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Molecular Complexes Exhibiting Polarization Bonding. XI. The Crystal and Molecular Structure of the 7,7,8,8-Tetracyanoquinodimethane-Anthracene Complex

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The 1:1 complex formed between 7,7,8,8-tetracyanoquinodimethane and anthracene crystallizes as deep green needles, space group $C2/m$, with two molecules of complex in the unit cell of dimensions $a = 11{\cdot}476 \pm 0{\cdot}011$, $b = 12{\cdot}947 \pm 0{\cdot}013$, $c = 7{\cdot}004 \pm 0{\cdot}007$ Å, $\beta = 105{\cdot}4 \pm 0{\cdot}2°$. The structure was solved by Patterson methods and refined by least-squares methods using 469 independent reflexions measured on a linear diffractometer. The final residual, R, was 0·111. The component molecules are stacked alternately in infinite columns which are parallel to the c axis with the mean plane of the molecules perpendicular to the stacking axis and a mean perpendicular separation of 3·50 Å. The central six-membered rings of the two types of molecule are orientated at 30° to each other.

Introduction

The 1:1 complex formed between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and anthracene was first described by Melby, Harder, Hertler, Mahler, Benson & Mochel (1962). The investigation of the crystal and molecular structure of the complex was carried out to provide comparison with the structures of complexes of aromatic molecules with tetracyanoethylene (TCNE) as exemplified by the naphthalene–TCNE complex described in Part IX (Williams & Wallwork, 1967).

Experimental

Deep-green needles of the complex were deposited after hot equimolar solutions of the components in tetrahydrofuran were mixed and allowed to cool very slowly. Microanalyses for carbon, nitrogen and hydrogen confirmed the 1:1 ratio of the component molecules in the complex. In plane polarized light the crystals exhibited strong pleochroism. The colours ranged from deep green to a straw colour as the plane of polarization of the light was rotated and maximum absorption occurred when the electric vector of the polarized light was vibrating parallel to the needle axis.

Oscillation and Weissenberg X-ray photographs were taken, using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å), with the crystal rotating about the b and the c (needle) axes. The cell dimensions, determined from the Weissenberg photographs, were refined with the use of a linear diffractometer (Arndt & Phillips, 1961), and intensity data for the $h0l$, $h1l$, ..., $h11l$ and the $hk0$, $hk1$, ..., $hk6$ reciprocal lattice levels were then collected with Mo $K\alpha$ radiation. A total of 469 independent reflexions with $\theta < 32{\cdot}5°$ were observed out of a possible total of 1800 accessible reflexions. Intensity measurements were made with a scintillation counter and a pulse height selector. The moving-crystal stationary-counter technique was employed. The crystal used was approximately cylindrical with a radius of 0·2 mm. No absorption corrections were applied to the data.

Crystal data

$C_8H_4(CN)_4.C_{14}H_{10}$, $M = 382{\cdot}43$. Monoclinic, $a = 11{\cdot}476 \pm 0{\cdot}011$, $b = 12{\cdot}947 \pm 0{\cdot}013$, $c = 7{\cdot}004 \pm 0{\cdot}007$ Å, $\beta = 105{\cdot}4° \pm 0{\cdot}2°$, $U = 1003$ Å^3, $D_m = 1{\cdot}25$ g.cm^{-3}, $Z = 2$, $D_c = 1{\cdot}26$ g.cm^{-3}, $F(000) = 396$. Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å), $\mu = 0{\cdot}84$ cm^{-1}. Absent spectra, hkl when $h+k$ odd. Space group $C2$ (no. 5), Cm (no. 8) or $C2/m$ (no. 12). Negative piezoelectric and pyroelectric tests indicate $C2/m$ and this is confirmed by refinement of the structure.

