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The Refinement of the Crystal Structure of the Pyrene–Tetracyanoethylene Complex

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Crystals of the 1:1 complex of pyrene and tetracyanoethylene (TCNE) are monoclinic, space group $P2_1/a$ with $a=14{\cdot}333$, $b=7{\cdot}242$, $c=7{\cdot}978$ Å, $\beta=92{\cdot}36°$, $Z=2$. The structure was refined by three-dimensional analysis by the block-diagonal least-squares method. Pyrene and TCNE molecules are stacked alternately along the *c* axis direction, making their molecular planes almost parallel to each other. The mean separation of the molecular planes is 3·323 Å.

Introduction

The crystal structures of π-molecular compounds usually have a common feature, namely that donor and acceptor molecules are alternately stacked, plane-to-plane, along one of the crystal axes with relatively small separation between molecular planes. This is in accord with the prediction based on the charge-transfer theory (Mulliken, 1952). It is not known, however, if the further details of mutual orientation of donor and acceptor molecules can be predicted from the charge-transfer theory. In order to clarify this problem, detailed theoretical and experimental investigations have to be carried out on some typical π-molecular compounds.

From this point of view, the molecular compound formed between pyrene and tetracyanoethylene (TCNE) is of particular interest, since, in the first place, the charge-transfer interaction is expected to be strong in this case because of the large electron affinity of TCNE, and, in the second place, this compound is suited for the theoretical treatment because the component molecules are of simple molecular structure with high symmetry. We have studied the visible and ultraviolet absorption spectrum of the crystal of this compound and have carried out a theoretical investigation of the charge-transfer interaction between pyrene and TCNE (Kuroda, Ikemoto & Akamatu, 1966*a*). We have already reported the results of the preliminary analysis of the crystal structure by using the two-dimensional method (Kuroda, Ikemoto & Akamatu, 1966*b*). The purpose of the present study is to elucidate the further details of the crystal structure of this molecular compound by the three-dimensional analysis.

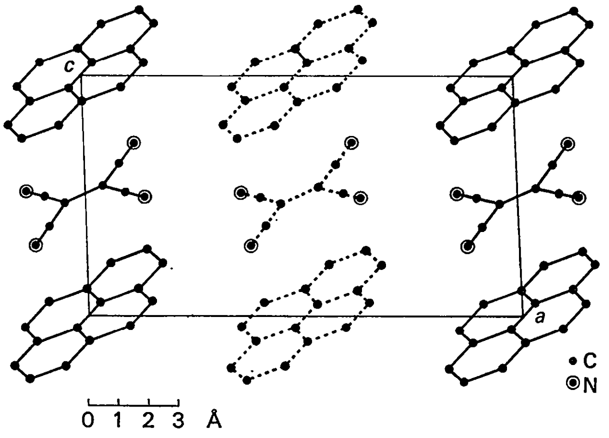

Fig. 1. Projection of the molecular arrangement on to the (010) plane.

Experimental

Lattice constants were redetermined by least-squares calculation based on the measurement of 10 diffraction lines with a diffractometer, Geigerflex. Quartz powder was used as the internal standard.

Crystal data

Monoclinic
$a=14{\cdot}333\pm0{\cdot}009$ Å
$b=\ 7{\cdot}242\pm0{\cdot}008$
$c=\ 7{\cdot}978\pm0{\cdot}004$
$\beta=92{\cdot}36°\pm0{\cdot}04°$
$V=827{\cdot}5$ Å^3
Formula $C_{16}H_{10}.C_6N_4$; F.W. 330·4
D_x (calculated density) $=1{\cdot}285$ g.cm^{-3}
D_m (measured density) $=1{\cdot}3\pm0{\cdot}02$ g.cm^{-3}
$Z=2$
$\mu=7{\cdot}5$ cm^{-1} (Cu $K\alpha$)
Space group $P2_1/a$ (from Weissenberg photographs)
(Absent spectra $h0l$ when h is odd, $0k0$ when k is odd).

The dark purple crystal of a lath shape of 0·3 mm length was used for data collection on a Weissenberg goniometer. A set of intensity data was obtained up to the 3rd layer around the *b* and *c* axes and the zero layer around [$\bar{1}$01]. The intensities were measured visually from multi-film Weissenberg photographs. Ni-filtered Cu $K\alpha$ radiation was used. No correction was made for absorption, while the correction for the Lorentz and polarization factors was made in the usual way. The data were placed on the same relative scale by the method of Rollett & Sparks (1960). In all, 1438 independent reflexions from 1889 possible reflexions were obtained, but the intensity was not measurable on 429 of them.

Refinement

The structure was refined by the least-squares method. The calculation was carried out by means of the computer program written by Y. Okaya and modified by T. Ashida. This program uses the block-diagonal approximation with a 9×9 matrix for each atom with anisotropic temperature factors and a 4×4 matrix for each atom with an isotropic temperature factor. The scale factor is refined by assuming the overall temperature factor. The weighting scheme used was $W = 1{\cdot}0$ for $F_o \geq 2{\cdot}7$ and $W = 0{\cdot}5$ for $F_o < 2{\cdot}7$.

