Although the molecules are close-packed according to the requirements of Kitaigorodsky (1961) the packing appears to be quite loose and may offer opportunities for stacking faults and disordering phenomena. One observed stacking fault is the bending of the crystal face (100) about the direction [001]. Apparently helices of hydrogen-bonded molecules can be slightly bent.

We thank Prof. E. Havinga for his continuous interest in this investigation and are indebted to Miss C. Schattenkerk who prepared the crystals.

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Molecular Complexes Exhibiting Polarization Bonding. IX. The Crystal and Molecular Structure of the Tetracyanoethylene – Naphthalene Complex

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The 1:1 complex formed between tetracyanoethylene and naphthalene crystallizes as red-brown prisms, space group $C2/m$, with two molecules of complex in the unit cell of dimensions $a = 7{\cdot}26 \pm 0{\cdot}01$, $b = 12{\cdot}69 \pm 0{\cdot}01$, $c = 7{\cdot}21 \pm 0{\cdot}01$ Å, $\beta = 94{\cdot}4 \pm 0{\cdot}2°$. The structure was solved by Patterson methods and refined to $R = 0{\cdot}137$ by least-squares methods using 512 independent reflexions measured on a linear diffractometer. The component molecules are stacked alternately in infinite columns which are parallel to the c axis. The normals to the mean molecular planes are inclined at approximately 28·5° to the stacking axis. This positions the C=C group of a tetracyanoethylene molecule adjacent to each ring of the naphthalene molecule, so that the relative molecular orientations are those necessary for a Diels–Alder reaction. The mean perpendicular separation of the molecules is 3·30 Å.

Introduction

The 1:1 molecular complex formed between tetracyanoethylene (TCNE) and naphthalene was first described by Merrifield & Phillips (1958). They postulated a sandwich type structure in which the components lie in planes parallel to each other. The structure of the complex was investigated to determine the separations and the relative orientations of the component molecules in view of the strong acceptor properties of TCNE.

Experimental

Red-brown crystals of the complex were deposited slowly after warm equimolar proportions of concentrated solutions of the components in ethyl acetate were mixed and allowed to cool. Micro-analysis indi-

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cated a 1:1 ratio of the components in the crystals. In plane polarized light the crystals exhibited pleochroism. The colours ranged from wine red to dark brown as the plane of polarization of the light was rotated, but the direction of maximum absorption did not appear to correspond to any of the crystal axes.

Weissenberg X-ray photographs were taken with crystals rotating about each of the three crystallographic axes, using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å). The cell dimensions, determined from the Weissenberg photographs, were refined with the use of a linear diffractometer (Arndt & Phillips, 1961). Intensity data for the *hk*0, *hkl*, ..., *hk*7 reciprocal lattice levels were then collected on the linear diffractometer, using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). A total of 512 independent reflexions with $\theta < 32{\cdot}5°$ were observed out of a possible total of 1200 independent reflexions within this range. Intensity measurements were made with a scintillation counter and a pulse height selector. The moving-crystal stationary-counter technique was employed. The crystal from which the data were collected was approximately cylindrical, with a radius of 0·25 mm. No absorption or extinction corrections were applied to the data.

Crystal data

$C_6N_4.C_{10}H_8$, $M = 256{\cdot}3$. Monoclinic. $a = 7{\cdot}26 \pm 0{\cdot}01$, $b = 12{\cdot}69 \pm 0{\cdot}01$, $c = 7{\cdot}21 \pm 0{\cdot}01$ Å, $\beta = 94{\cdot}4° \pm 0{\cdot}2°$, $U = 662{\cdot}3$ Å^3, $D_m = 1{\cdot}29$ g.cm^{-3}, $D_c = 1{\cdot}28$ g.cm^{-3}, $Z = 4$, $F(000) = 528$, Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å), $\mu = 0{\cdot}88$ cm^{-1}. Absent spectra, *hkl* when $h+k$ odd. Space group *C*2 (no. 5), *Cm* (no. 8) or *C*2/*m* (no. 12). Negative piezoelectric and pyroelectric tests indicate *C*2/*m* and this is confirmed by refinement of the structure.

Determination and refinement of the structure

A trial structure was deduced from the 0*kl* and *hk*0 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 0·25 and 0·23 for the 0*kl* and *hk*0 zones respectively. Structure factors were then calculated for the *hkl* reflexions followed by a three-dimensional electron distribution calculation, from which improved atomic coordinates were obtained.