Determination and refinement of the structure

A trial structure was deduced from the $hk0$ and $h0l$ Patterson projections. The structure was partially refined through structure-factor, electron-density projection calculations to the stage where the reliability index,

$$R = \Sigma \,||F_o| - |F_c|| / \Sigma \,|F_o|\,,$$

was 0·21 and 0·16 for the $hk0$ and $h0l$ zones respectively. Structure factors were then calculated for the hkl reflexions followed by a three-dimensional Fourier electron-density summation, from which improved atomic coordinates were obtained.

Refinement was continued by the block-diagonal least-squares method with a program written by Dr R. D. Diamand. The weighting scheme employed was $\sqrt{w} = 1$ if $|F_o| < F^*$ otherwise $\sqrt{w} = F^*/|F_o|$, and the scattering factors of Hoerni & Ibers (1954) for carbon and nitrogen were used. The reflexions too weak to be observed were omitted from the analysis. Hydrogen atom parameters were not included. Four cycles of structure-factor least-squares using individual isotropic temperature factors improved R to 0·165. Refinement

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was then continued allowing the temperature factors of the atoms to vary individually and anisotropically. After four cycles of least-squares the refinement converged with $R=0{\cdot}111$ for observed reflexions. The comparison of observed and final calculated structure factors is shown in Table 6.

The final atomic coordinates and their estimated standard deviations (derived from the least-squares normal equations block-diagonal matrix) are summarized in Table 1. The anisotropic temperature factors are given in Table 2.

Table 1. *Final positional parameters* (*upper line*) *and their estimated standard deviations* (*lower line*)

	$10^4x/a$	$10^4y/b$	$10^4z/c$
C(1)	0000	1088	0000
	—	9	—
C(2)	1077	0551	0475
	7	6	12
C(3)	2214	1127	0938
	10	12	16
C(4)	3228	0499	1382
	9	13	15
C(5)	1271	0000	5509
	9	—	14
C(6)	0617	0975	5241
	6	5	11
C(7)	2506	0000	6026
	9	—	15
C(8)	3198	0929	6325
	6	6	12
N	3764	1657	6574
	6	6	12

Table 2. *Final atomic thermal parameters* ($\times 10^4$)

B_{ij} are coefficients in the temperature factor expression $\exp\,[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	198	87	367	000	205	000
C(2)	145	122	367	−55	140	−37
C(3)	230	297	443	−214	235	−116
C(4)	217	432	433	−152	156	−65
C(5)	116	69	268	000	129	000
C(6)	132	71	306	13	124	9
C(7)	122	72	318	000	83	000
C(8)	114	91	442	−1	123	28
N	149	100	634	−54	120	−3

Sections of the three-dimensional electron-density distribution and of the difference electron-density distribution were then calculated. These syntheses showed no unexpected features, confirmed the marked anisotropy of the anthracene molecule and clearly indicated the positions of the hydrogen atoms of the TCNQ molecule.

Least-squares planes through each of the molecules were calculated by the modification (Blow, 1960) of the method of Schomaker, Waser, Marsh & Bergman (1959). All of the atoms, other than hydrogen, in each molecule were used to define the planes and each atom used was given unit weight. The pertinent parameters of the planes, and the deviations of the atoms from them, are summarized in Table 3.

Table 3. *Molecular least-squares planes*

	TCNQ	Anthracene
Perpendicular distance in Å from the origin		
	3·502	0·000
Direction cosines of normal relative to orthogonal axes		
a	0·2533	0·2612
b	0·0000	0·0000
c^*	−0·9674	−0·9653

Perpendicular distance in Å of atoms from the mean planes

C(5)	0·013	C(1)	0·000
C(6)	0·010	C(2)	−0·010
C(7)	0·009	C(3)	0·006
C(8)	0·001	C(4)	−0·001
N(1)	−0·008		

The anisotropic thermal parameters of the atoms were used in an analysis of the rigid-body translational and librational motion (Cruickshank, 1956) of each molecule. The results of the analyses are given in Table 4 for the TCNQ molecule and in Table 5 for the anthracene molecule. The r.m.s. discrepancies between the observed and calculated U_{ij} values are 0·004 and 0·017 Å^2 for the TCNQ and anthracene molecules respectively. The method of Busing & Levy (1964) was used to correct the bond lengths of the TCNQ molecule for libration. The corrected bond lengths are illustrated in Fig. 1(*a*) together with the uncorrected bond lengths and angles and their e.s.d.'s. The bond lengths and angles and their e.s.d.'s for the anthracene molecule are illustrated in Fig. 1(*b*). No attempt was made to correct these for librational motion because it was so extreme as to cause atoms C(4) and C(4′) to be unresolved in one electron-density peak.