The parameters previously reported (Kuroda, Ikemoto & Akamatu, 1966*b*) were used as the starting values of the refinements, by introducing anisotropic temperature factors in place of the previous isotropic temperature factors. After several cycles of refinement neglecting hydrogen atoms, the R value decreased to 15%. The positions of all hydrogen atoms were determined by the usual $(F_o - F_c)$ synthesis. These hydrogen atoms were then included in the subsequent refinements assuming a common isotropic temperature factor.

Finally R decreased to 13·8%, excluding non-observable reflexions. Final parameters with their standard deviations are given in Table 1 and F_o and F_c are compared in Table 2.

Discussion

The arrangement of molecules in the crystal is shown in Fig. 1. The donor and acceptor molecules are stacked alternately along the c axis.

The molecules can be considered planar. The equations of the planes of pyrene and TCNE were calculated by the method of least-squares. The equations are:

$$-0{\cdot}4274X + 0{\cdot}4265Y + 0{\cdot}8141Z = 0$$

Table 1

(*a*) Atomic coordinates in fractions of cell edges and their standard deviations in 10^{-3} Å

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Pyrene						
C(1)	0·1433	9	−0·2742	10	0·2663	8
C(2)	0·1750	8	−0·1041	10	0·2157	8
C(3)	0·1193	7	0·0101	9	0·1078	7
C(4)	0·0291	7	−0·0571	8	0·0550	7
C(5)	−0·0027	7	−0·2304	8	0·1089	7
C(6)	0·0558	9	−0·3402	9	0·2114	8
C(7)	0·1502	8	0·1854	9	0·0525	8
C(8)	0·0935	4	0·2939	9	−0·0517	8
H(1)	0·177		−0·349		0·374	
H(2)	0·229		−0·060		0·271	
H(3)	0·024		−0·439		0·239	
H(4)	0·218		0·246		0·095	
H(5)	0·093		0·448		−0·073	
TCNE						
C(9)	0·0423	8	0·0097	10	0·5328	8
C(10)	0·0849	8	−0·1374	9	0·6360	8
C(11)	0·0968	8	0·1788	10	0·5066	8
N(1)	0·1213	8	−0·2454	9	0·7159	8
N(2)	0·1406	8	0·3038	9	0·4902	8

(*b*) Thermal parameters. The β's are used in the expression: $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})\}$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pyrene						
C(1)	0·00596	0·02462	0·01379	0·00771	0·00182	0·00155
C(2)	0·00385	0·02425	0·01486	0·00267	−0·00129	0·00090
C(3)	0·00370	0·01853	0·01096	0·00032	0·00043	−0·00169
C(4)	0·00325	0·01533	0·00932	0·00121	0·00054	−0·00358
C(5)	0·00417	0·01390	0·01154	−0·00104	0·00119	−0·00208
C(6)	0·00646	0·01562	0·01145	0·00030	0·00205	0·00281
C(7)	0·00428	0·02071	0·01379	−0·00375	−0·00006	−0·00236
C(8)	0·00570	0·01744	0·01411	−0·00646	0·00306	−0·00157
TCNE						
C(9)	0·00526	0·02152	0·01325	0·00184	−0·00207	−0·00820
C(10)	0·00487	0·01915	0·01153	0·00404	−0·00446	0·00262
C(11)	0·00489	0·02130	0·01393	0·00135	−0·00284	0·00272
N(1)	0·00707	0·02566	0·01858	0·00667	−0·00316	0·00804
N(2)	0·00585	0·02477	0·02240	−0·00588	−0·00148	−0·00001

Table 2. *Observed and calculated structure factors and their difference* (× 10)