Refinement was continued by the block-diagonal least-squares method using 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. Five cycles of isotropic structure-factor least-squares improved R from 0·29 to 0·24. Refinement was then continued, allowing the temperature factors of each atom to vary anisotropically. After seven further cycles of least-squares, the refinement converged with $R = 0{\cdot}137$, or 0·130 omitting the $\bar{1}12$ reflexion. The 47 positional, thermal and scale parameters have been refined using 512 independent reflexions and the problem is therefore well overdetermined. The measured structure factors are compared in Table 1 with the values calculated from the penultimate set of atomic parameters.

The final positional parameters together with their standard deviations, obtained from the least-squares normal equations matrix, are summarized in Table 2. The anisotropic temperature factors are listed in Table 3.

A final three-dimensional electron density distribution and a difference electron density distribution were calculated. The composite electron density distributions, projected down the *a* axis, are shown in Figs. 1 and 2 respectively. The interpretation of the difference synthesis is discussed below.

The bond lengths and angles, together with their standard deviations, are shown in Fig. 3. Least-squares planes, one for each molecule, were calculated by using the modification (Blow, 1960) of the method of Schomaker, Waser, Marsh & Bergman (1959). Each plane was defined by all the atoms, except hydrogen, of one molecule and each atom was given unit weight. The relevant parameters of the planes and the distances of the atoms from the planes are given in Table 4.

Attempts were made to explain the observed thermal parameters, U_{ij}, of the atoms on the basis of rigid-body molecular vibrations and librations, using the method of Cruickshank (1956), but the attempts were unsuccessful. This might be because only sixteen independent observations (U_{ij}) were used to determine

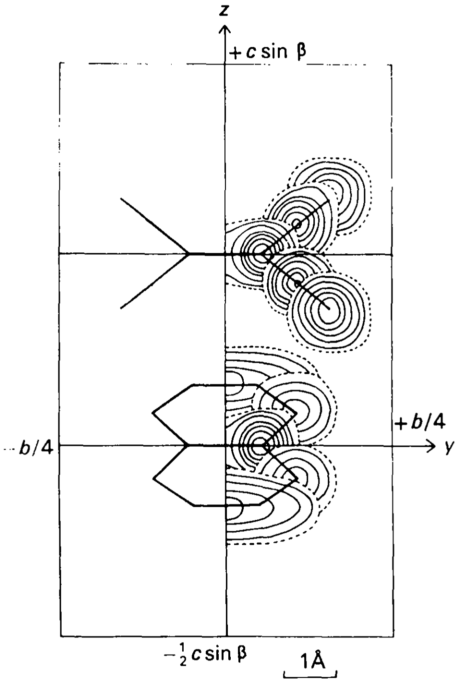

Fig. 1. Composite map, viewed along the *a* axis, of Fourier electron density sections near to atomic centres. Contours at 0·5 e.Å^{-3} (broken line), and 1,2,... e.Å^{-3} (full lines).

Table 1. *Comparison of observed and final calculated structure factors* (*on twenty-five times the absolute scale*)
Lines marked with an asterisk give (left to right) l and k. The other lines give (left to right) h, F_o, F_c.