Description and discussion of the structure

The structure consists of infinite columns of alternate TCNQ and anthracene molecules stacked in a plane-to-plane manner in columns parallel to the *c* axis of the unit cell with the mean molecular planes perpendicular to this axis. Each cell contains two columns of molecules and the structure, projected along the *c* axis, is illustrated in Fig. 2. The mode of molecular overlap is such that the long axes of each molecule are parallel, and their centres are superimposed. The central hexagonal ring systems of the two types of molecule are orientated at 30° to each other, thereby avoiding direct overlap of the majority of the atoms. This relative orientation is not that for the optimum overlap of the π-orbital systems of the molecules but the structure is such that the aromatic system of the TCNQ molecule is overlapped by the entire aromatic system of the anthracene molecule. There is no suggestion of specific interaction involving C = C bonds as found in the structure of the naphthalene–TCNE complex (Williams & Wallwork, 1967).

The most surprising aspect of the structure is the relatively large intermolecular spacing (3·50 Å) of the

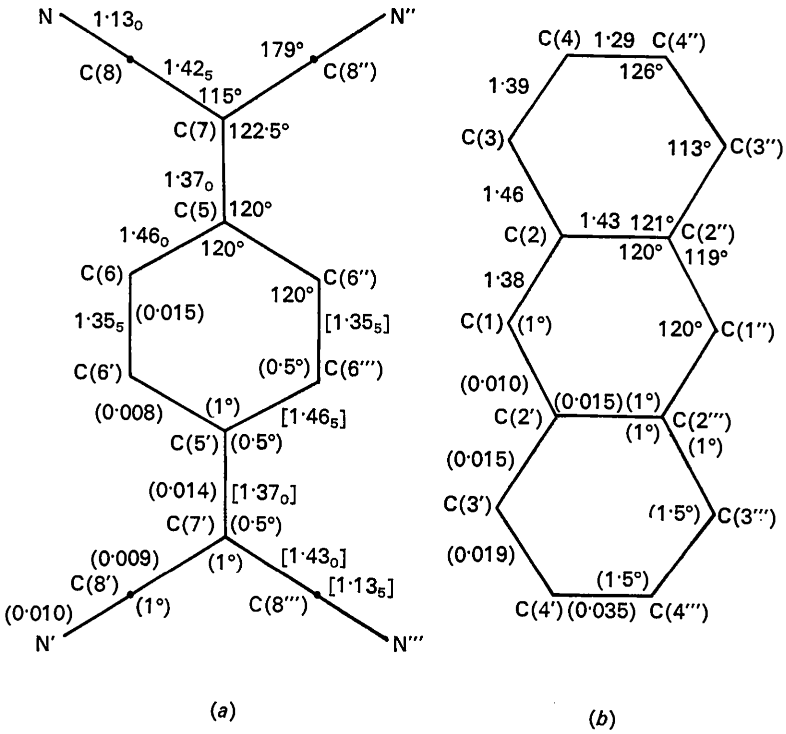

Fig. 1. Bond lengths (Å) and bond angles, with (in parentheses) their standard deviations, for (*a*) TCNQ, (*b*) anthracene. Values for TCNQ in square brackets are bond lengths corrected for libration.