H	FO	FC	DF
K,L= 0 0			
2	695	725	-30
4	713	-782	69
6	130	105	25
8	240	198	42
10*	27	-32	4
16*	23	-31	7
K,L= 1 0			
1	565	608	-42
4	63	55	7
5	49	41	8
6	211	165	46
7	62	41	20
8	113	75	37
10*	9	-11	2
11*	9	10	0
12*	23	-1	-22
13	62	-65	3
14	60	-53	-6
15	64	-66	1
16*	19	-22	3
18	42	37	4
K,L= 2 0			
0	549	-618	69
1	118	115	3
2	104	48	55
4	432	442	-10
5	50	-32	-17
6	55	-58	2
7*	14	20	-6
8	194	-177	-16
9	37	-45	7
10	38	-32	-5
11*	12	14	-2
12	117	-109	-8
13	80	69	11
14	127	-124	-3
17*	11	20	-8
K,L= 3 0			
1	254	226	28
2	149	130	19
3	75	73	2
4	49	37	12
5	60	-44	-15
6	170	153	17
7*	14	8	5
8*	28	32	-4
9	30	-20	-10
10	54	-49	-4
11	158	-154	-4
12	66	63	2
13	116	-105	-10
14	72	74	-1
17*	18	16	2
K,L= 4 0			
0	263	243	20
1	98	76	21
2	120	98	21
3	40	32	7
4	58	-58	0
5	46	44	2
6	80	84	-3
7	108	111	-3
8	214	207	7
9	37	45	-7
11*	12	12	0
12	84	-85	0
13*	22	35	-13
16*	13	20	-6
K,L= 5 0			
2	38	37	1
3	83	87	-3
4	62	-66	4
5*	20	19	1
6	61	-61	0
7	35	38	-2
8	54	60	-5
9	31	43	-12
10	66	68	-2
11	42	-32	-10
12*	15	18	-3
13*	20	-18	-1
14*	18	17	1
15*	8	11	-3
K,L= 6 0			
0	65	67	-2
1*	27	-30	2
2	33	38	-5
4	65	-73	8
5	39	42	-3
6	109	-102	-7
7*	19	16	3
8	42	-46	4
9*	17	18	0
10	37	-39	1
11*	25	18	6
12*	26	-23	-2
K,L= 7 0			
1*	26	24	2
2	105	-118	13
3	76	-78	2
4	30	33	-2
5	100	-99	-1
6	72	83	-10
7*	17	-20	3
K,L= 8 0			
1	31	-34	2
3*	29	-31	1
K,L= 9 0			
2	41	45	-4
3*	13	16	-3
K,L= 0 1			
-16*	12	-16	4
-14*	23	-25	2
-12	33	-23	-10
-10	32	46	-13
-8	323	339	-15
-6	318	319	0
-4	69	-60	-8
-2	449	411	37
0	193	186	7
2	199	-153	-46
4	565	495	70
6	74	70	3
8	152	-155	2
10	54	60	-5
12	56	68	-11
16	32	37	-5
K,L= 1 1			
-16*	18	27	-8
-15*	17	-16	0
-14*	22	38	-15
-12	39	33	5
-10	94	-83	-11
-9	87	64	23
-8	176	-136	-39
-7	305	251	53
-6	172	151	20
-5	78	-57	-21
-4	233	194	39
-3	331	-301	-30
-2	229	208	20
-1	185	155	30
0	301	303	-2
1	163	-152	-10
2	67	70	-2
3	85	-77	-8
4	248	208	39
5	349	294	55
6	274	206	67
7	277	224	53
10	41	6	35
11	101	-86	-15
12	62	52	9
13	74	-60	-14
15	41	37	4
18*	18	18	0
K,L= 2 1			
-17	33	36	-2
-16*	16	-19	2
-14	39	-44	4
-13	94	-94	0
-12	32	29	3
-11*	8	-22	14
-10	61	56	4
-9	57	64	-7
-8*	6	-18	11
-7	71	71	0
-6	138	-122	-16
-5	46	47	-1
-4	202	-202	0
-3	81	-84	3
-1	155	-140	-14
0	38	45	-7
1	307	-278	-29
2	304	-261	-42
4	389	-331	-58
5	442	378	64
6	68	62	6
7	101	87	13
8	193	171	21
9	63	-59	-4
10	63	-55	-8
11	133	114	18
12	154	-143	-10
13	44	41	2
14*	13	-20	7
15	44	-46	2
16*	11	17	-5
K,L= 3 1			
-17*	16	17	0
-15	38	-43	4
-14	78	-75	-3
-13	69	-74	4
-12	80	-75	-5
-11	124	118	5
-10	64	-64	0
-9	138	131	7
-8	101	-103	2
-7	235	-222	-13