*	0	0										
	2	-1235	-1391	4	407	432	6	255	282			
*	0	1										
	1	1246	1436	3	422	432	7	241	265			
*	0	2										
	0	1286	1549	2	389	351	4	178	131	6	244	247
*	0	3										
	1	-88	-45	3	532	545	5	234	210	7	-65	-68
	9	68	79									
*	0	4										
	0	-1643	-1732	2	933	878	4	175	129	6	-52	-7
	8	-47	-19									
*	0	5										
	1	-649	-650	3	597	566	5	-90	-96	7	-95	-103
	9	44	37									
*	0	6										
	0	-301	-192	2	-306	-306	4	67	94	6	-118	-146
*	0	7										
	1	-325	-264	5	-290	-245						
*	0	8										
	0	132	85	2	-315	-294	4	-338	-358	6	-67	-45
*	0	9										
	3	-433	-503	5	-79	-34						
*	0	10										
	0	-105	-144	2	-180	-129	4	-226	-273			
*	0	11										
	1	-134	-100	3	-169	-188						
*	0	12										
	0	-65	-92	2	-181	-124	4	85	55	6	-54	-74
*	0	13										
	1	-111	-119	3	93	111						
*	0	15										
	3	59	62									
*	1	0										
	2	429	390	4	-93	-78	6	-118	-119			
*	1	1										
	-7	-64	-41	-5	-51	-49	-3	78	148	-1	244	118
	1	-374	-357	3	140	166	5	-50	-2			
*	1	2										
	-6	-84	-90	-4	338	352	-2	-852	-829	0	601	640
	2	-84	-92	4	-81	-108	6	76	57			
*	1	3										
	-7	123	124	-5	-88	-99	-3	-244	-232	-1	717	821
	1	-1138	-1235	3	575	573	5	-120	-158	9	-44	-21
*	1	4										
	-4	125	145	-2	-569	-586	0	497	540	2	-162	-163
	4	-172	-166	6	214	184	8	-66	-58			
*	1	5										
	-7	115	92	-5	-148	-156	-3	90	88	1	111	91
	3	-241	-237	5	149	124						
*	1	6										
	-6	129	116	-4	-280	-277	-2	394	403	0	-278	-279
	2	221	260	4	-165	-133	6	48	20			
*	1	7										
	-7	-35	-27	-5	-93	-53	-3	213	180	-1	-278	-274
	1	352	391	3	-240	-253	5	55	91			
*	1	8										
	-6	-59	-15	-4	63	19	0	-118	-137	2	132	111
	6	-78	-63									
*	1	9										
	-1	50	14	1	-220	-155	3	262	214	5	-131	-91
*	1	10										
	-6	-52	-27	-4	187	143	-2	-206	-149	0	52	34
*	1	11										
	1	-119	-57	3	98	62						
*	1	12										
	-6	70	57	-4	-46	-42	4	39	27			
*	1	13										
	-3	-38	-26	1	41	73	3	-105	-98	5	74	68
*	1	14										
	-4	-59	-46	-2	36	40	0	72	55	2	-38	-38
*	1	15										
	-1	71	45									
*	2	0										
	-8	150	187	-4	233	208	-2	1155	1162	2	460	489
	4	-155	-132	6	441	464						
*	2	1										
	-7	151	165	-5	212	198	-3	-388	-392	-1	2242	3168
	1	-734	-731	3	348	337	5	361	376	9	47	30
*	2	2										
	-8	59	65	-6	84	77	-4	275	287	-2	410	412
	0	592	501	2	462	452	4	225	208	6	111	108
	8	77	65									
*	2	3										
	-7	116	93	-5	73	60	-3	584	544	-1	-810	-685
	1	1112	1019	3	144	61	5	194	165			
*	2	4										
	-8	-31	-64	-6	37	44	-4	391	397	-2	-451	-410
	0	-339	-326	2	666	631	4	167	139	6	-174	-193
	9	117	111									
*	2	5										
	-5	54	104	-3	155	119	-1	-791	-745	1	271	221
	3	194	222	5	-124	-178	7	-67	-14			
*	2	6										
	-6	-151	-130	-4	213	172	-2	-364	-322	0	-500	-467
	2	372	325	4	-321	-306						
*	2	7										
	-7	-47	-41	-5	-135	-123	-3	-252	-245	-1	121	94
	1	-449	-437	3	-163	-144	5	-95	-89			
*	2	8										
	-6	-149	-105	-4	-209	-262	-2	-74	-53	0	-123	-81
	2	-354	-423									
*	2	9										
	-7	57	31	-5	-252	-283	-3	-145	-122	1	-207	-185
	3	-391	-419	5	41	75						
*	2	10										
	-4	-251	-292	-2	-52	-41	0	-76	-33	2	-358	-412
	6	-49	-61									
*	2	11										
	-3	-184	-179	-1	-89	-105	1	-176	-123	3	-52	-95
*	2	12										
	-2	-133	-115	0	-147	-124						
*	2	13										
	-5	57	69	-3	-67	-49	-1	-37	-75	1	-44	-44
	3	78	92	5	-73	-87						

Table 1 (*cont.*)

