m.s. deviations for the bond lengths are comparable with those obtained from the least-squares results; however the r.m.s. deviations for the angles are larger, in general.

Table 6. Bond lengths and angles

	Bond lengths			
	A	B	C	D
C(1)–C(2)	1.41 Å	1.38 Å	1.39 Å	1.40 Å
C(2)–C(3)	1.39	1.42	1.38	1.43
C(3)–C(4)	1.42	1.39	1.40	1.38
C(4)–C(5)	1.42	1.39	1.42	1.43
C(5)–C(6)	1.40	1.38	1.38	1.46
C(6)–C(1)	1.41	1.39	1.41	1.31
C(8)–C(9)	1.43	1.43	1.37	1.40
C(9)–C(10)	1.36	1.35	1.43	1.44
C(10)–C(11)	1.41	1.41	1.42	1.37
C(11)–C(12)	1.40	1.43	1.43	1.40
C(12)–C(13)	1.40	1.36	1.37	1.40
C(13)–C(8)	1.41	1.40	1.39	1.40
C(6)–C(7)	1.52	1.54	1.54	1.55
C(7)–C(8)	1.47	1.48	1.53	1.54
C(13)–C(14)	1.50	1.55	1.52	1.51
C(14)–C(1)	1.49	1.51	1.51	1.54
C(14)–C(15)	1.59	1.57	1.59	1.59
C(15)–C(16)	1.63	1.62	1.62	1.60
C(16)–C(7)	1.59	1.59	1.59	1.59
C(16)–C(17)	1.46	1.46	1.43	1.49
C(16)–C(18)	1.46	1.47	1.46	1.47
C(15)–C(19)	1.44	1.44	1.46	1.49
C(15)–C(20)	1.45	1.47	1.47	1.48
N(1)–C(17)	1.16	1.16	1.13	1.14
N(2)–C(18)	1.13	1.13	1.13	1.12
N(3)–C(19)	1.16	1.15	1.17	1.15
N(4)–C(20)	1.19	1.15	1.16	1.15
*C(21)–C(21')	1.14			
*C(21)–C(22)	1.48			
*C(21)–C(23)	1.57			
C(22)–N(5)	1.12			
C(23)–N(6)	1.12			
*C(24)Cl(1)	1.82			
*C(24)Cl(2)	1.74			

Table 6 (cont.)

	A	B	C	D
C(6)C(1)C(2)	120°	121°	121°	124°
C(1)C(2)C(3)	120	118	119	113
C(2)C(3)C(4)	120	121	122	123
C(3)C(4)C(5)	120	120	119	122
C(4)C(5)C(6)	119	120	119	112
C(5)C(6)C(1)	120	121	121	124
C(13)C(8)C(9)	118	118	122	124
C(8)C(9)C(10)	120	119	120	114
C(9)C(10)C(11)	122	123	118	121
C(10)C(11)C(12)	120	118	121	123
C(11)C(12)C(13)	119	118	118	116
C(12)C(13)C(8)	122	124	122	120
C(5)C(6)C(7)	126	126	127	118
C(7)C(8)C(9)	127	127	126	123
C(12)C(13)C(14)	126	125	125	124
C(14)C(1)C(2)	126	126	125	121
C(6)C(7)C(8)	109	109	109	106
C(13)C(14)C(1)	111	110	110	107
C(1)C(6)C(7)	113	113	112	118
C(7)C(8)C(13)	115	116	113	113
C(8)C(13)C(14)	113	111	114	116
C(14)C(1)C(6)	114	113	114	114
C(6)C(7)C(16)	106	105	107	104
C(8)C(7)C(16)	106	108	105	107
C(1)C(14)C(15)	107	108	108	106
C(13)C(14)C(15)	105	105	104	104
C(7)C(16)C(15)	108	108	108	109
C(14)C(15)C(16)	110	108	108	110
C(7)C(16)C(18)	109	111	110	110
C(7)C(16)C(17)	109	110	109	109
C(14)C(15)C(19)	110	111	109	108
C(14)C(15)C(20)	108	107	109	108
C(15)C(16)C(17)	112	111	111	110
C(15)C(16)C(18)	110	111	110	111
C(16)C(15)C(19)	112	111	112	112
C(16)C(15)C(20)	112	110	111	111
C(17)C(16)C(18)	108	106	109	108
C(19)C(15)C(20)	108	109	108	107
C(15)C(20)N(4)	177	180	177	174
C(15)C(19)N(3)	175	177	178	175
C(16)C(18)N(2)	178	178	178	177
C(16)C(17)N(1)	177	178	178	175
*C(21)C(21)C(22)	125			
*C(21)C(21)C(23)	113			
*C(22)C(21)C(23)	121			
*C(21)C(22)N(5)	165			
*C(21)C(23)N(6)	164			
*Cl(1)C(24)Cl(2)	109			

\* These bond lengths and angles involve atoms with large thermal factors.

