

**The Crystal Structures of the Molecular Complexes between Benzidine
and 7,7,8,8-Tetracyano-*p*-quinodimethane.
I. Benzidine-TCNQ Complex Containing Dichloromethane**

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Crystals of the 1:1 complex of benzidine and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), containing dichloromethane in the crystal lattice, are monoclinic, space group $I2/m$, with $a = 20.892$, $b = 9.950$, $c = 6.445$ Å, $\beta = 91.92^\circ$, $Z = 2$. The structure was refined by three-dimensional analysis using the block-diagonal and full-matrix least-squares method. Benzidine and TCNQ molecules are alternately stacked along the c axis to form columns, with the molecular planes almost parallel to each other. Between the columns there are channels running along the c axis, in which dichloromethane molecules are sited.

Introduction

Benzidine (BD) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) were found to form solid molecular complexes, which contain solvent molecules in the crystal lattice as well as the solvent-free complex (Ohmasa, Kinoshita & Akamatu, 1969). Examples of the solvent that can enter into the lattice of the BD-TCNQ complex are acetone, acetonitrile, dichloromethane, 1,2-dichloroethane and benzene.

From the X-ray powder diffraction patterns, the crystal structures of the solvent-containing complexes were found to vary more or less depending on the solvent contained. It was also known that a solvent-containing complex gradually loses solvent molecules to form the solvent-free complex when the crystals are kept in vacuum for a long period.

The electrical and magnetic properties of the solvent-containing complexes differ markedly from those of the solvent-free complex, and are appreciably dependent on the kind of solvent contained in the lattice (Ohmasa, Kinoshita & Akamatu, 1971*a, b*).

In view of these interesting behaviour of the solvent-containing complexes, it is of particular interest to elucidate the role of solvent molecules in the structural and physical aspects of these solids. Thus we have decided to perform the crystal-structure analysis on this series of molecular complexes. In the present paper we report the crystal structure of the BD-TCNQ complex that contains dichloromethane.

Experimental

Crystals of the complex were precipitated when dichloromethane solutions of benzidine and TCNQ were mixed. They were redissolved in hot solvent consisting of a 1:1 mixture of dichloromethane and 1,2-

dichloroethane. By allowing the solution to cool slowly, well-grown, dark-green needle-like crystals were obtained, which were elongated along the c axis. Chemical analysis of these crystals indicated the molecular ratio of the components, BD:TCNQ:CH₂Cl₂, to be 1:1:1.8.

Lattice constants were determined by a least-squares analysis of eight diffraction lines observed with an automatic recording X-ray diffractometer, Geigerflex, by using sodium chloride as an internal standard.

Crystal data

Monoclinic

$a = 20.982 \pm 0.019$ Å, $b = 9.950 \pm 0.005$,

$c = 6.445 \pm 0.005$

$\beta = 91.92 \pm 0.13^\circ$

$V = 1338.8$ Å³

Formula: C₁₂H₁₂N₂ · C₁₂H₄N₄ · 1.8 CH₂Cl₂;

F.W.541

D_x (calculated density) = 1.349 cm⁻³

D_m (measured density) = 1.40

$Z = 2$

$\mu = 4.68$ cm⁻¹ (Mo $K\alpha$)

Space group $I2/m$ (from Weissenberg and precession photographs)

(Absent spectra: hkl when $h+k+l$ is odd,

$h0l$ when $h+l$ is odd, $0k0$ when k is odd).

Intensity data were first obtained up to the fourth layer around the c axis from the Weissenberg photographs by using the multiple-film technique. The data on the $h0l$, $1kl$, $2kl$ reflexions were collected from the precession photographs. Ni-filtered Cu $K\alpha$ radiation was used and the intensities were determined visually. The corrections for the Lorentz and polarization factors were made in the usual way, but no correction was made for absorption. The number of observed reflexions was 320 at this stage. These data were used in the preliminary analysis to obtain an approximate structure.