Table 4. *Rigid-body thermal parameters for the TCNQ molecule*

(For the molecule centred at 0,0,½).

$$\tau\dagger=\begin{pmatrix}746 & -1 & 729\\ & 547 & 2\\ & & 536\end{pmatrix}\times 10^{-4}\ \text{Å}^2 \qquad \omega\dagger=\begin{pmatrix}32\cdot5 & 0\cdot1 & 8\cdot1\\ & 9\cdot3 & -0\cdot7\\ & & 8\cdot1\end{pmatrix}\ (^\circ)^2$$

Direction cosines ($\times 10^4$) for principal axes relative to orthogonal axes:

Eigenvalue	*a*	*b*	*c**	Eigenvalue	*a*	*b*	*c**
τ 0·0769 Å^2	9543	−7	2987	ω 34·8 (°)^2	9596	−32	2814
0·0547	139	−9988	−469	9·6	−450	−9888	1425
0·0513	−2984	−489	9593	5·8	−2778	1494	9490

U_{ij} (Å)$^2 \times 10^3$†‡

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(5)	79	56	71	−2	3	0
	1	4	0	6	2	2
C(6)	75	59	59	0	6	0
	−7	1	3	0	2	0
C(7)	76	68	75	0	2	1
	2	−7	−2	0	−6	−1
C(8)	80	77	102	−8	−5	2
	−9	0	0	6	1	9
N(1)	89	86	147	−16	−16	2
	8	−1	−1	−4	0	−3

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

‡ The numbers below the U_{ij} are the differences ($\times 10^3$) of U_{ij} derived from B_{ij} and those calculated from rigid-body parameters. The r.m.s. difference is 0·004 (Å)^2.

molecules within one stack, presumably due to the unfavourable relative orientation of the components. The four shortest approaches between atoms of adjacent molecules of the same column (C(1)–C(6) 3·57, C(2)–C(6) 3·58, C(2)–C(5) 3·58, C(4)–C(8) 3·58 Å) are, if anything, greater than the expected van der Waals distances. This implies that any charge-transfer interaction between the molecules is weak. This does not conflict with the existence of a low-energy, charge-transfer band in the spectrum of the complex, which causes its deep green colour. The fairly low ionization potential of anthracene and the high electron affinity of TCNQ inevitably produce an excited state of fairly low energy, but this will not stabilize the ground state of the complex by admixture of the two wave functions if the symmetries are inappropriate for overlap.

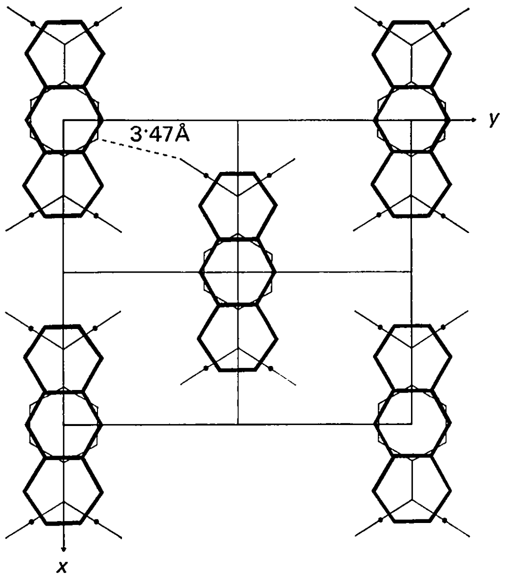

Fig. 2. The molecular arrangement, viewed along the c axis.

Both molecules are planar within experimental error and the molecular planes are inclined to each other at the small angle of ½°. The structure projected along the b axis is illustrated in Fig. 3.

The libration-corrected dimensions of the TCNQ molecule are in good agreement with the dimensions of the uncomplexed molecule (Long, Sparks & Trueblood, 1965). The r.m.s. discrepancy between the two determinations is 0·007 Å, much less than one e.s.d. No bond length differs by more than 1½ e.s.d. The maximum difference in the bond angles is also 1½ e.s.d., the r.m.s. difference being one degree.