• 2	14										
-4	94	57	2	68	108						
• 2	15										
1	59	54									
• 2	16										
0	48	42									
• 2	17										
-1	58	53	1	39	30						
• 3	0										
-6	-41	-19	-4	142	104	-2	-36	-24	2	-129	-78
6	-157	-177	8	98	75						
• 3	1										
-9	-55	-27	-5	130	103	-3	-155	-134	-1	90	58
1	175	155	3	-99	-87	5	-76	-68			
• 3	2										
-4	-64	-68	-2	309	314	0	-632	-607	2	426	411
4	-136	-125									
• 3	3										
-5	135	158	-3	-459	-449	-1	404	414	1	-129	-124
3	-135	-146	5	217	181	7	-108	-91			
• 3	4										
-8	69	66	-6	-85	-83	-4	-56	-46	-2	212	210
0	-401	-396	2	201	206						
• 3	5										
-7	52	43	-5	-96	-64	-1	61	38	3	-155	-138
5	130	109									
• 3	6										
-8	46	21	-6	-85	-79	-4	143	134	-2	-181	-181
0	328	316	2	-360	-341	4	173	168	6	-55	-55
• 3	7										
-5	-72	-84	-3	175	191	-1	-164	-177	1	139	126
3	-69	-49	5	-64	-59	7	83	72			
• 3	8										
-8	-43	-21	-4	73	53	2	74	31	4	-85	-42
• 3	9										
-7	-36	-20	-5	94	68	-3	-98	-53	1	64	50
7	59	12									
• 3	10										
-6	46	26	-2	37	24	0	-186	-121	2	218	177
4	-97	-56	6	39	11						
• 3	11										
-5	51	25	-3	-90	-48	3	39	43	5	41	19
• 3	12										
-6	56	14	4	70	79						
• 3	13										
-1	43	36	1	-40	-38						
• 4	0										
-8	75	81	-6	124	116	-4	-195	-203	-2	1552	1589
2	240	261	4	389	393	8	77	36			
• 4	1										
-9	57	69	-5	115	101	-3	471	437	-1	434	397
1	261	274	5	342	338						
• 4	2										
-8	53	66	-6	82	71	-4	64	63	-2	509	470
0	202	187	2	147	109	4	292	281			
• 4	3										
-7	52	35	-5	175	194	-3	-94	-81	-1	110	107
1	391	334	3	266	242	5	-119	-127	7	115	135
• 4	4										
-8	47	6	-6	37	57	-4	189	167	-2	-544	-496
0	513	-73	2	161	127						
• 4	5										
-5	163	171	-3	-253	-231	-1	-274	-266	1	419	401
3	-107	-120	5	-119	-120	7	62	52			
• 4	6										
-4	-56	-54	-2	-140	-139	0	-159	-161	2	52	64
4	-149	-175									
• 4	7										
-7	-92	-75	-3	-78	-77	-1	-200	-183	1	-45	-80
3	-269	-243	7	-36	-60						
• 4	8										
-6	-134	-144	-4	-91	-93	-2	41	24	0	-257	-251
2	-276	-279									
• 4	9										
-5	-154	-191	-3	-35	-17	-1	-47	-17	1	-341	-408
3	-55	-17	7	-76	-44						
• 4	10										
-6	-78	-74	-4	-101	-89	-2	-46	-59	0	-141	-112
2	-156	-229	6	-36	-44						
• 4	11										
-5	-50	-91	-3	-77	-63	-1	-88	-67	1	-114	-132
3	-36	-15									
• 4	12										
-4	-93	-73	-2	-49	-63	0	-78	-60	4	-50	-79
• 4	13										
-3	-55	-59	-1	-66	-67	1	83	86	3	-52	-56
• 4	14										
2	47	53									
• 5	0										
2	-56	-51	4	-89	-87	6	37	51			
• 5	1										
-7	-35	-5	-3	63	79	-1	-96	-102	1	54	43
5	-117	-106	7	58	53						
• 5	2										
-6	73	66	-4	-131	-137	-2	111	112	2	-78	-79
4	72	61	6	-71	-43	8	36	7			
• 5	3										
-5	-52	-42	-3	118	125	-1	-263	-264	1	249	249
3	-79	-96									
• 5	4										
-6	57	3	-4	-88	-117	-2	95	103	2	-87	-87
4	163	135	6	-73	-66	8	-39	-6			
• 5	5										
-7	-58	-46	-5	47	41	-1	46	29	1	-46	-80
3	111	105									
• 5	6										
-6	-56	-41	-4	55	68	-2	-51	-58	2	-58	-54
6	54	51									
• 5	7										
-5	65	61	-3	-53	-63	-1	76	96	1	-111	-122
3	46	41									
• 5	8										
-2	-49	-57	0	41	52	2	-35	-17	4	-41	-39
6	46	41									
• 5	9										
-1	-91	-62	1	139	111	5	42	28	3	-96	-69
• 5	10										
-6	38	21	-4	-45	-38	0	52	11			
• 5	11										
-1	-55	-14	1	41	35						