The benzene rings in the adduct have normal C-C bond lengths and they are essentially planar. The largest deviation from least-squares planes computed for each benzene ring is 0.017 Å except for molecule *D* where it is 0.030 Å.

The eight-membered cage, formed by bridging the C(7) and C(14) atoms of anthracene by the TCNE molecule, has some unusual properties. The apical atoms C(7) and C(14) and C(15) and C(16), the two central atoms of the TCNE molecule which were connected by a double bond, have become tetrahedrally bonded as a result of the Diels-Alder reaction. The bond lengths from C(7) and C(14) to the benzene rings

are of the order of 1.50–1.54 Å as found in triptycene (Karle & Estlin, 1969; Palmer & Templeton, 1968), a molecule with many similarities to the TCNE-anthracene adduct. However, bonds C(7)–C(16) and C(14)–C(15) which link the apical atoms with the tetracyanoethane are 1.58–1.59 Å and C(15)–C(16) which had been an ethylenic linkage before the adduct formation is 1.62 Å. These values were found in each of the four independent molecules. Each of these bonds is significantly longer than the usual value of ~1.54 Å for a single bond. The angles about C(15) and C(16) are nearly tetrahedral. The closing of the cage has affected the angles adjacent to the benzene rings. They have decreased from 120 to 113–114°. Since they still are larger than the tetrahedral value, the angles about the apical atoms C(7) and C(14) are forced to become smaller than 109.5°. The same disposition of angle values exists in the cage of the triptycene molecule.

In the tetracyanoethane group, the C–C and C≡N distances are ~1.46 and ~1.15 Å respectively. In free tetracyanoethylene (Bekoe & Trueblood, 1964) and in the TCNE-naphthalene complex (Williams & Wallwork, 1967) these distances are 1.43–1.44 Å and ~1.13 Å.

The thermal parameters for the adduct are largest at the periphery of the molecule. That is, they are largest for the N atoms, which have *B* values of 3 to 4 Å<sup>2</sup>, and for C(3), C(4), C(10) and C(11) of the benzene rings, which have *B* values up to 4.9 Å<sup>2</sup>. The cage appears to be very rigid. The solvent molecule, CH<sub>2</sub>Cl<sub>2</sub>, has large thermal factors, 6.4–7.7 Å<sup>2</sup>. This is often the case for solvent molecules which have been incorporated in a crystal structure. Atom C(21), part of the free TCNE molecule, has an unusually large thermal factor, not consistent with the *B* values for the other atoms in this molecule. The value is probably an artifact of the large number of variables and incomplete refinement. The coordinates of this atom are not well defined and consequently the bond lengths and angles about C(21) are not reliable.

We wish to express our appreciation to Mrs Janet Estlin for her aid in the data collection and intensity estimation.

#### References

- BEKOE, D. A. & TRUEBLOOD, K. N. (1964). *Abstr. Amer. Cryst. Assoc. Meeting*, Bozeman, Montana, p. 87.  
 GREENBERG, B. & POST, B. (1968). *Acta Cryst.* B24, 918.  
 JOHNSON, C. K. (1965). *ORTEP*, ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 KARLE, I. L. & ESTLIN, J. A. (1969). *Z. Kristallogr.* 128, 371.  
 KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* 16, 969.  
 KARLE, I. L. & KARLE, J. (1964). *Acta Cryst.* 17, 1356.  
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849.  
 MIDDLETON, W. J., HECKERT, R. E., LITTLE, E. L. & KRESPAN, C. G. (1958). *J. Amer. Chem. Soc.* 80, 2783.  
 PALMER, K. J. & TEMPLETON, D. H. (1968). *Acta Cryst.* B24, 1048.  
 WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* 22, 899.