The dimensions of the anthracene molecule [apart from the bonds and angles involving the atom C(4)] are in reasonable agreement with the weighted mean of the bond lengths determined by various authors and discussed by Cruickshank & Sparks (1960). The dimensions involving the atom C(4) are invalid for the reasons discussed above.

The thermal parameters, U_{ij} of the TCNQ molecule appear to be adequately explained on the basis of rigid-body librations and vibrations. The principal axes of both libration and of vibration correspond to within a few degrees of the natural molecular axes and there is appreciable libration only about the long axis in the plane of the molecule. The thermal parameters, U_{ij}, of the anthracene molecule are reasonably well explained on the basis of rigid-body motions. The dis-

Table 5. *Rigid-body parameters for the anthracene molecule*

(For the molecule centred at 0,0,0).

$$\tau\dagger = \begin{pmatrix} 973 & 32 & 89 \\ & 1192 & -1 \\ & & 583 \end{pmatrix} \times 10^{-4}\,(\text{Å})^2 \qquad \omega\dagger = \begin{pmatrix} 74{\cdot}0 & -0{\cdot}6 & -9{\cdot}3 \\ & 7{\cdot}0 & -1{\cdot}1 \\ & & 59{\cdot}3 \end{pmatrix} (^\circ)^2$$

Direction cosines (× 10^4) for principal axes relative to orthogonal axes:

Eigenvalue	a	b	c^*	Eigenvalue	a	b	c^*
τ 0·1196 (Å)^2	−1425	−9898	−67	ω 78·6 (°)^2	8954	−2	−4452
0·0989	9662	−1405	2159	54·7	−4451	259	−8951
0·0563	−2147	243	9764	4·3	117	9997	230

U_{ij} (Å)^2 × 10^3†‡

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	133	119	103	3	15	−1
	−17	−45	−18	−3	2	1
C(2)	107	147	73	−15	10	−7
	−15	−43	12	−4	−5	−1
C(3)	137	239	119	−65	12	−30
	−1	14	17	−9	6	4
C(4)	107	373	93	−42	3	−20
	−29	−7	7	−11	0	6

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

‡ The numbers below the U_{ij} are the differences (× 10^3) of U_{ij} derived from B_{ij} and those calculated from rigid-body parameters. The r.m.s. difference is 0·017 (Å)^2.

Table 6. *Comparison of observed and final calculated structure factors*

The asterisked line gives l, h; subsequent lines give k, $25F_o$, $25F_c$.)