-6	71	-67	-3
-5	183	-160	-22
-4	116	-99	-17
-3	284	257	27
-2	172	-144	-27
-1	213	175	38
0	95	86	9
1	36	-44	8
2*	27	-32	4
3	140	-126	-14
4*	27	20	7
5	342	-282	-59
6	122	103	19
7	142	-129	-13
9	101	95	6
10*	22	22	0
11	102	89	12
14	47	-42	-4
15*	14	-24	10
17*	15	-20	5
K,L= 4 1			
-10	148	124	24
-9	237	-218	-18
-8	49	49	0
-7	174	-175	0
-6	106	-110	3
-5*	25	25	0
-4*	24	-40	16
-3	73	-70	-3
-2	39	15	24
-1	58	62	-4
0	115	94	21
1	231	207	24
2	90	84	6
3	72	-64	-7
4	52	-51	-1
5	79	-63	-15
7	156	138	18
8	151	121	29
9	93	86	6
10	116	97	18
11	54	-51	-2
12	44	53	-8
13*	28	-36	8
15*	11	20	-8
16*	13	-16	3
K,L= 5 1			
-10*	9	27	-17
-8	45	-47	1
-7	50	51	0
-5*	28	34	-6
-4*	15	28	-12
-3	76	-81	5
-2*	26	31	-4
-1	36	-42	6
0*	8	13	-4
1	40	26	13
3	121	-124	2
4	56	64	-7
6	145	125	19
7	251	210	40
8	92	82	9
9	60	43	17
11	52	-61	9
12*	27	41	-13
14	41	45	-3
15	41	38	2
K,L= 6 1			
-9	48	59	-10
-7*	14	-23	9
-5	81	-85	4
-2*	29	-42	13
-1*	15	14	1
0	68	-71	2
2	117	-117	0
3	167	159	8
4	106	-101	-5
5	129	115	14
6	38	38	0
7	38	-50	12
8*	12	15	-2
9*	27	-32	5
10	49	-65	15
11	40	49	-8
13	41	47	-5
K,L= 7 1			
-9	59	58	0
-7	33	-43	9
-6	58	-72	13
-5	100	-118	17
-4	49	-46	-2
-3	59	-81	21
-1	62	-66	4
1	56	-63	7
2	62	50	11
4	36	38	-1
6	52	-46	-5
10*	17	26	-8
11*	9	6	2
K,L= 8 1			
-8	31	29	2
-4	44	-42	-1
-2	39	-35	-4
-1*	19	-24	4
1	30	-46	16
3*	24	-35	11
7	36	38	-1
8*	21	28	-6
9	30	30	0
K,L= 0 2			
-16	88	-95	6
-14*	26	-33	6
-10	87	82	4
-8	156	154	1
-6	48	-53	5
-4	154	142	11
-2	746	805	-59
0	266	308	-42
2	194	-189	-4
4	180	-174	-6
6	61	-59	-1
8	35	31	3
16	60	-61	1
K,L= 1 2			
-17	33	-27	-6
-15*	17	-28	11
-10	128	114	13
-8	88	70	17
-7	34	-23	-11
-6	415	-349	-66
-5*	29	-29	0
-4	71	66	4
-3	584	608	-24
-2	1201	1357	-156
-1	573	644	-70
0	417	450	-33
1	35	27	8
2	587	-622	34
4	39	35	3
5	42	18	23
6	288	231	57
9	57	-46	-10
10	117	92	24
11	169	-131	-38
12	141	99	41
13	86	-78	-7
14*	12	-11	0
17*	15	-26	11
K,L= 2 2			
-17*	16	-23	6
-14*	25	-34	9
-13	56	55	0
-12	40	-45	5
-11*	24	26	-2
-10*	8	-17	8
-9	64	-66	2
-8*	21	21	0
-7*	28	-20	-7
-6	31	17	13
-5	80	-73	-7
-4	209	169	40
-3	74	-65	-8
-2	319	297	22
-1	166	141	24
0	102	101	0
2	115	58	56
3	205	163	41
4*	14	-4	-9
5	232	175	57
6*	9	1	7
8	39	-30	-9
9	100	97	3
10	169	-145	-24
11	115	92	22
12	178	-167	-10
13	42	-52	9
16	41	27	14
17*	5	12	-7
K,L= 3 2			
-16	69	-70	0
-15	80	-71	-9
-14	42	-44	1
-13	65	-65	0
-11	48	56	-8
-10	163	-164	0
-9	76	75	0
-8	136	-133	-3
-7	68	63	4
-6	159	137	21
-5	144	119	24
-4	102	-67	-35
-3	59	34	25
-2	355	-307	-47
1	113	97	15
2	228	194	33
4	39	29	9
5*	16	-17	0
6	208	-181	-27
8	57	-59	1