Table 1 (*cont.*)

•	5	13										
	1	-47	-57	3	48	52						
•	6	0										
	4	330	316	6	-46	-38	0	36	38			
•	6	1										
	-9	40	34	-7	45	46	-3	466	482	-1	-70	-188
	1	62	92	3	270	275						
•	6	2										
	-6	65	69	-4	90	83	-2	125	134	0	138	141
	2	110	122	4	77	67	6	55	64			
•	6	3										
	-5	46	54	-3	-38	-44	-1	200	219	1	96	78
	3	85	66									
•	6	4										
	-6	72	95	-4	-101	-110	0	213	234	2	61	41
	4	-130	-133	6	102	100	8	-44	-12			
•	6	5										
	-5	40	24	-3	-153	-174	-1	78	83	1	76	81
	3	-98	-128									
•	6	6										
	-4	-69	-76	-2	-123	-140	0	104	103	2	-144	-169
•	6	7										
	-1	-135	-151	1	-82	-85	3	-56	-59	5	-59	-37
	7	-40	-19									
•	6	8										
	-6	-49	-67	-2	-68	-57	0	-154	-202	2	-99	-75
	6	-38	-55									
•	6	9										
	-7	-57	-68	-5	-51	-46	-1	-112	-121	1	-158	-188
	5	-49	-48	7	-40	-48						
•	6	10										
	-6	-53	-78	-4	-62	-23	0	-122	-182			
•	6	11										
	-5	-55	-54	-3	-35	-34	-1	-40	-50	5	-55	-27
•	6	12										
	-4	-53	-45	0	35	8	4	-68	-32			
•	6	13										
	1	42	34									
•	6	14										
	0	42	44									
•	7	0										
	4	-85	-84	6	66	52						
•	7	2										
	0	74	80									
•	7	3										
	-5	-41	-61	-3	48	48	3	71	72	5	-64	-94
•	7	4										
	-6	38	1	-2	-35	-40						
•	7	5										
	3	41	20									
•	7	6										
	-8	-37	-18									

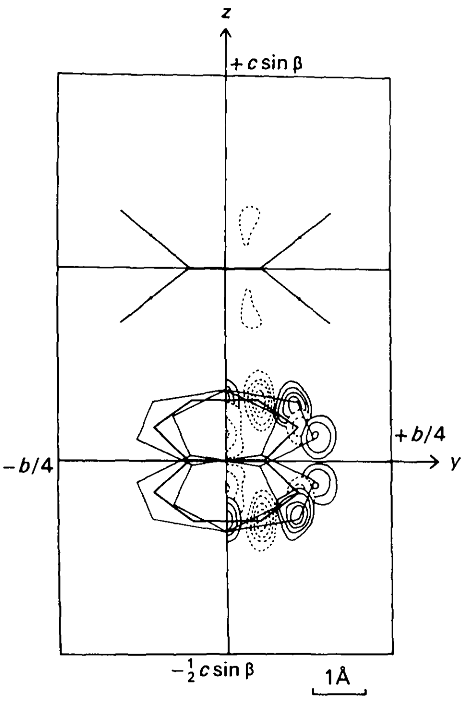

Fig. 2. Composite difference density map from the final $(F_o - F_c)$ Fourier summation. Contours at −0·5, −0·4, −0·3, 0·2 e.Å⁻ (broken lines) and +0·2, +0·3, +0·4, +0·5 e.Å⁻ (full lines). The positions of the atoms assumed in the calculation of F_c are shown, together with two disordered naphthalene positions.

twelve parameters (six ω_{ij} and six τ_{ij}) by the method of least squares. On the basis of other studies (Bekoe & Trueblood, 1960; Long, Sparks & Trueblood, 1965), it now appears that the nitrogen atoms of the cyano

Table 2. *Final positional parameters* (× 10⁴) *and their estimated standard deviations*