•	0	0										
	12	392	311	10	418	431	8	184	185	6	-287	-246
	4	-1939	-1927	2	2728	3038						
•	0	1										
	9	411	374	7	-355	-220	5	-694	-765	3	673	787
	1	1193	1290									
•	0	2										
	8	-132	-100	6	-295	-311	4	-379	-342	2	-720	-696
	0	-1246	-1258									
•	0	3										
	15	-106	-108	13	-130	-20	11	-192	202	9	231	46
	7	-250	-227	5	-742	-702	3	-858	-852	1	1370	1371
•	0	4										
	12	-133	-68	10	170	196	8	245	314	6	-463	-508
	4	-205	-202	0	-991	-931						
•	0	5										
	9	-59	-89	7	306	392	5	203	418	3	-856	-832
	1	-714	-716									
•	0	6										
	12	-77	-26	10	96	18	8	-80	-41	4	-114	-105
	2	-144	-102	0	-120	-21						
•	0	7										
	1	-106	-214	9	91	58	5	156	149	3	314	347
	1	-214	-214									
•	0	8										
	6	413	434	4	276	297	2	59	24	0	97	113
•	0	9										
	3	179	188	1	184	214						
•	0	10										
	4	-87	-82									
•	0	11										
	9	-131	-71	5	116	81	3	-83	-94	1	-113	-116
•	0	12										
	2	85	32									
•	0	13										
	5	-82	-49									
•	1	0										
	10	-386	-414	8	-250	-283	6	-460	-435	4	-53	-99
	2	191	145	0	-198	-296						
•	1	1										
	7	103	98	5	190	150	3	-972	-964	1	397	471
•	1	2										
	10	89	122	8	255	244	6	132	67	4	1117	1125
	2	739	713	0	-1237	-1234						
•	1	3										
	7	275	312	5	338	271	3	-108	-101	1	-113	-140
•	1	4										
	14	-81	-55	10	162	224	6	-63	-51	4	-834	-846
	2	-519	-480	0	746	648						
•	1	5										
	9	379	383	5	-143	-183	3	224	298	1	129	69
•	1	6										
	6	265	265	2	-79	-74	0	336	292			
•	1	7										
	7	-244	-253	5	-373	-397	3	-175	-171	1	45	42
•	1	8										
	6	-292	-326	4	-188	-239	2	132	108	0	169	183
•	1	9										
	9	-68	-47	3	-56	-67	1	234	218			
•	1	10										
	8	74	25	6	-150	-90	2	71	119	0	77	114
•	1	11										
	1	70	69									
•	1	12										
	2	-77	-28									
•	1	-1										
	13	-114	-123	11	-313	-348	9	-360	-346	7	-272	-257
	5	-291	-332	3	-152	-167						
•	1	-2										
	12	76	99	8	-145	-118	6	348	331	4	-221	-260
•	1	-3										
	15	74	95	11	-73	-49	9	294	269	7	220	124
	5	545	485	3	1508	1494	1	-661	-699			
•	1	-4										
	12	89	14	8	211	155	6	429	379	4	-231	-252
	2	-453	-359	0	320	291						
•	1	-5										
	11	176	203	5	-469	-487	3	-782	-712	1	310	267
•	1	-6										
	10	324	205	8	318	340	4	57	94	2	226	273
	0	-59	-67									
•	1	-7										
	5	125	139	3	-232	-258	1	166	147			
•	1	-8										
	10	122	91	8	-87	-47	6	-454	-470	4	-297	-324
	0	57	44									
•	1	-9										
	11	-154	-29	7	-159	-127	5	-230	-282	3	-78	-66
	1	189	235									
•	1	-10										
	4	-81	-32	2	154	60	0	287	282			
•	1	-11										
	9	111	74	5	-85	-94	1	69	122			
•	2	0										
	10	253	263	8	134	199	6	-462	-470	4	-297	-315
	2	1124	1176	0	2056	2015						
•	2	1										
	11	-64	-62	7	-196	-189	5	-267	-280	3	-103	-91
	1	-893	-932									
•	2	2										
	12	86	85	10	136	106	8	-151	-116	6	-277	-259
	4	-795	-777	2	-41	-71	0	1328	1307			
•	2	3										
	9	263	302	7	-151	-66	5	-502	-470	3	69	25
	1	-241	-292									
•	2	4										
	10	-54	-75	8	102	125	6	264	310	4	-205	-201
	2	-699	-587	0	-645	-613						
•	2	5										
	7	-73	-42	5	-45	-29	3	-266	-243	1	-91	-56
•	2	6										
	8	93	54	4	199	204	2	117	120	0	-288	-289
•	2	7										
	7	189	223	5	309	309	3	91	108			
•	2	8										
	4	134	135	2	169	183	0	183	181			
•	2	9										
	5	-85	-92									
•	2	10										
	6	87	65	2	-82	-103	0	-105	-94			
•	2	12										
	6	-110	-31	4	-78	-57						

Table 6 (*cont.*)