In the next stage of analysis, the intensity data were

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redetermined with Rigaku-Denki computer-controlled four-circle diffractometer using monochromatized Mo $K\alpha$ radiation. The reproducibility of the measurement was checked by measuring the $00\bar{2}$ and 020 reflexions every fifty reflexions. Among the 1670 independent reflexions in the range $2\theta \leq 55^\circ$, intensity data were obtained for 828 (729 of which were three times larger than their standard deviations) and used in the refinement. All the reflexions were measured by the θ - 2θ scan technique at a 2θ scan rate of $1.0^\circ \text{ min}^{-1}$. The scan range $\Delta 2\theta$ was varied according to the formula: $\Delta 2\theta = 2^\circ + 0.9^\circ \tan \theta$. The background settings were those given by the expression $2\theta \pm 0.9 \times \Delta 2\theta$, and at each point background counts were taken for 10 sec. For a count rate above 16,000 c.p.s., attenuators were automatically inserted in the incident beam. The intensities were corrected for background and for Lorentz and polarization effects, and were reduced to the structure amplitude, $|F_o|$.

Structure determination and refinement

From the consideration of the space group, the symmetry of the component molecules and the number of molecules in the unit cell, the position of molecular centre was easily determined as $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$ respectively for benzidine and TCNQ. There are two possible orientations for each molecule. Hence we can consider four possible structures. The structure factor was calculated for these four trial structures, and the one which gave the lowest R value was chosen as the

starting model. The position of dichloromethane was determined from the difference Fourier map.

When we calculated the R value for this approximate structure, using the intensity data from the diffractometer, we obtained 0.45. Block-diagonal least-squares refinement with isotropic temperature factors reduced the R value to 0.23. With anisotropic temperature factors, the R value became 0.20. The number of dichloromethane molecules in the unit cell has to be considered as more or less uncertain, since the solvent molecules tend to be lost from the crystal. We took this factor into account by allowing the multiplicity of the dichloromethane molecule to be variable in the full-matrix least-squares refinement.

Although the reproducibility of measurement was ensured after every fifty measurements, one of these sets, comprising 50 reflexions, was suspected to be spurious since the coincidence between F_o and F_c was unsatisfactory, while a good agreement was found when photographic data were used. Thus in the final least-squares analysis we eliminated the data belonging to this particular set, as well as those obtained by the measurement following this spurious set. Using the remaining 605 reflexions, a full-matrix refinement with anisotropic temperature factors was carried out, which brought the R value down to 0.12 and the multiplicity of the dichloromethane molecule to 0.42. This value of the multiplicity corresponds to 1.7 dichloromethane molecules per unit formula, which is in satisfactory agreement with the value estimated from the chemical analysis, 1.8.

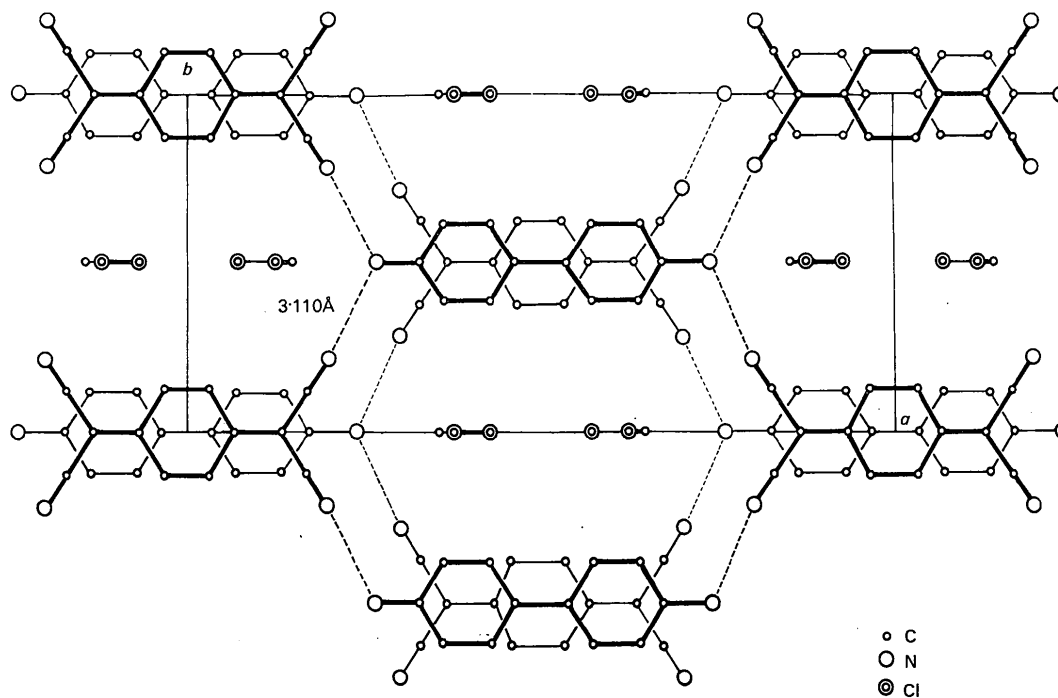


Fig. 1. Projection of molecular arrangement onto the (001) plane.