The number below each parameter is its e.s.d.

	x/a	*y/b*	*z/c*
C(1)	0000	0532	5000
	—	5	—
C(2)	1547	1109	5806
	8	4	8
C(3)	0000	0552	0000
	—	6	—
C(4)	1591	1079	0840
	14	7	10
C(5)	2993	0474	1594
	10	15	10
N	2791	1548	6452
	7	4	8

Table 3. *Final atomic thermal parameters* (× 10⁴)

B_{ij} are coefficients in the temperature factor expression $\exp\,[-(B_{11}h^3 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0197	0063	0200	0000	0006	0000
C(2)	0241	0061	0264	0017	−0022	0003
C(3)	0267	0067	0185	0000	0059	0000
C(4)	0728	0155	0219	−0073	0274	−0420
C(5)	0374	0701	0245	−0089	0076	−0713
N	0290	0096	0321	0012	−0104	−0076

groups cannot be considered as part of the rigid body. Full analysis of the rigid-body motions of TCNE in the present structure is therefore precluded.

Description and discussion of the structure

The structure consists of infinite columns of alternate TCNE and naphthalene molecules, the columns being parallel to the *c* crystal axis. The normals to the planes of the TCNE and naphthalene molecules are inclined at angles of 28·2° and 28·8° respectively to the stacking axis. This has the effect of positioning one TCNE

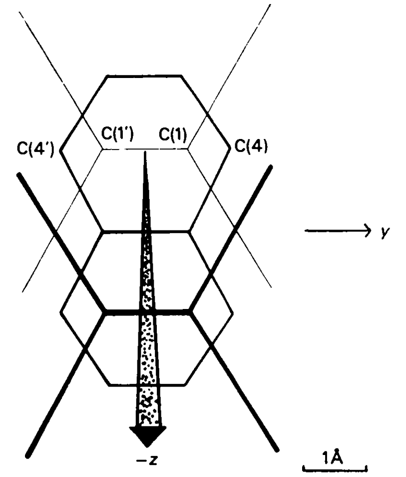

Fig. 4. Diagrammatic representation of the molecular overlap as seen perpendicular to the mean molecular planes.

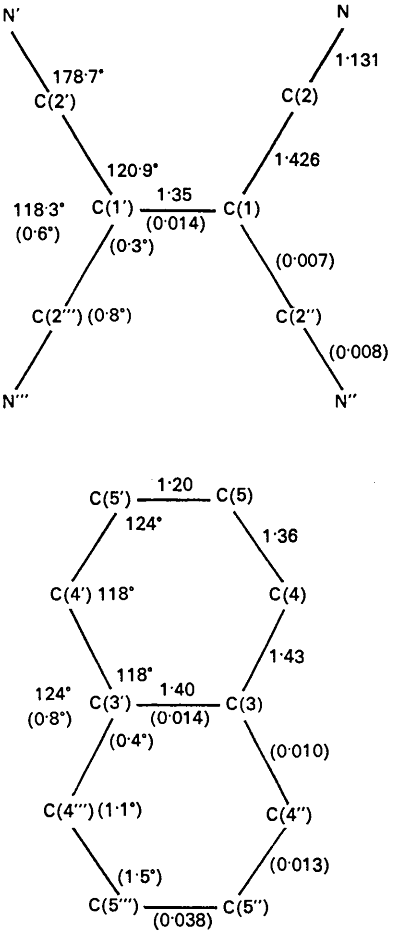

Fig. 3. Molecular dimensions (Å) and their standard deviations (in parenthesis).

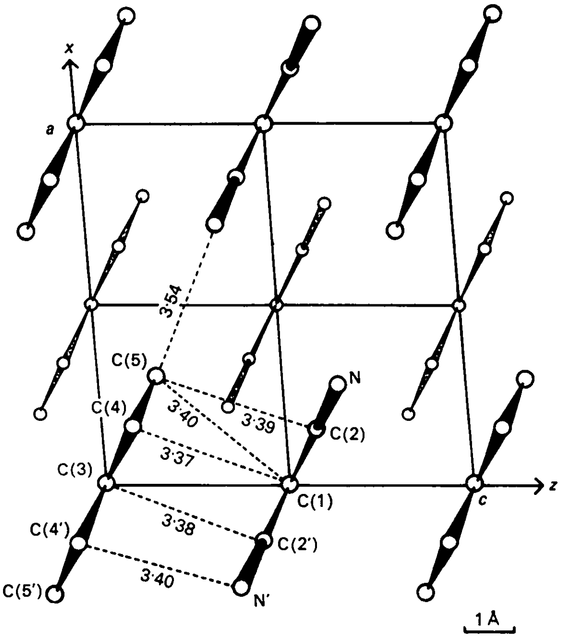

Fig. 5. The molecular arrangement, viewed along the *b* axis, showing the principal molecular contact distances.