• 2	-1										
11	385	360	9	229	275	7	57	48	5	-682	-702
3	-287	-293	1	4812	4746						
• 2	-2										
10	154	162	8	84	151	6	-554	-551	2	548	594
0	-25	-62									
• 2	-3										
9	-101	-82	7	-165	-157	5	-389	-314	3	-578	-529
1	-347	-334									
• 2	-4										
10	205	193	6	-432	-391	4	-655	-642	2	212	135
0	1097	1112									
• 2	-5										
9	225	245	5	-285	-253	3	-64	-62	1	-654	-634
• 2	-6										
10	-84	-107	8	69	37	6	341	343	4	-334	-289
2	-680	-681	0	-292	-279						
• 2	-7										
5	-56	-80	1	-79	-67						
• 2	-8										
6	175	172	4	269	282	0	-251	-254			
• 2	-9										
9	-99	-57	7	168	175	5	342	338	3	137	112
• 2	-10										
6	-191	-109	2	177	182	0	160	156			
• 2	-12										
0	-105	-99									
• 2	-13										
1	73	17									
• 3	0										
10	-108	-111	8	-140	-143	6	121	137	4	-273	-291
2	-348	-312									
• 3	1										
9	104	130	7	98	82	5	283	250	3	554	556
1	-170	-157									
• 3	2										
12	-69	-35	8	122	144	6	225	201	4	263	231
0	-261	-243									
• 3	3										
11	114	107	9	70	117	7	78	122	5	-286	-289
3	-608	-586	1	138	113						
• 3	4										
12	76	19	10	156	204	8	208	235	4	-92	-55
2	114	145	0	66	35						
• 3	5										
11	87	24	7	130	144	5	128	124	1	114	111
• 3	6										
8	-96	-56	6	-183	-190	4	-192	-208			
• 3	7										
13	-137	-46	7	-193	-173	5	-253	-299	1	90	101
• 3	8										
10	-64	-22	0	240	211						
• 3	-1										
13	-132	-137	11	-331	-343	9	-234	-250	7	-255	-248
5	-227	-227	3	129	141						
• 3	-2										
12	-111	-125	10	-233	-249	8	-187	-192	6	-102	-93
4	-223	-252	2	-56	-62	0	280	323			
• 3	-3										
11	64	63	7	82	60	5	160	169			
• 3	-4										
10	69	45	8	197	192	6	176	128	4	614	621
2	308	321	0	-638	-626						
• 3	-5										
7	171	199	3	-362	-419	1	125	120			
• 3	-6										
12	92	93	10	178	241	8	144	200	6	-170	-147
4	-381	-365	2	-109	-75	0	276	230			
• 3	-7										
9	187	196	7	169	157	3	84	111	1	95	57
• 3	-8										
10	82	14	4	-100	-129	2	-79	-93	0	178	155
• 3	-9										
7	-253	-232	5	-359	-371						
• 3	-10										
6	-127	-115	4	-128	-141	0	136	203			
• 3	-11										
1	152	149									
• 4	0										
6	-178	-189	4	-155	-43	2	-103	-86			
• 4	1										
7	-136	-107	5	-247	-259	3	-340	-319	1	227	248
• 4	2										
10	111	127	8	81	98	6	-256	-213	4	-228	-207
2	40	23									
• 4	3										
9	99	33	7	149	133	5	54	37	3	-204	-211
1	-391	-350									
• 4	4										
6	56	52	4	-124	-101	2	-188	-161	0	-69	-36
• 4	5										
3	111	111	1	-70	-60						
• 4	6										
6	191	206	4	171	182						
• 4	7										
3	91	100	1	110	110						
• 4	8										
2	68	31									
• 4	9										
3	-75	-44	1	-75	-64						
• 4	-1										
11	149	143	9	143	197	5	-309	-305	3	111	107
1	1111	1081									
• 4	-2										
10	215	236	6	-197	-166	4	-345	-337	2	818	815
0	1876	2026									
• 4	-3										
7	-112	-106	5	-205	-221	3	124	147	1	-42	-33
• 4	-4										
8	-87	-82	6	-140	-149	4	-299	-288	2	-186	-164
0	74	80									
• 4	-5										
11	90	86	9	114	109	7	-135	-108	5	-311	-300
3	-120	-144	1	235	236						
• 4	-6										
8	132	134	4	-152	-107	2	-251	-221	0	-427	-393
• 4	-7										
7	129	97	3	-334	-293	1	-226	-198			
• 4	-8										
4	52	37	0	-87	-88						
• 4	-9										
7	133	123	5	213	201	3	140	134	1	-59	-61
• 4	-10										
6	226	147	4	77	144	2	59	78	0	63	92
• 5	0										
6	76	67	4	146	142	2	60	74	0	-57	-55
• 5	1										
7	120	94	3	149	133	1	-65	-64			
• 5	2										
4	-179	-180	2	-143	-131	0	85	78			
• 5	3										
9	127	141	7	80	46	5	-98	-89	1	49	59
• 5	4										
8	61	69	6	66	68	4	59	34	0	82	74
• 5	5										
5	-99	-91	3	-86	-78	1	92	81			
• 5	6										
6	-152	-165	4	-98	-126	0	72	54			
• 5	7										
5	-95	-39	1	79	81						
• 5	8										
2	69	40									
• 5	9										
5	-88	-26									