The final parameters are given in Table 1 together with their standard deviations. The observed and calculated structure factors are listed in Table 2.

Table 1. Atomic parameters

(a) Atomic coordinates ($\times 10^4$) as fractions of the cell edges and their standard deviations ($\times 10^3 \text{ \AA}$) in parentheses

	x	y	z
BD			
C(1)	361 (14)	0 (0)	50 (11)
C(2)	711 (9)	1198 (9)	85 (7)
C(3)	1370 (8)	1207 (9)	162 (7)
C(4)	1721 (12)	0 (0)	212 (11)
N(1)	2390 (14)	0 (0)	299 (13)
TCNQ			
C(5)	329 (9)	1250 (9)	5018 (8)
C(6)	666 (13)	0 (0)	5055 (12)
C(7)	1327 (14)	0 (0)	5104 (11)
C(8)	1707 (11)	1203 (11)	5148 (8)
N(2)	1992 (10)	2177 (11)	5157 (8)
CH₂Cl₂			
C(9)	3548 (30)	0 (0)	6623 (18)
Cl(1)	3738 (12)	0 (0)	4064 (7)
Cl(2)	4253 (16)	0 (0)	8182 (11)

(b) Thermal parameters ($\times 10^5$). The β_{ij} values refer to 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}
BD						
C(1)	234	455	1437	0	-184	0
C(2)	141	673	1565	55	-42	100
C(3)	83	624	2380	-142	96	101
C(4)	79	785	1962	0	33	0
N(1)	196	1128	4121	0	-27	0
TCNQ						
C(5)	184	811	1829	125	178	178
C(6)	77	1101	1880	0	-139	0
C(7)	179	585	1396	0	13	0
C(8)	189	952	2228	21	36	-73
N(2)	255	1253	3487	-209	-46	-126
CH₂Cl₂						
C(9)	503	1015	4084	0	560	0
Cl(1)	849	1406	5539	0	-282	0
Cl(2)	1190	2193	8613	0	-1219	0