9	94	-90	-4
10	56	52	3
11	109	-106	-2
12*	15	-18	3
15	48	47	1
K,L= 4 2			
-9	71	-60	-10
-8	76	-65	-11
-7*	18	-17	0
-6	37	-42	4
-5	35	-38	3
-4	63	66	-2
-2	86	78	8
-1	157	132	24
0	118	105	13
2	89	89	0
3	59	-55	-4
4	145	115	30
5*	11	19	-8
6	59	56	2
8	145	-106	-39
10	127	-105	-22
11*	8	16	-7
13*	22	31	-8
K,L= 5 2			
-8	45	44	1
-7	45	-43	-1
-4*	12	-8	-3
-3	37	47	-9
-2	31	33	-1
-1	155	135	20
0	36	26	10
1	31	23	7
2*	24	37	-13
3	77	-80	2
4	148	132	16
5	55	63	-8
6	195	171	24
7*	26	41	-15
8	91	79	12
9	77	-68	-8
K,L= 6 2			
-8*	12	25	-13
-7*	25	27	-1
-5	104	107	-3
-4	53	-68	15
-3*	21	49	-28
-2*	22	20	2
-1	65	-61	-4
0	107	108	-1
1	30	24	5
2	102	-86	-15
3	125	108	16
4	156	-132	-24
5	65	63	2
6*	21	31	-10
7	44	48	-4
8*	12	27	-15
K,L= 7 2			
-8	50	-53	2
-7	60	-54	-5
-6	33	-37	3
-5*	24	-32	8
-4	55	60	-5
-2*	25	33	-7
-1*	25	35	-9
0	41	-41	0
1*	20	18	2
2	32	-28	-4
3*	20	-22	2
4*	20	-20	0
K,L= 8 2			
-7	65	-55	-10
-6	33	-29	-3
-5	55	-48	-6
-4	67	59	8
-2	31	28	2
0	67	-65	-1
1*	26	-30	4
2*	29	-30	0
3*	24	-24	0
4	50	27	22
K,L= 9 2			
1	44	-39	-4
K,L= 0 3			
-16*	29	-35	5
-12	32	40	-8
-10	178	187	-8
-8	60	70	-10
-6	221	-235	13
-4	232	-179	-53
-2	159	-162	3
0	202	-204	1
2	54	-11	-43
4	86	86	0
6	103	96	7
8	31	-38	6
10	159	-144	-14
14	53	59	-5
16	57	-42	-14
K,L= 1 3			
-17*	22	-20	-2
-14	43	-35	-7
-11	39	38	0
-10	122	104	18
-9	99	79	20
-8	182	141	41
-7	37	-40	3
-6	87	80	6
-5*	13	2	10
-4	115	99	16
-3	264	209	55
-1	36	25	11
0	70	-62	-7
1	110	-76	-33
2	514	446	67
3	149	-107	-41
4	243	183	60
6	267	-216	-51
7	65	58	7
8	75	62	13
9	137	-101	-35
10	260	213	47
11	111	-77	-33
13	73	64	9
14*	16	-13	-2
16	49	42	7
17	58	-38	-20
K,L= 2 3			
-14	38	33	4
-13	53	-60	6
-12	72	69	2
-11	99	-99	0
-10	47	56	-9
-9	97	95	1
-8*	7	-10	3
-7	98	88	9
-6*	6	14	-7
-5	228	-185	-43
-4	263	228	34
-2	146	116	30
-1	51	35	16
0	88	-73	-15
2	56	-43	-12
3	480	424	56
5	353	284	68
6	74	56	18
7	67	-45	-21
8*	7	36	-28
9	79	-63	-15
11	47	-49	1
15	36	38	-2
16*	27	-19	-7
K,L= 3 3			
-16	43	-44	0
-15	49	-48	-1
-13	35	37	-1
-12	70	-71	1
-11	158	158	0
-10	133	-115	-18
-9	42	50	-8
-7	85	-77	-8
-6*	27	-31	3
-5*	22	-7	-14
-4	108	-76	-31
-3*	6	-4	-1
-2*	9	31	-21
-1	175	-144	-30
0	144	-126	-17
1	87	-90	3
2	116	-107	-9
3	80	64	16
4	156	141	14
5	49	49	0
6	102	96	6
7*	16	24	-7
8	66	-58	-8
9	109	95	14
10	110	-103	-7
11	35	35	0
12*	24	-33	9
13	45	-45	0
14*	29	29	0
16*	27	-28	1
K,L= 4 3			
-9	147	-127	-19
-8	46	-51	4
-7	67	-70	3
-6	41	-35	-6
-5	68	69	0
-4	33	-37	4
-3	102	71	30
-2	45	35	9
2	178	-161	-17
4	64	-63	0
5	103	-87	-16
6	59	53	5
7*	16	32	-16
8	60	38	22
9	108	102	6
12*	28	-30	2