Table 6 (*cont.*)

5	-1											
9	-104	-107	7	-47	-29	3	-172	-154	1	-85	-14
5	-2											
4	-123	-130	6	-237	-124						
5	-3											
9	-106	-121	7	-65	-50	5	-70	-58	3	-112	-108
1	72	85									
5	-4											
6	64	70	4	119	106	2	38	45			
5	-5											
9	85	66	7	95	101	5	186	150	3	202	203
5	-6											
8	52	75	4	-151	-150						
5	-7											
9	135	161	5	-142	-128	3	-87	-83			
5	-8											
8	117	101	6	69	50						
5	-9											
3	-86	-90									
5	-10											
4	-130	-151									
6	-2											
2	241	283	6	535	587						
6	-3											
·	465	518									

crepancies are probably due to the inaccuracies of the U_{ij} values for the atom C(4), caused by the interaction of thermal and positional parameters for this atom and its mirror-related atom C(4′). For anthracene, however, the axes of libration are not simply related to the molecular axes, except that both axes about which the libration is large are nearly perpendicular to the short axis in the plane of the molecule. Their combined effect is to add libration of the molecule in its own plane to the type of motion found for TCNQ.

There are no abnormal sideways intermolecular contacts in the structure. The closest approach, $d_{\mathrm{C}\cdots\mathrm{N}}=$ 3·47 Å, is shown in Fig. 2. There are no other intermolecular approaches of less than 3·57 Å. The *b* cell length seems to be determined by the size of the TCNQ molecule. The evidence for this is that the shortest intermolecular contacts, between stacks, involve only the TCNQ molecules. This explains the relatively small thermal librations and vibrations of the TCNQ molecule as compared with those of the anthracene molecule and the fact that anthracene, but not TCNQ, has librational motion in its own plane.

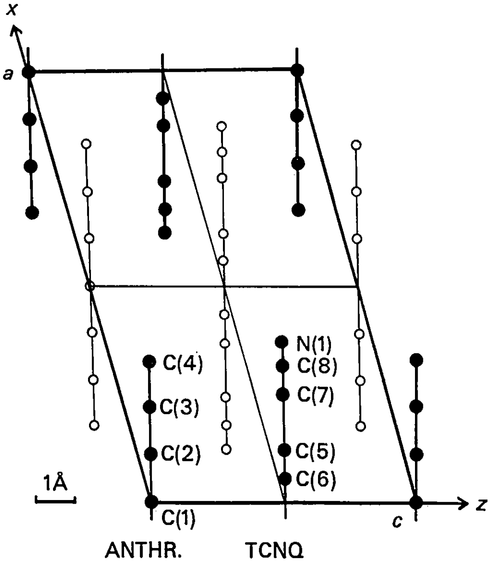

Fig. 3. The molecular arrangement, viewed along the *b* axis. Atoms belonging to molecules centred at $y=0$ and $y=0{\cdot}5$ are represented by full and open circles respectively.

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