Table 2. Observed and calculated structure factors

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
M.L. -3	1		M.L. #4	1		3	70	103	2	87	83	1	140	130	M.L. -6	5		u	v	+22
M.L. -4	54		M.L. #5	3		5	87	103	5	87	103	5	87	103	M.L. -7	8		u	v	+22
M.L. -5	75		M.L. #6	7		7	103	140	7	103	140	7	103	140	M.L. -8	10		u	v	+22
M.L. -6	103		M.L. #7	10		10	140	187	10	140	187	10	140	187	M.L. -9	13		u	v	+22
M.L. -7	140		M.L. #8	13		13	187	234	13	187	234	13	187	234	M.L. -10	16		u	v	+22
M.L. -8	187		M.L. #9	16		16	234	281	16	234	281	16	234	281	M.L. -11	19		u	v	+22
M.L. -9	234		M.L. #10	19		19	281	328	19	281	328	19	281	328	M.L. -12	22		u	v	+22
M.L. -10	281		M.L. #11	22		22	328	375	22	328	375	22	328	375	M.L. -13	25		u	v	+22
M.L. -11	328		M.L. #12	25		25	375	422	25	375	422	25	375	422	M.L. -14	28		u	v	+22
M.L. -12	375		M.L. #13	28		28	422	469	28	422	469	28	422	469	M.L. -15	31		u	v	+22
M.L. -13	422		M.L. #14	31		31	469	516	31	469	516	31	469	516	M.L. -16	34		u	v	+22
M.L. -14	469		M.L. #15	34		34	516	563	34	516	563	34	516	563	M.L. -17	37		u	v	+22
M.L. -15	516		M.L. #16	37		37	563	610	37	563	610	37	563	610	M.L. -18	40		u	v	+22
M.L. -16	563		M.L. #17	40		40	610	657	40	610	657	40	610	657	M.L. -19	43		u	v	+22
M.L. -17	610		M.L. #18	43		43	657	704	43	657	704	43	657	704	M.L. -20	46		u	v	+22
M.L. -18	657		M.L. #19	46		46	704	751	46	704	751	46	704	751	M.L. -21	49		u	v	+22
M.L. -19	704		M.L. #20	49		49	751	798	49	704	798	49	704	798	M.L. -22	52		u	v	+22
M.L. -20	751		M.L. #21	52		52	798	845	52	751	845	52	751	845	M.L. -23	55		u	v	+22
M.L. -21	798		M.L. #22	55		55	845	892	55	798	892	55	798	892	M.L. -24	58		u	v	+22
M.L. -22	845		M.L. #23	58		58	892	939	58	845	939	58	845	939	M.L. -25	61		u	v	+22
M.L. -23	892		M.L. #24	61		61	939	986	61	892	986	61	892	986	M.L. -26	64		u	v	+22
M.L. -24	939		M.L. #25	64		64	986	1033	64	939	1033	64	939	1033	M.L. -27	67		u	v	+22
M.L. -25	986		M.L. #26	67		67	1033	1080	67	986	1080	67	986	1080	M.L. -28	70		u	v	+22
M.L. -26	1033		M.L. #27	70		70	1080	1127	70	1033	1127	70	1033	1127	M.L. -29	73		u	v	+22
M.L. -27	1080		M.L. #28	73		73	1127	1174	73	1080	1174	73	1080	1174	M.L. -30	76		u	v	+22
M.L. -28	1127		M.L. #29	76		76	1174	1221	76	1127	1221	76	1127	1221	M.L. -31	79		u	v	+22
M.L. -29	1174		M.L. #30	79		79	1221	1268	79	1174	1268	79	1174	1268	M.L. -32	82		u	v	+22
M.L. -30	1221		M.L. #31	82		82	1268	1315	82	1221	1315	82	1221	1315	M.L. -33	85		u	v	+22
M.L. -31	1268		M.L. #32	85		85	1315	1362	85	1268	1362	85	1268	1362	M.L. -34	88		u	v	+22
M.L. -32	1315		M.L. #33	88		88	1362	1409	88	1315	1409	88	1315	1409	M.L. -35	91		u	v	+22
M.L. -33	1362		M.L. #34	91		91	1409	1456	91	1362	1456	91	1362	1456	M.L. -36	94		u	v	+22
M.L. -34	1409		M.L. #35	94		94	1456	1503	94	1409	1503	94	1409	1503	M.L. -37	97		u	v	+22
M.L. -35	1456		M.L. #36	97		97	1503	1550	97	1456	1550	97	1456	1550	M.L. -38	100		u	v	+22
M.L. -36	1503		M.L. #37	100		100	1550	1597	100	1503	1597	100	1503	1597	M.L. -39	103		u	v	+22
M.L. -37	1550		M.L. #38	103		103	1597	1644	103	1550	1644	103	1550	1644	M.L. -40	106		u	v	+22
M.L. -38	1597		M.L. #39	106		106	1644	1691	106	1597	1691	106	1597	1691	M.L. -41	109		u	v	+22
M.L. -39	1644		M.L. #40	109		109	1691	1738	109	1644	1738	109	1644	1738	M.L. -42	112		u	v	+22
M.L. -40	1691		M.L. #41	112		112	1738	1785	112	1691	1785	112	1691	1785	M.L. -43	115		u	v	+22
M.L. -41	1738		M.L. #42	115		115	1785	1832	115	1738	1832	115	1738	1832	M.L. -44	118		u	v	+22
M.L. -42	1785		M.L. #43	118		118	1832	1879	118	1785	1879	118	1785	1879	M.L. -45	121		u	v	+22
M.L. -43	1832		M.L. #44	121		121	1879	1926	121	1832	1926	121	1832	1926	M.L. -46	124		u	v	+22
M.L. -44	1879		M.L. #45	124		124	1926	1973	124	1879	1973	124	1879	1973	M.L. -47	127		u	v	+22
M.L. -45	1926		M.L. #46	127		127	1973	2020	127	1926	2020	127	1926	2020	M.L. -48	130		u	v	+22
M.L. -46	1973		M.L. #47	130		130	2020	2067	130	1973	2067	130	1973	2067	M.L. -49	133		u	v	+22
M.L. -47	2020		M.L. #48	133		133	2067	2114	133	2020	2114	133	2020	2114	M.L. -50	136		u	v	+22
M.L. -48	2067		M.L. #49	136		136	2114	2161	136	2067	2161	136	2067	2161	M.L. -51	139		u	v	+22
M.L. -49	2114		M.L. #50	139		139	2161	2208	139	2114	2208	139	2114	2208	M.L. -52	142		u	v	+22
M.L. -50	2161		M.L. #51	142		142	2208	2255	142	2161	2255	142	2161	2255	M.L. -53	145		u	v	+22
M.L. -51	2208		M.L. #52	145		145	2255	2302	145	2208	2302	145	2208	2302	M.L. -54	148		u	v	+22
M.L. -52	2255		M.L. #53	148		148	2302	2349	148	2255	2349	148	2255	2349	M.L. -55	151		u	v	+22
M.L. -53	2302		M.L. #54	151		151	2349	2396	151	2302	2396	151	2302	2396	M.L. -56	154		u	v	+22
M.L. -54	2349		M.L. #55	154		154	2396	2443	154	2349	2443	154	2349	2443	M.L. -57	157		u	v	+22
M.L. -55	2396		M.L. #56	157		157	2443	2490	157	2396	2490	157	2396	2490	M.L. -58	160		u	v	+22
M.L. -56	2443		M.L. #57	160	</															