Table 2 (*cont.*)

H	FO	FC	DF
13•	28	-32	4
15	36	-27	-8
K,L= 5 3			
-9	56	-66	10
-8	75	-72	-2
-6	37	-33	-3
-5•	17	-34	16
-4	37	34	3
-2	117	97	19
-1	48	47	1
0	168	153	15
1	197	-185	-12
2	149	138	10
3	167	-144	-23
4	33	25	8
5	179	157	22
6	38	41	-2
7	127	101	26
8	98	93	4
9	42	-54	12
10	38	50	-12
11•	15	-20	4
12•	13	-8	-5
13	31	26	5
14•	29	-24	-5
K,L= 6 3			
-7•	10	24	-14
-6•	10	-27	16
-4	42	-53	10
-3•	23	28	-4
-2•	25	-30	4
-1	64	56	8
0	86	-78	-7
1	46	39	7
2	54	-50	-4
3•	28	28	0
4	150	135	15
5	97	86	11
6	119	104	15
7	58	53	5
8	31	-31	0
12	43	50	-6
K,L= 7 3			
-8	35	-38	3
-7	33	-38	4
-5•	16	-29	13
-3•	20	-20	0
1•	24	31	-7
3	43	44	0
8•	15	-34	18
9•	24	23	0
10•	17	6	10
K,L= 8 3			
-8	40	-41	1
-7	56	-55	-1
-5•	8	-24	16
-4	32	-25	-7
-3	30	-25	-4
-2•	24	-17	-6
1•	26	17	9
2•	16	-11	-4
3	40	31	8
4	42	-40	-2
K,L= 0 4			
-16•	12	-24	11
-12	37	-57	19
-10•	14	-21	6
-8	94	110	-16
-6	100	90	9
-4	243	-247	3
-2	127	-127	0
0	328	333	-5
2•	22	29	-6
4	175	-179	3
8	138	-172	34
10	200	-233	33
14•	10	-42	32
16	45	-50	5
K,L= 1 4			
-17•	25	-22	-3
-15	31	-31	0
-14•	23	30	-7
-11	57	58	-1
-10	34	32	1
-9•	28	24	3
-8	56	-41	-14
-7•	16	20	-3
-6	67	-64	-2
-5	301	247	54
-4	224	163	61
-3	302	226	75
-2	179	120	59
0	130	-95	-34
1	160	-123	-37
2	33	11	22
3	198	-133	-64
4	33	21	12
6	34	34	0
7	76	-74	-2
8	186	131	55
9	204	-166	-37
10	139	99	39
11	39	-39	0
14	61	-40	-21
15	58	-39	-18
16	30	-27	-3
K,L= 2 4			
-16•	6	-11	5
-15•	24	20	4
-13•	26	-38	11
-12	97	106	-8
-11	55	-57	2
-10	97	101	-4
-9	39	-43	4
-8	98	-95	-3
-7	97	-90	-6
-6	120	103	17
-5	172	168	3
-4	598	550	48
-3	402	348	54
-2	300	247	53
0	220	-184	-36
1	34	-24	-9
2	37	-32	-5
3	81	58	22
4	210	168	42
5	46	-58	11
6•	7	16	-9
7	39	36	3
8	99	-95	-4
9	89	81	7
10	35	-51	16
11•	23	-30	7
13	36	-48	11
16•	22	20	1
K,L= 3 4			
-13	34	41	-6
-12	58	-70	11
-10•	18	-11	-7
-8•	16	23	-6
-7•	17	17	0
-6•	29	-26	-2
-5	70	66	4
-4	59	65	-6
-3	56	56	0
-2	47	46	1
-1	59	61	-2
0•	18	-20	2
1	137	132	5
3	129	118	11
6	30	21	8
7	62	-58	-3
8	60	60	0
9	92	-87	-5
10	34	-45	10
11	73	-83	10
12	35	-44	8
13•	22	19	2
15	43	45	-1
K,L= 4 4			
-4	39	-35	-4
K,L= 5 4			
-4•	26	33	-6
K,L= 6 4			
-4•	16	18	-1
K,L= 8 4			
-4•	29	26	2
K,L= 0 5			
-16•	23	25	-2
-10	46	-44	-1
-8	76	-78	1
-4	57	57	0
0	281	-286	4
2	176	-186	10
4	189	209	-20
6	34	-45	10
8	257	-331	73
10•	25	-26	0
12	70	87	-16
14	62	-64	1
K,L= 1 5			
-15	37	29	7
-14	49	-38	-10
-13	105	85	19
-11	45	42	3
-10	82	73	9
-9	60	-49	-10
-8	59	-48	-11
-7•	18	27	-9
-6	185	-149	-35
-5	68	50	17
-4	105	-84	-20
-3	74	-50	-24
-2	57	-44	-13
-1	68	-61	-7
0	171	115	56
1	207	-150	-57
2	282	191	91
3	93	-80	-12
5	77	56	21
6	65	-58	-7
8	83	-69	-14
10•	18	-17	-1
11	49	48	0
12	35	34	1
13•	18	-15	-3
K,L= 2 5			
-15•	19	-22	3
-14	63	63	0
-13	78	-71	-7
-12	158	133	25
-11•	11	15	-3
-10	36	34	2
-9	57	49	8
-7•	8	-4	-4
-6	123	107	15
-5	59	72	-12
-4	30	17	13
-3	38	36	2
-2	47	-51	4
-1•	7	-13	6
0	135	112	23
1	91	77	13
2	34	35	0
3	51	54	-2
4	86	-86	0
6	55	59	-3
7	70	-69	0
8	155	142	13
9	65	-56	-8
10•	20	34	-14
11	35	43	-8
12•	28	-21	-7
13	32	44	-12
15•	22	-20	-1
K,L= 3 5			
-12•	9	-8	0
-11	52	57	-5