Table 4. *Molecular least-squares planes*

	TCNE		Naphthalene	
Perpendicular distance from origin		−3·298 Å		0·000 Å
Direction cosines of plane-normal relative to				
a		0·4727		0·4811
b		0·0000		0·0000
*c**		−0·8812		−0·8766
		D		*D*
Deviations (*D*) of atoms from the least-squares planes	C(1)	0·000 Å	C(3)	0·000 Å
	C(2)	−0·001	C(4)	0·003
	N	+0·001	C(5)	−0·002

molecule over one ring of each naphthalene molecule and a centrosymmetrically related TCNE molecule below the other ring when the structure is viewed perpendicular to the mean molecular planes as illustrated in Fig. 4. The structure viewed along the *b* axis is shown in Fig. 5 together with the principal molecular contact distances. These and the interplanar perpendicular separation of 3·30 Å are indicative of interaction between the TCNE and naphthalene molecules.

The molecular overlap is particularly interesting in that the molecules are positioned as for a Diels–Alder reaction. A Diels–Alder reaction does in fact occur between TCNE and anthracene at room temperature (Middleton, Heckert, Little & Krespan, 1958). The C(1)···C(4) and C(1′)···C(4′) contacts of 3·37 Å may represent weak partial bond formation in preparation for a Diels–Alder reaction and this might be expected to lengthen the C(1)–C(1′) bond. The observed bond distance of 1·35 Å is 0·012 Å longer than the corresponding distance in the crystal structure of TCNE itself (Bekoe & Trueblood, 1964), but it is not possible to state that any lengthening has occurred because the high e.s.d. of this bond in the complex (due to its special position in the structure) makes this change insignificant. The dimensions of the naphthalene molecule in the complex are similarly not sufficiently accurate to detect any small changes which might have occurred compared with the uncomplexed molecule.

The *b* cell length seems to be determined by the size of the cyanocarbon molecule. The evidence for this is that all approaches of less than 3·54 Å, between molecules in adjacent stacks, involve only the TCNE molecules. All intermolecular contacts, between stacks, which involve the naphathalene molecules are greater than the sum of the van der Waals radii of the atoms concerned. The naphthalene molecule has a large amount of free space in the *y* direction. This is consistent with the large B_{22} parameter of the atom C(5), which indicates large thermal librations of the naphthalene molecule about an axis normal to the molecular plane.

Sections through the three-dimensional difference electron density distribution (Fig. 2) showed significant peaks and troughs in the region of the naphthalene molecule. These observations can be explained on the basis of a disordered structure in which there are small contributions to the final structure from the additional molecular orientations indicated in Fig. 2. The peaks and troughs might also be due to an interaction of the thermal and positional parameters of the naphthalene molecule.

Bekoe & Trueblood (1960, 1964) have determined the structure of TCNE itself. The molecular dimensions of the uncomplexed TCNE molecule are compared in Table 5 with the dimensions obtained in the present study. The overall agreement is seen to be good; however, as the bond lengths of the uncomplexed molecule have been corrected for the effects of libration, a strict comparison cannot be made. The disorder in the position of the naphthalene molecule, mentioned above, results in misleading apparent dimensions for this molecule and comparison with uncomplexed naphthalene molecular dimensions would be meaningless.

An explanation of the factors influencing the relative orientations of the donor and acceptor molecules has been suggested. The crystallographic evidence for interaction between the molecules is the reduced interplanar distance. Although TCNE is regarded as being a powerful electron acceptor this structure shows no evidence for particularly strong interaction. The most interesting feature which has been revealed is the specific interaction between the C=C groups and the 1,4 positions of the naphthalene ring. Other examples of this type of interaction involving C=C and C=O groups have already been discussed briefly (Prout & Wallwork, 1966).