thermal ellipsoids of the individual atoms drawn by the *ORTEP* program (Johnson, 1965) are shown in Fig. 3.

Benzidine and TCNQ molecules form columns along the *c* axis, in which benzidine and TCNQ are alternately stacked with their molecular planes almost parallel to each other. Between these molecular columns, channels run along the *c* axis. Each channel is surrounded by four columns composed of benzidine and TCNQ. It is in these channels that the dichloromethane molecules are sited. The distance between an N atom of a benzidine molecule and the nearest N atom of a TCNQ molecule in the neighbouring molecular column is 3.110 Å (as shown in Fig. 1). This N...N distance is shorter than the value expected for a van der Waals contact. Thus it is likely that the benzidine-TCNQ columns are linked together by N...N≡C hydrogen-bond network to stabilize the channelled structure.

The arrangement of donor and acceptor molecules described above resembles that in the anthracene-TCNQ complex (Williams & Wallwork, 1968). In the latter, however, no solvent-containing complex is obtainable. Seemingly this difference is associated with the situation that a channelled structure is stabilized by the intermolecular hydrogen bonds in the benzidine-TCNQ system but not in the anthracene-TCNQ system.

The relative orientation of TCNQ with respect to the neighbouring benzidine molecule is shown in Fig. 4. In the polarized absorption spectrum of this complex,

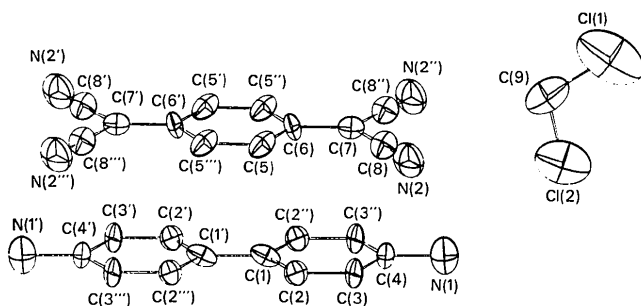


Fig. 3. The atomic numbering of the molecules. Ellipsoids represent anisotropic thermal parameters.

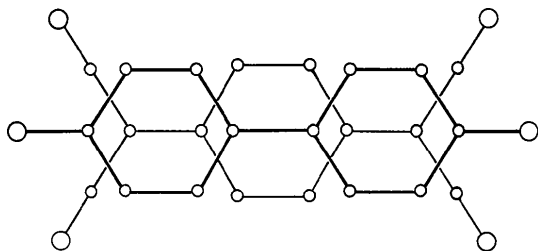


Fig. 4. Relative orientation of BD with respect to TCNQ found in the crystal.

it has been found that the direction of the transition moment of the second charge-transfer band is nearly perpendicular to that of the first charge-transfer band (Amano, Kuroda & Akamatu, 1969). We have carried out a theoretical investigation on the electronic transitions expected for the molecular arrangement shown in Fig. 4, and found that the anomalous polarization of the second charge-transfer bands can be understood with this molecular arrangement.