-9•	12	18	-5
-7	46	-45	-1
-6	60	68	-7
-5•	25	29	-3
-4	67	68	0
-3•	26	27	0
-2•	26	-27	1
-1	70	-68	-2
0	97	98	0
1	47	47	0
2	155	141	13
3	166	151	15
4•	8	23	-15
5•	26	26	0
7	54	-55	0
9•	27	-38	10
13	37	37	0
14	36	-29	-6
K,L= 4 5			
-5•	21	18	2
K,L= 6 5			
-5	31	26	5
K,L= 0 6			
-14•	27	-7	-19
-8	93	105	-11
-6	60	65	-5
-2•	27	28	0
0	86	-89	3
2	66	-60	-5
6	179	-218	38
8	170	-207	36
K,L= 1 6			
-14	79	-58	-21
-13	64	51	12
-11	55	23	32
-10•	18	20	-1
-9	39	34	5
-7	87	55	31
-6	124	-105	-18
-4	49	-45	-3
-2	123	92	30
0	48	39	8
1	57	-37	-19
2	134	-93	-41
5	50	-46	-4
7	220	-174	-46
8	60	-54	-5
9	73	-62	-11
10•	17	-36	18
11•	19	18	1
12	37	-50	12
14	63	-45	-18
K,L= 2 6			
-14	59	57	1
-13•	17	-7	-9
-12	41	41	0
-11•	9	16	-7
-10•	13	-23	10
-9•	14	-19	5
-8	45	32	12
-7	54	54	0
-6	154	121	32
-5	146	126	20
-4	83	72	11
-1	87	-92	5
1	70	-78	7
2	33	28	4
3•	8	-19	11
5	61	51	9
6	64	-64	0
7	49	47	1
8•	28	-40	12
9•	8	17	-8
13	68	-73	4
K,L= 3 6			
-12•	28	36	-7
-11•	21	-23	1
-10•	9	-16	6
-9	30	-39	9
-8•	8	16	-7
-7	113	115	-2
-6	189	173	16
-5	246	218	28
-4	113	90	22
-3•	9	27	-18
-2•	9	-11	2
-1	90	-86	-4
0	47	57	-9
1•	9	11	-2
2	70	67	2
3•	9	-25	16
4	63	58	4
5	79	-81	1
6	53	48	5
7•	20	-19	0
9•	22	-17	-5
10•	9	-22	13
11•	15	-27	12
13•	23	13	10
K,L= 4 6			
-6	35	32	3
K,L= 6 6			
-6	35	38	-3
K,L= 0 7			
-12•	25	-34	8
-8	95	112	-17
-6	59	74	-14
-2	127	-139	11
0	196	-208	11
4	44	60	-15
12	36	-38	1
K,L= 1 7			
-13	35	28	6
-11	44	-31	-12
-8	48	-38	-10
-7•	21	10	10
-2	104	-73	-30
-1	101	-73	-28
0	39	-38	-1
1	39	-34	-4
2	122	88	34
3	48	41	7
4	51	-44	-6
6	254	-214	-40
8	75	-51	-23
10	110	74	36
12•	12	-18	5
K,L= 2 7			
-12•	28	28	0
-10•	11	-13	1
-8•	25	-36	11
-6•	26	-36	9
-5	30	-30	0
-4•	23	-28	5
-2•	25	-28	3
-1	42	41	1
2	30	28	2
6	40	-50	9
7•	18	-15	-2
10•	27	27	0
K,L= 3 7			
-12•	5	14	-9
-11•	22	22	0
-8	55	60	-5
-7•	24	36	-12
-6	41	44	-3
-4•	28	31	-2
-3	105	-112	6
-2	162	159	2
-1	55	-61	6
0	79	77	2
1	55	57	-1
2	67	-70	2
3•	18	13	4
5	36	-48	12
6	80	79	0
7•	9	-18	9
9	35	34	0
11	37	50	-12
K,L= 4 7			
-7	53	53	0
K,L= 5 7			
-7•	12	-13	0
K,L= 0 8			
-10	39	49	-10
-8	82	78	3
-4•	11	-30	19
-2	38	-40	2
0•	25	30	-5
2•	23	29	-6
4	66	-81	14
6	61	-69	8
10•	17	43	-25
K,L= 1 8			
-8	71	15	56
-3	37	16	21
-2	66	-52	-13
0	73	-48	-24
3	79	-63	-15
5	204	-139	-65
6	63	-48	-14
7	80	-62	-17
K,L= 2 8			
-7•	21	-31	10
-4	33	5	28
-3	43	52	-9
-2•	28	-37	8
0	30	-33	3
2	37	-40	3
3	42	46	-3
4	85	-93	8
5	41	-41	0
6	94	-72	-21
7	35	-45	9
K,L= 3 8			
-10	36	40	-3
-9•	6	11	-4
-8	70	63	6
-7	99	91	8
-5•	9	19	-10
-4•	25	31	-6
-3	111	-102	-9
-2	71	62	9
-1	71	-69	-2
0•	9	12	-3
1•	9	-15	5
2•	19	15	4
3•	15	-14	-1
4•	7	3	3
9•	25	-32	6
K,L= 4 8			
-8	69	67	2
K,L= 0 9			
-2•	26	-26	0
0	32	-40	7
2	31	39	-8
4	105	118	-12
6	46	55	-8
K,L= 1 9			
-3	114	-71	-43
-2	61	-54	-6
-1•	18	-31	12
K,L= 2 9			
-6•	21	-21	0
-5	48	54	-6
-4	128	-107	-20
-3	36	38	-2
-2	68	-63	-5
-1•	7	-20	12
0	63	55	7
4	120	-116	-4
5	33	-33	0
6•	28	-27	-1
K,L= 3 9			
-7•	25	-27	1
-6•	13	16	-2
-5	58	-54	-4
-4	56	49	7
-3•	21	-22	0
-1•	23	30	-6
0•	18	-25	6
4•	19	-7	-11
K,L= 0 10			
-2•	27	33	-5
2	45	-48	2