We are indebted to the Director of the Manchester University Department of Computer Science for allowing computing facilities on the Atlas computer, to the Director of the Oxford University Computing Laboratory for allowing computing facilities on the Mercury computer, and to M. M. Harding, R. D. Diamand and J. S. Rollett for the use of their computer programs. We also thank Dr J. S. Rollett for assistance with the Mercury computing and the Science Research Council for a maintenance grant (to R.M.W.) and for contributing the cost of the linear diffractometer.

Table 5. *Comparison of molecular dimensions of complexed and uncomplexed* TCNE

	Present study		Uncomplexed TCNE*	
Bond		σ		σ
C(1)–C(1′)	1·351 Å	0·014 Å	1·339 Å	0·008 Å
C(1)–C(2)	1·426	0·007	1·442 1·441	0·005 0·005
C(2)–N	1·131	0·008	1·135 1·133	0·006 0·005
Angle		σ		σ
C(1′)–C(1)–C(2)	120·9°	0·3°	121·0° 120·9	0·3° 0·3
C(2)–C(1)–C(2″)	118·3	0·6	118·1	0·3
C(1)–C(2)–N	178·7	0·8	179·1 179·4	0·4 0·4

* Trueblood (1965)

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The Crystal Structure of Lithium Sodium Sulfate*

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The crystal structure of $LiNaSO_4$ has been determined by three-dimensional Fourier methods and refined by full-matrix least-squares procedures. The space group is $P31c$ with cell dimensions $a_0 = 7{\cdot}6270$, $c_0 = 9{\cdot}8579$ Å. Three crystallographically different sulfate groups are situated on two different threefold axes. The lithium and sodium ions are surrounded by irregular arrangements of four and eight oxygen atoms, respectively.

Introduction

In the course of studying the phase diagram of the Li_2SO_4–Na_2SO_4–H_2O system, Cavalca & Nardelli (1952) isolated and reported the space group and lattice constants for $LiNaSO_4$. They pointed out that this compound is not isomorphous with $LiKSO_4$. A compound containing both sodium and lithium ions was considered of interest to complement nuclear magnetic resonance studies in our laboratory (Anderson, 1961). Therefore, the current structure determination of $LiNaSO_4$ was undertaken to establish positional parameters and nearest neighbors of the alkaline metal ions.

Experimental

Lattice constants for $LiNaSO_4$ ($a_0 = 7{\cdot}6270(7)$ and $c_0 = 9{\cdot}8579(10)$ Å) were obtained with Cu $K\alpha$ radiation (λ for $K\alpha_1 = 1{\cdot}54050$ Å) by least-squares fit of high 2θ values measured on films taken with a 115 mm diameter Weissenberg camera which accepts Straumanis film loading. Systematic absences of $hh\overline{2h}l$ for l odd and evidence of a piezoelectric effect indicate the space group is $P31c$. Cavalca & Nardelli reported an experimental density of $2{\cdot}536$ g.cm^{-3} compared with $2{\cdot}527$ g.cm^{-3} calculated from the above lattice constants and six molecular weights of $LiNaSO_4$ per cell. No evidence of ferroelectricity was found in this noncentrosymmetric compound.

Three-dimensional Mo $K\alpha$ intensity data were measured using balanced filters with a Picker diffractometer equipped with a General Electric single-crystal orienter and scintillation counter. A unique set of 496 reflections (27 were considered unobserved) was obtained by averaging symmetry-equivalent reflections. No absorption corrections were necessary for the spherically ground crystal ($\mu R = 0{\cdot}5$).

Lorentz and polarization factors were applied and structure factors calculated using both neutral and charged (extrapolated) scattering factors from Table 3.3.1A of *International Tables for X-ray Crystallography* (1962, p. 202) (denoted hereafter ITXC).

Structure determination

A three-dimensional Patterson function was calculated, and the sulfur–sulfur vectors were found to be consistent with sulfate groups situated on the threefold axes (special positions (a) and (b) in space group $P31c$) rather than in general positions. Succeeding Fourier syntheses resolved the sodium ion and oxygen atoms for the final structure as well as weaker oxygen 'ghosts' corresponding to sulfate ions oriented in the opposite direction. Full-matrix least-squares refinement of positional and isotropic thermal parameters was attempted for several models differing only in the arrangements of oxygen atoms. The 'ghost' peaks vanished and the oxygen thermal parameters successfully converged only

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