The benzidine and TCNQ molecules can be considered to be planar. The equations of the molecular planes were calculated by the method of least squares. The equations thus obtained are:

$$-0.0378 X + 0.0 Y + 1.0000 Z = 0.00$$

for benzidine, and

$$-0.0259 X + 0.0 Y + 1.0000 Z = 3.222$$

for TCNQ, where *X*, *Y* and *Z* are coordinates with respect to the crystal axes *a*, *b* and *c* (in Å units). These two planes make an angle of 0.7° with each other. The mean separation between the molecular planes is 3.22 Å which is smaller than the usual van der Waals separation. The deviations of atoms from the least-squares planes are listed in Table 3.

Table 3. Atomic deviations (Å) from the least-squares planes of the BD and TCNQ molecules

BD		TCNQ	
C(1)	0.004	C(5)	0.006
C(2)	-0.001	C(6)	0.001
C(3)	-0.004	C(7)	0.003
C(4)	0.001	C(8)	-0.006
N(1)	0.004	N(2)	-0.003

The distances between the atoms of the neighbouring benzidine and TCNQ molecules are listed in Table 4.

Table 4. Distances less than 3.5 Å between atoms of the nearest-neighbour BD and TCNQ molecules and their standard deviations (Å)

BD...TCNQ	
C(4)...C(8)	3.475 (14)
C(4)...C(7)	3.366 (15)
C(2)...C(6)	3.452 (14)
C(2)...C(5)	3.336 (11)
C(1)...C(5)	3.472 (13)
C(1)...C(6)	3.302 (17)
C(3)...C(7)	3.472 (12)
C(3)...C(8)	3.330 (12)

The bond lengths and bond angles in each molecule are illustrated in Figs. 5 and 6, together with the standard deviations. These values have not been corrected for thermal motion.

The molecular dimensions of TCNQ have been reported for the TCNQ crystal and for various TCNQ complexes. It is well known that the bond lengths of

TCNQ vary systematically with its formal charge. The bond lengths found in the present complex fall between those for the neutral TCNQ and mononegative TCNQ ion, but are closer to the former. In the benzidine molecules, the C-C bonds in its benzene rings are of almost equal length, but the bond connecting the two benzene rings is rather long, 1.509 Å. Unfortunately no data are available for the molecular dimensions of benzidine, or of its ion, with which the present results can be compared.

As shown in Table 1, the standard deviations of the atomic coordinates (especially those of the carbon atoms) and temperature factors of the dichloromethane molecule are rather large. This is naturally to be expected from the presence of appreciable defects in the lattice of this complex; for example, there are only 3.4 dichloromethane molecules in the unit cell, although there are four sites for dichloromethane. It was also found that the correlation among the atomic parameters of dichloromethane is large. Consequently, the atomic parameters of the molecule could not be accurately determined.

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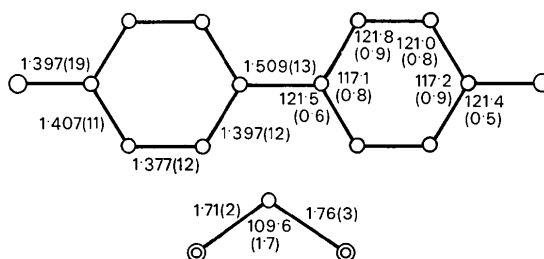


Fig. 5. Bond lengths and their e.s.d.'s (Å), and bond angles and their e.s.d.'s (°) in BD and dichloromethane.

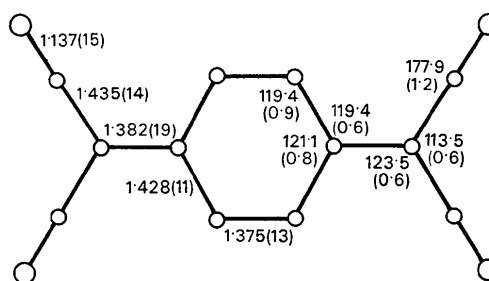


Fig. 6. Bond lengths and their e.s.d.'s (Å), and bond angles and their e.s.d.'s (°) in TCNQ.