for pyrene (without the hydrogen atoms) and

$$-0{\cdot}4104X+0{\cdot}4056Y+0{\cdot}8330Z=3{\cdot}323$$

for TCNE, where X, Y and Z are coordinates with respect to the crystal axes a, b and c in Å. The deviations of the atoms from the each least-squares plane are listed in Table 3. These two planes make an angle of about 2° with each other. The mean separation between the planes is 3·323 Å, which is smaller than the usual van der Waals separation.

Table 3. *Atomic deviations from the least-squares planes of the pyrene and TCNE molecules*

Pyrene		TCNE	
C(1)	0·005 Å	C(9)	−0·003 Å
C(2)	0·008	C(10)	0·001
C(3)	0·001	C(11)	−0·000
C(4)	0·003	N(1)	−0·000
C(5)	0·012	N(2)	0·001
C(6)	−0·019		
C(7)	−0·006		
C(8)	−0·001		

The distances between the atoms of the nearest neighbor pyrene and TCNE molecules are listed in Table 4, where the shortest one is C(1)–C(10), 3·253 Å. Such close contact between the donor and the acceptor molecules suggests the presence of a strong intermolecular interaction. The relative orientation of TCNE to pyrene found in the crystal is shown in Fig. 2.

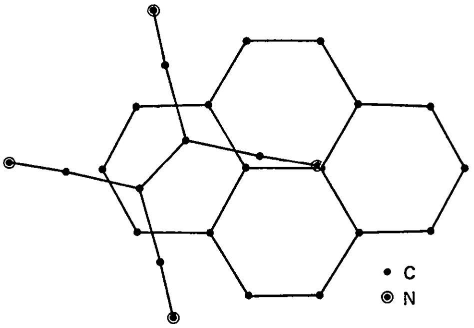

Fig. 2. Relative orientation of pyrene to TCNE found in the crystal.

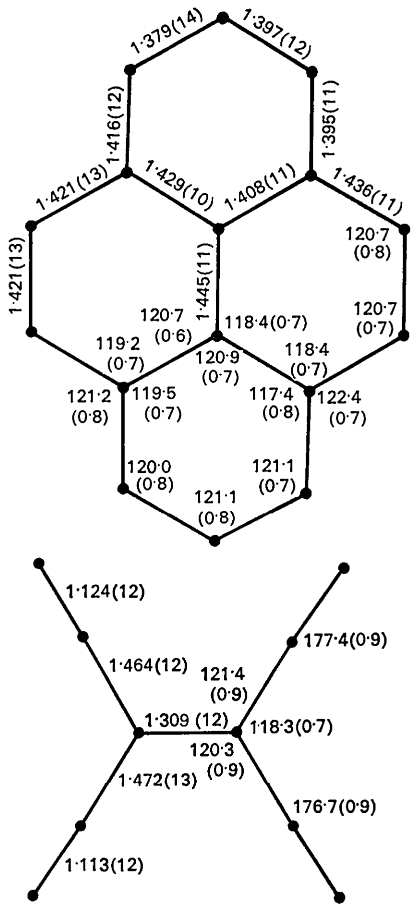

Fig. 3. Bond lengths and their e.s.d.'s (Å) and bond angles and their e.s.d.'s (°).

Table 4. *Distances between atoms of the nearest neighbor pyrene and TCNE less than* 3·5 Å *and their standard deviations*

Pyrene–TCNE	
C(1)–C(9)	3·331 (0·013) Å
C(1)–C(10)	3·253 (0·012)
C(2)–C(9)	3·330 (0·012)
C(2)–C(11)	3·325 (0·013)
C(3)–C(11)	3·435 (0·011)
C(4)–C(9′)	3·501 (0·011)
C(4)–C(10′)	3·326 (0·011)
C(5)–C(9′)	3·344 (0·012)
C(5)–C(11′)	3·422 (0·012)
C(6)–C(9′)	3·480 (0·013)
C(6)–C(11′)	3·408 (0·012)

The molecular structures of the constitutent molecules are illustrated in Fig. 3. The bond lengths given in Fig. 3 have not been corrected for thermal motions.

The bond lengths and bond angles of TCNE are in good agreement with those found by Bekoe & Trueblood (1960), if the standard deviations are taken into account. The largest discrepancy is found in the C–C≡N angle, which differs by about 3° from their value. According to our results, C–C≡N seems to be not linear but bent slightly.

The bond lengths of pyrene agree very well with the values reported by Robertson (1948), but some bond distances differ by about 0·1 Å from the values reported by Damiani, De Santis, Giglio, Liquori, Puliti & Ripamonti (1965) for the crystal structure of the molecular complex between pyrene and 1,3,7,9-tetramethyluric acid.

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